

Application of Extended Nernst Planck Model in Nano Filtration Process –A Critical Review

Manoj Kumaran¹, Shailendra Bajpai²

M.Tech¹, Associate Professor², Department of Chemical Engineering,
^{1,2}Dr. B.R. Ambedkar National Institute of Technology, Jalandhar, India

Abstract: Organic pollutants were widely used in various industries including electroplating, mining, painting etc. Theirs effective reuse and disposal before discharge is a challenging work. Various methods such as Ion exchange, Solvent extraction, Adsorption, Advanced oxidation process, Membrane separation processes have been studied earlier. Of these nano filtration possess the major applications in wide range of industries. In this review the modeling for the treatment of wastewater using various transport models is discussed. This review also depicts the various approach of Extended Nernst Planck Model for determination of transport phenomena and improved performance in detail. Research work related to modeling in nanofiltration for waste water treatment, heavy metal removal, charged ion removal has been reviewed individually by ENP model or by coupling it with other models such as Donnan steric Polarization Model(DSPM) etc. This review also provides the clear information regarding the other sophisticated model. It equips the author with the knowledge about the significance of Donnan, steric, dielectric and transport effects separation of solute particles by nanofiltration.

Keywords: Coupled modeling, Donnan Steric Polarization Model, Extended Nernst Planck model, Nanofiltration, Separation mechanism.

I. INTRODUCTION

Nano filtration (NF) is one of the important pressure driven membrane separation processes which hold the properties intermediate between Reverse osmosis (RO) and Ultrafiltration (UF). NF carries the advantages of both RO and UF such as higher flux, lower operating pressure, comparatively higher retention, lower operating and maintenance costs[1]. NF has been widely used in different applications ranging from desalination, softening and waste water treatment. It is effective for separation of sugars and divalent ions where particle size ranges from 0.5-5 nm [2, 3].

There are various membrane transport models to predict the phenomena of solute particles transport through the membranes such as Solution Diffusion (SD), Solution Diffusion Imperfection(SDI), Preferential Sorption Capillary Flow (PSCF), Donnan Exclusion(DE), Extended Nernst Planck(ENP) Model etc., [4]. Nernst Planck equation itself possess limitations which includes intrinsic limitations such as hindrance in dealing with bulk phase, finite-ion-size transport, fail to deal explicitly with discrete energetic barriers, proportionality or friction coefficients, mobilities and diffusion coefficients are not defined microscopically etc. Therefore in order to overcome these disadvantages few modifications in Nernst Planck equation has been done which result in Extended Nernst Planck equation. ENP Model is used to describe flux of ions through charged membrane and to determine which mechanism is more predominant for solute removal whether diffusive or convective [5]. The transport equations of ions through the membrane include three components such as ionic diffusion, electro migration and convective flow. According to Scopus database it is found that nearly 1738 articles have been published for NF membranes in different areas, among which the modeling has gained only the least importance and only scarce reported the extended Nernst Planck model Fig 1. The present work summarises the basics of NF modeling and especially the ENP model.

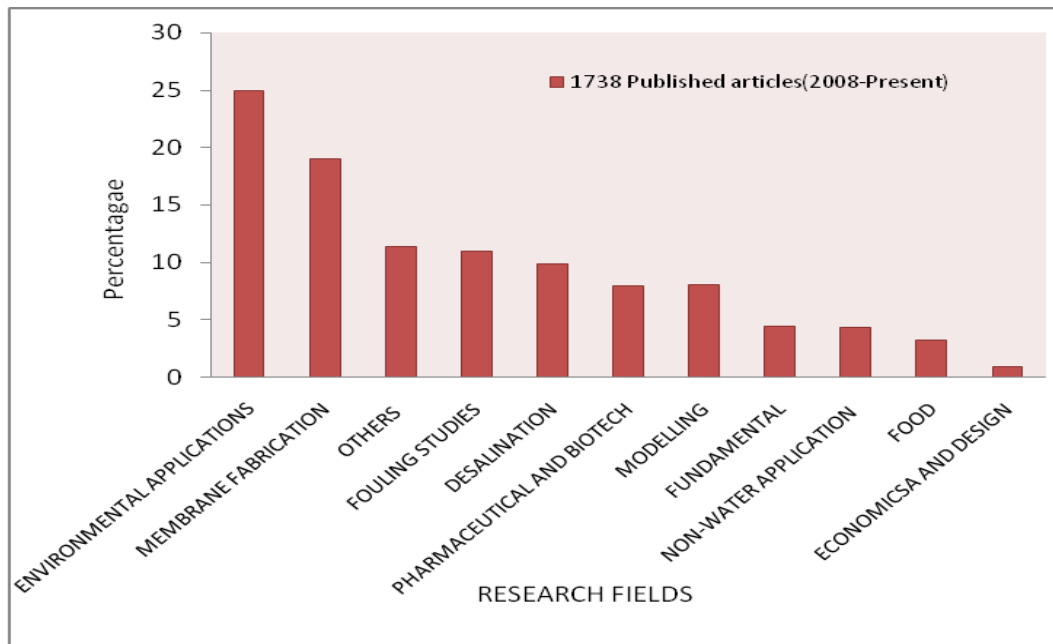


Fig 1. Research fields related to Nanofiltration (SCOPUS DATABASE-2014)

This paper reviews the transport model for both industrial based module and lab scale test cell. In addition to this application of NF modeling using other sophisticated models in treatment of ground, surface, and wastewater will also be reviewed. The review also deals at the prospective recommendations for future works that should be addressed in order to make significant improvement in modeling of transport phenomena NF membrane processes.

II. PRINCIPLE OF MEMBRANE SEPARATION

Nanofiltration (NF) develops the pressure gradient across the membrane which aids the separation. This selectively transports the solvent and certain solutes through the membrane. The main driving force for the separation process is the pressure difference between feed and the permeate side of the membrane. Despite this force the removal of solute from waste water is also achieved by co-interaction of Donnan, steric, dielectric and transport effects. Charge of the ions also plays a key role in separation. The steric effect such as size based separation occurs for the transport of neutral solutes [7].

In case of charged ions, Donnan effect plays a major role by describing the membrane potential interactions and equilibrium maintenance at charged solute and membrane interface [7]. The charge of the membrane is based on the material used for its fabrication. However its charge is developed mainly due to dissociation of ionic functional groups in membrane surface and pores[8]. This in turn decides whether the membrane is acidic or basic. But the greater disadvantage is weaker ion exchanging ability which also alters the membrane charge [9]. The dielectric effect is not clearly explained due to irregular electrostatic attraction & repulsion due to variation of ionic surrounding.[10] The movement of solute through the membrane is pressure dependent which is known as drag force. The drag force facilitates the removal of solute through porous membrane resulting in hindrance of its transport. The transport effects is of three components may be convective, diffusive and electromigration. Thus the overall transport is given by the solute flux. This transport phenomenon is explained briefly by a unique membrane transport model know as Extended Nernst Planck (ENP) model. Thus the four factors involve in separation of solute from the solution using Nanofiltration [11].

Besides the above mentioned factors the Nanofiltration separation also depends on salt type and membrane type known as the salt permeability. Lower salt permeability signifies that osmotic pressure varies at both compartment whereas the higher permeability signifies the same osmotic pressure [12].

The efficiency of the separation is well understood based on the two parameters such as Permeate flux and Rejection. The factors that influence the two parameters are [13]

- Transmembrane Pressure
- Temperature

- Feed concentration of solute
- Flow rate
- Presence of co-ions etc.,

III. MODELING OF NF MEMBRANES

Predictive Modeling is an important step to develop a successful model by determining the membrane characteristics, to improve efficiency by varying influencing parameters and optimizing the separation process. Many literatures reviewed the optimization process of the NF process [14]. To review the optimization process it is essential to understand the NF process and its various modules. Thus, Marriot and Sorensen (2003) have investigated the general approach of modeling membrane for different modules. They developed mathematical models of hollow fibre and spiral-wound membrane modules. These models describe the generic membrane separation based on mass, momentum and energy balances. Thus, it is unique and overcomes the limitation of operating range and convergence of process specificity. These models were tested using various case studies of gas separation, pervaporation, and reverse osmosis followed by its simulation to test its accuracy [15].

A. Membrane Transport Models and its Classifications:

Membrane transport models are used to predict the solute and solvent flux through the membrane. Some of them are discussed below in following subheadings. The table 1 briefly explains different transport models used by the authors to determine the rejection using Nanofiltration process

TABLE 1. CRITICAL REVIEW OF NANOFILTRATION AND ITS TRANSPORT MODELS

Membrane	Manufacturer	MWCO G mol ⁻¹	Temp. Max.	pH Optimum	Model Type	Author
Nanomax50	Millipore	350	40°C	2-10	Coupled –(Film theory and ENP)	Chaabane et al.
DL	GE Osmonics	200-400	50°C	3-9	SD model based on ENP	Neiwersch et al
Desal HL	GE Osmonics	150-300	45°C	2-9	DSPM-DE Model	Wang et al.
HDS-12-2540	Hyflux Corp.	250	45°C	2-10	Coupled –(Film theory and ENP)	Hua et al.
NF-270	DSS Labstack [®] M20	200-400	45°C	3-10	ENP Model	Bargeman et al.
NF-90	DSS Labstack [®] M20	200-400	45°C	3-10	ENP Model	Bargeman et al
NTR-7450	DSS Labstack [®] M20	600-800	90°C	2-11	ENP Model	Bargeman et al
NTR-7410	DSS Labstack [®] M20	600	90°C	2-11	ENP Model	Bargeman et al
NTR-7470	DSS Labstack [®] M20	600-800	40°C	2-11	ENP Model	Bargeman et al
NTR-7250	DSS Labstack [®] M20	800	40°C	2-8	ENP Model	Bargeman et al
Desal 5DK	DSS Labstack [®] M20	150-300	50°C	2-11	ENP Model	Bargeman et al
TS 80	DSS Labstack [®] M20	150		4-11	ENP Model	Bargeman et al
TS 82	DSS Labstack [®] M20	175		4-11	ENP Model	Bargeman et al
XN-45	DSS Labstack [®] M20	500		4-11	ENP Model	Bargeman et al
DK	GE Power & Water	150-300		2-10	Pore Transport	Eflegenir et al
EFC40	PCI Membrane Syst.	300		3-9	Pore Transport	Eflegenir et al

a. Solution diffusion model (SD):

It is based on principle of diffusion of the solute and the solvent through the membrane. The main assumption of this model is that the membrane has a homogeneous non porous membrane. Both the solute and solvent dissolve in the membrane and diffuse through the membrane. The solute solvent diffusion is uncoupled and the diffusion takes place due to its own chemical potential (Chaabane et al., 2004). These gradients are result of concentration and pressure differences across the membrane. This concentration gradient is created by molecules which cannot pass through the membrane and its effect is referred to as **concentration polarization**(Figure 3) which leads to a reduced trans-membrane flow (flux). The differences in the solubility and diffusivities of the solute and solvent are extremely important in this model.

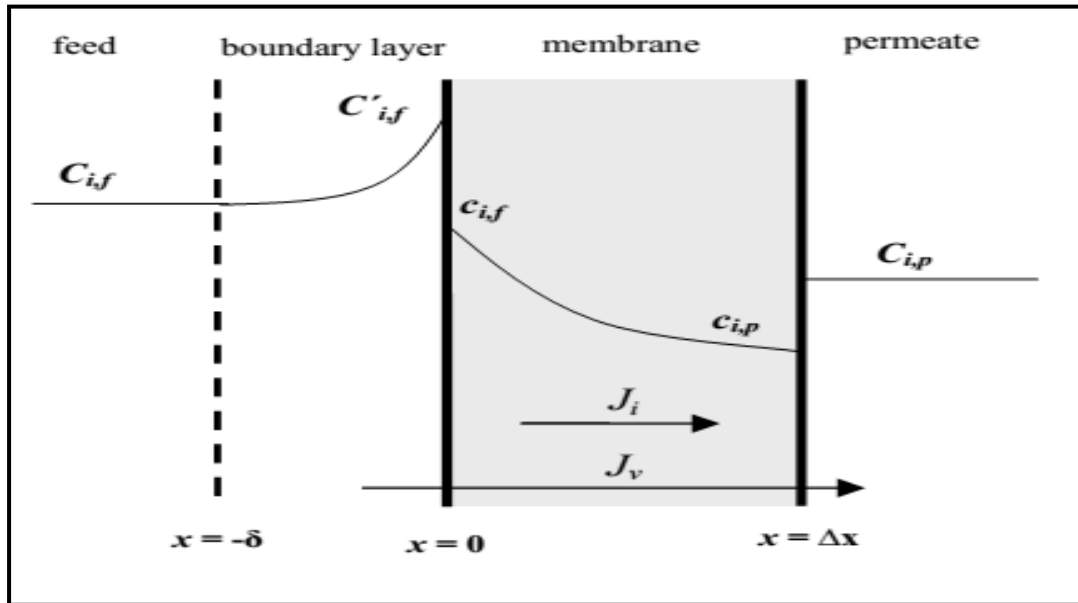


Fig 2. Phenomena of Concentration Polarization (Zafrilla et al., 2008)

The solute and solution flux through the membrane can be explained in following equations:

$$J_w = \frac{P_w}{l} (\Delta p - \Delta \pi) \quad (1)$$

$$J_s = \frac{P_s}{l} (C_m - C_p) \quad (2)$$

$$R' = \left(1 + \frac{P_s}{J_w} \right)^{-1} = \left[1 + \left(\frac{P_s}{P_w} \right) + \left(\frac{1}{\Delta p - \Delta \pi} \right) \right]^{-1} \quad (3)$$

b. Solution-Diffusion-Imperfection Model (SDI):

The solution-diffusion-imperfection model was an early modification of the solution-diffusion model to include pore flow in addition to diffusion of solvent and solute through the membrane as the mechanisms of transport (Chaabane et al., 2004). This model recognizes that there may be small imperfections or pores on the surface of membranes through which transport can occur. The governing equations are as:

$$J_w = \frac{P_w}{l} (\Delta p - \Delta \pi) + \frac{P_s}{l} \Delta p \quad (4)$$

$$J_s = \frac{P_s}{l} (C_m - C_p) + \frac{P_s}{l} \Delta p C_m \quad (5)$$

$$R' = \left[1 + \left(\frac{P_2}{P_w} \right) \left(\frac{1}{\Delta p - \Delta \pi} \right) + \left(\frac{P_3}{P_w} \right) \left(\frac{1}{\Delta p - \Delta \pi} \right) \right]^{-1} \quad (6)$$

Where P_3 is coupling coefficient and P_2 is solute permeability coefficient and R' is true rejection

c. Preferential Sorption-Capillary Flow Model (PSCF):

Sourirajan in 1977 has proposed the early pore model named preferential sorption capillary model. The major assumption used in this model for the separation mechanism is inclusion of both surface phenomena and fluid transport through pores in the membrane. The membrane is considered to be micro porous in nature which is totally in contrast with the SD model. The significant statement of this model is that the membrane barrier layer has chemical properties which has property of preferential sorption for the solvent or preferential repulsion for the solutes of the feed solution. Thus a layer of almost pure solvent is preferentially sorbed on the surface and in the pores of the membrane. Solvent transport occurs as solvent from this layer is forced through the membrane capillary pores under pressure (Ho and Sirkar, 1992). The water flux according to model is given by:

$$N_w = A \{ \Delta p - [\pi x'_s - \pi x''_s] \} \quad (7)$$

The solute flux is expressed by

$$N_s = \frac{c_T K_s D_{sm}}{l} (x'_s - x''_s) \quad (8)$$

Where N_w is water flux, N_s is solute flux, A is Pure water permeability, and $\Pi(x_s)$ is Osmotic pressure of solution with molefraction x_s

d. Donnan Exclusion Model (DE):

NF membranes are often negatively charged. When a charged membrane is placed in a salt solution, a dynamic equilibrium occurs. The counter ion (opposite to that of membrane charge) concentration is higher while the co-ion (same sign charge as the fixed membrane charge) concentration is lower in the membrane phase than in the bulk solution, creating a "Donnan potential" (Feynman et al., 1963). This potential prevents the diffusion of the counter ion from the membrane phase to the bulk solution and the diffusion of the co-ion from the bulk solution to the membrane phase. A potential also occurs when an applied pressure gradient forces water flow through the membrane. The effect of "Donnan potential" is to repel the co-ion from the membrane, and because of electroneutrality requirements, the counter ion is also rejected. The Donnan potential is given by following equation

$$\Delta\psi_{Don} = \psi - \psi' = \frac{1}{z_i F} [RT \ln \frac{a_i}{a'_i} - \bar{v}_i \pi_i] \quad (9)$$

$\psi - \psi'$ is electric potential difference, z_i is the valency of ionic species i , F is Faraday's constant, R gas constant, T absolute temperature, a_i is the activities, v_i is partial molar volume of component i , π_i is swelling pressure

B. Predictive Modeling- Extended Nernst Planck Model:

The ENP modeling gains major importance compared to other models because it provides the information regarding the properties of both membrane and the process stream. The objective of these models is to predict the actual conditions of membrane process and compare it with measurable parameters of the process thereby predicting the consistency and accuracy of the model. The most common drawbacks of NF modeling is to predict the essential membrane characteristics such as pore radius and its charge. As already mentioned in the above section the Donnan and transport effects are clearly explained by ENP Modeling [12].

Extended Nernst Planck equation governs the transport of ionic species through membrane. This model describes the flux of ions through a charged membrane. Rejection of ions through pores is manifested at the pore solution interface and the ionic fluxes generated through Convective, diffusive and electrostatic migration forces [16]. This model assumes that both the solute and solvent dissolve in the nonporous and homogeneous surface layers of the membrane and then each diffuses across it due to the chemical potential gradient which is the result of both concentration and pressure difference across the membrane. Solubility and diffusivity of solute and solvent in the membrane phase are important in this model. The ENP equation varies for different type of modeling based on the properties of membrane and solute, other variable and operational parameters, type of NF process and application of NF process etc., [17]. Few forms of ENP equation are discussed and also explains briefly about its former equation from where it is obtained.

Rather than accounting the steric component at the interfaces, reflection coefficient of each solute was included to determine the transport mechanism of diffusive and convective flow [18-20].

$$J_i = C_i v_s (1 - \sigma) - D_i \left[\frac{\partial C_i}{\partial x} + C_i \frac{\partial \ln \gamma_i}{\partial x} + z_i \frac{F}{RT} C_i \frac{\partial \phi}{\partial x} + \frac{C_i}{RT} \left(v_i - \frac{M_i}{M_s} v_s \right) \frac{\partial p}{\partial x} \right] \quad (1)$$

This equation gives the contribution of Schlogl's to develop Nernst Planck equation. Thus Schlogl equation is significantly useful in application of ENP equation for describing the movement of electrolytes through ionic membranes has been used in recent times. The equation is particularly useful for considering the mechanisms of transport and the adjustable fitting parameters required, based on the real measurable membrane properties. In the above equation, the first two terms represents the salt flux due to diffusion, the third term accounts for flux due to Donnan potential, and the last two terms describes solute flux due to convection. As coincidence with the Donnan equilibrium model, this model predicts the solute rejection is a function of feed concentration and charge of the ion. However, the Nernst-Planck equation includes the effects of convective and diffusional fluxes, which can be important for NF membrane [21]

The transport of electrolytes through the membrane is explained by the following ENP equation.

$$J_i = - \frac{c_i K_i d D_{i\infty}}{RT} \frac{d\mu}{dx} + K_{i,c} c_i V \quad (2)$$

$K_{i,c}$ and $K_{i,d}$ are hindrance factors which accounts the limitation occurred due to convection and diffusion in a confined area [6,7]. The above equation is used to develop into full form of ENP equation which is altered form of equation 1.

$$J_i = -D_i \left[\frac{\partial C_i}{\partial x} + C_i \frac{\partial \ln \gamma_i}{\partial x} + z_i \frac{F}{RT} C_i \frac{\partial \psi}{\partial x} + \frac{C_i}{RT} V_{s,i} \frac{dP}{dx} \right] + K_{i,c} c_i V \quad (3)$$

The entrance and exit of ion through the pore at equilibria is well defined by the activity coefficient which is clearly explained by the following equation [12].

$$\frac{\gamma_i c_i}{\gamma_i^0 c_i} = \phi_i \exp \left(\frac{z_i F}{RT} \Delta \psi_D \right) \exp \left(- \frac{\Delta W_i}{k_B T} \right) \quad (4)$$

The three terms on R.H.S explains briefly about steric, Donnan, and dielectric effects respectively.

Thus Nernst Planck equation for dilute solution by Garba [22] is given as follows

$$J_i = -D_i \left[\frac{\partial C_i}{\partial x} + C_i \frac{\partial \ln \gamma_i}{\partial x} + z_i \frac{F}{RT} C_i \frac{\partial \phi}{\partial x} \right] \quad (5)$$

For a unidirectional flow of dilute solutions through the membrane [23], the transport equation is given by

$$J_i = -P_i \left[\frac{\partial C_{i(x)}}{\partial x} + \frac{C_{i(x)} z_i F}{RT} \frac{\partial \psi}{\partial x} \right] + J_v C_{i(x)} (1 - \sigma_i) \quad (6)$$

The above mentioned description provides the outline about the detailed study of different approaches of extended Nernst Planck equation. The theoretical study not only provides the data regarding membrane and pore characteristics but also provides linearized membrane transport model by avoiding the computational approach.

C. Review of present work of Extended Nernst Planck Modeling in NF process

This section reviews the recent involvement of ENP in Nanofiltration process. Since ENP is one of most successful; model for Nano filtration few literatures are referred as follows: Radcliffe studied the set of PEG solutions of varying molecular weight of varying pore size to determine the particle size. The results were compared with that experimentally obtained rejection values to determine the reliability of the model. As mentioned in equation 2 hindrance factors obtained from experiments were found to be in good agreement with hydrodynamic theory predictions. This study also proved to be the first work to relate the hindrance factor to drag force in modeling [24].

Bargeman investigated the effect of membrane characteristics on Nanofiltration membrane performance during processing of practically saturated sodium chloride solutions. The two important principles for determination of retention was fixed, sulfate retention was calculated based on inverse relation with pore radius and chloride retention by measuring the sulfate concentration difference on either side. This was mainly fixed based on the solutions obtained from ENP equation. Based on the results obtained from chloride and sulfate retention Bargeman concluded that processing of salt solution can be done by simple experiment [25].

Neiwersch developed a mass transport model for removal of phosphorous using the Nanofiltration process. He developed for treating phosphoric acid and sulphuric acid containing waste water. This work involves experimentation followed by multi-ion transport modeling. This work mainly involved the solution diffusion model which incorporates permeability coefficients leading to development of ENP equation. Several combination of synthetic solution proved to fit the ENP model and thereby it was validated [26]. Efligenir elaborated the decontamination of effluents from surface treatment industries by three types of pressure driven membrane separation process such as Reverse osmosis (RO), Ultrafiltration (UF) and Nanofiltration (NF). The removal efficiency of heavy metals was determined and from numerical solution it was concluded all steric, electric and dielectric effects are necessary to improve the separation process. Therefore ENP modeling was performed [27].

Lee et al., carried out a study to investigate the removal of phosphorus using nanofiltration technology. Lee elaborately studied the operational transport parameters such as diffusive and convective component of ENP equation. Their main aim of the study was to investigate the statistical analysis using central composite design to understand the interaction effect of the investigated process parameters on the rejection and permeate flux was performed. This was followed by optimizing the process condition. The transport mechanism of the phosphorus ions through the nanofiltration membrane was studied using extended Nernst Planck equation. The separation of binary system containing concentrated solutions by Nanofiltration was performed by Bargeman. The effect of charge of membrane over flux and retention of NaCl and

glucose were determined. The ENP equation was developed for as binary system and the model is checked for its accuracy based comparison experimental and predicted results [28].

In the case of Characterisation of membrane Ahmad et al. has studied the transport parameters of extended Nernst Planck equation using the two parameter model where he investigated the transport phenomena of salts through the polyamide membrane in terms of anion and cation. The investigation provided the information about the effect of TMC content and reaction time on the diffusive and convective flow of ions through the membrane. The operational parameters were determined mathematically based on the variation in above mentioned two factors Membrane flux and rejection are related to the TMC content and reaction time, when NaCl and CuSO₄ are used as testing solutes. An optimum membrane with high flux and high copper ion rejection could be obtained by incorporating 0.1% (w/v) of TMC in the polymerization reaction mixture under reaction time period of 5 s [29].

Mohammad and his co-workers investigate the treatment of industrial waste water using the Nickel Phosphorous electrode less plating using the HL composite Nanofiltration membrane. Here they consider the electro migration and diffusive component of the ENP equation for determining the transport phenomena. The analysis of experimental data were done by two predictive models, such as Donnan steric pore model (DSPM) and ion transport model which are based on the extended Nernst-Planck equation. The results obtained from these models were compared to choose the better fit with the experimental results [23].

ENP Modeling is generally used to study the removal of ions through the membrane but Diaper proved that ENP modeling can also be used to develop a membrane. The poly acrylic acid based membrane was developed and single electrolyte solution was allowed to pass through it and its rejection and flux data were recorded. These experimental data were interpreted based on ENP equation due to which the membrane characteristics such as effective membrane charge density, porosity and thickness were predicted [30].

D. Review of Coupled Modeling - ENP with other Modeling:

In some cases the ENP model alone cannot predict the behavior of solute due to various reasons including membrane characteristics, solute type, surrounding environment etc. In such cases ENP modeling cannot be used alone and there is a need to involve other transport models resulting in coupled model. The following review discusses about coupled model. For highly complex sugars such as sylo-oligosaccharides syrup coupled model is essential to obtain maximum retention. Therefore, Hua developed a coupled model of ENP equation and film theory. NF experiments were performed in batch recycling mode and experimental R_{obs} were obtained using other operational parameters. Based on the coupled model the theoretical R_{obs} was established and check for its precision. They also studied other model parameters such as solute permeability and reflection coefficient using Genetic algorithm(GA) [31].

Zafrilla and Moros has studied modeling of nanofiltration system based on the Extended Nernst Planck equation using different physical modes. These physical based models generally concentrate on the interaction between the membrane and multi-ionic feed solutions. They basically determine the permeate characteristics at different operating conditions and feed concentration. The prevalent fortunate nanofiltration models are developed based on combination of the ENPE with the Donnan steric equilibrium. This resulting equation is implicit because the transport of solute across the membrane is dependent of permeate. The modeling is done by iterative Runge-Kutta method followed by using COMSOL for Donnan Steric-partitioning Pore Model (DSPM) to overcome the convergence problem. Using COSMOL comparative study of three different physical models such as PDE coefficient form, Convection and Diffusion, Nernst-Planck without electro-neutrality were performed[32].

Chaabane and his co-workers first proposed the mathematical coupled model involving Film theory and ENP equation. Based on this model, Hua in 2015 has investigated removal of oligosaccharides. Thus this work has been the pioneer for future researchers. This mathematical modeling explained the influence of transmembrane pressure in concentration polarization. As it is coupled, Film theory explains the mechanism of transfer at polarization layer whereas the ENP equation elaborates the transport through membrane pores [33].

The ENP modeling is one of the derived models which is the extension of many other models. The basic model from which ENP is derived is known as Donnan-Steric-Pore-Model (DSPM). Few studies related to DSPM have been explained in the review below. Wang has investigated the rejection performance of the NF membranes for removal of various organic compounds. He initially studied the steric hindrance of NF membrane for rejection of 40 organic compounds. From his study it was evident that DSPM and Dielectric (DE) models proved to be successful in predicting

the rejection of remaining compounds also. He concluded that interfacial interaction is the primary reason for the prediction of model [34].

Roy and his co-workers have developed a DSPM with dielectric exclusion for different modules of Nanofiltration process. Comparative study of flat sheet and spiral wound module for varying membrane characteristics were performed. The influence of operating conditions such as feed pressure, recovery ratio and solute rejection of both modules were compared. The experimental values and DSPM-DE predicted values were found to be in good agreement. This study was also done for desalination process [35]. The classic Poisson Nernst Planck model was formulated to determine the ionic flow through the membrane by Liu and Xu. The most important parameter for modeling is boundary value problem which arise due to zero meromorphic function. They provided the relationship between the performance and BVP in this work[36]

IV. LIMITATIONS – NERNST PLANCK MODEL

Though Nernst Planck Model withholds major advantages and being successful in modeling nanofiltration membranes it is not used extensively due to the following reasons.

1. Nernst Planck equation (NPE) is imprecise with distinct energy barriers. This affects the prediction of surface ion exchange kinetics and other bulk phase heterogeneous barriers interpretation.
2. NPE affects the liquid junction potential because it is rarely applicable within $10^{-12} - 10^{-13}$ sec. Therefore during ensemble and average timing it cause negligence of these effects.
3. NPE in terms of point charge has intrinsic cons in finite ion size transport and also for the bulk phase.
4. It fails to investigate the mobilities, friction (proportionality) coefficients and diffusion coefficients in detail. This made it unsuitable for even homogeneous ion exchange membranes. This drawback has been overcome by few modifications in the model by incorporating the friction coefficients and diffusivities as mentioned in irreversible thermodynamics model leading to development of extended Nernst Planck Model.
5. NPE doesn't explain clearly regarding the range of mobility and diffusion coefficient for the solvent and cross linking component. This can be overcome by involving the percolation theory.
6. NPE is successful only when either the solution or the membrane is stationary. It fails when both are in motion. This also affects the size scale separation based on Debye Screening length. It fails for more heterogeneous solution [5].
7. Key deficiency of this type of ENP modeling is it lacks in clearly explaining the physicochemical properties in the pores of NF membrane especially it lacks to deal with activity coefficients and properties related to solid-liquid interface.

Thus the Nernst Planck equation itself proves to be most disadvantageous which encourages the modifications to make it most suitable for modeling which is universally applicable.

V. ADVANTAGES – NERNST PLANCK MODEL

The Extended Nernst Planck (ENP) model was developed to overcome the above mentioned drawbacks of the NPE by undergoing few modifications. ENP equation which is derived from NPE is considered to be the backbone for modeling the transport of wide variety of ions and solutes through NF membrane. This model is considered to be unique as it investigates the type of movement of the solute through the membrane either it may be diffusive or convective. However, this modeling proved to be more efficient for 3-4 ions separations from the mixture. For further removal of multi-component systems few other modifications are incorporated based on its industrial importance. Since the activity coefficients are not elaborately explained by NP modeling the few modifications are to be developed to study the complex interactions and other physicochemical phenomena.

VI. CONCLUSIONS

This review comprehends as given as (1) Principle of separation using nanofiltration, (2) importance of predictive modeling and various transport models (3) Research works related to ENP modeling (4) Importance and necessity of Coupled modeling (5) Prevalence of other sophisticated model in nanofiltration. Major importance drawn by Nanofiltration is due its unicity in selectivity for separation of specific compound. This property has developed a greater

attention among the other separation techniques for the waste water treatment. Based on this review it is evident that many factors are responsible for the separation process such as Donnan, steric, dielectric and transport effects. This review also explains the significance of predictive modeling for the elaborative study of membrane separation using nanofiltration. It investigates the essence of ENP which not only describes the flux of charged ions passing through the membrane but also its transport phenomena. Some cases does not fit into ENP modeling under such instances the coupled modeling plays a key role. ENP is generally coupled with DSPM –DE to provide better consistency and efficiency. It has been critically reviewed regarding the applicability of the current approaches of modeling with respect to separation process.

REFERENCES

- [1] X. Lu, X. Bian and L. Shi, 2002, Preparation and characterization of NF composite membrane, *J. Membr. Sci.*, 210, 3-11.
- [2] M. Frank, G. Bargeman, A. Zwijnenburg, M. Wessling, 2001, Capillary hollow fiber nanofiltration membranes, *Separation and purification technology*, 22, 499-506.
- [3] Y. Ji, Q. An, Q. Zhao, H. Chen, J. Qian, C. Gao, 2010, Fabrication and performance of a new type of charged nanofiltration membrane based on polyelectrolyte complex, *Journal of Membrane Science*, 357(1), 80-89.
- [4] W. S. W. Ho, K. K. Sirkar, 1992, *Membrane Handbook*, Springer Science, New York
- [5] R. P. Puck, 1984, Kinetics of bulk and interfacial ionic motion: microscopic bases and limits for the Nernst-Planck equation applied to membrane systems, *Journal of Membrane Science*, 17, 1-62.
- [6] W.M. Deen, 1987, Hindered transport of largemolecules in liquid-filled pores, *AIChE J.* 33, 1409–1425.
- [7] F.G. Donnan, 1995, Theory of membrane equilibria and membrane potentials in the presence of non-dialysing electrolytes. A contribution to physical–chemical physiology, *J. Membr. Sci.* 100, 45–55.
- [8] M. Ernst, A. Bismarck, J. Springer, M. Jekel, 2000, Zeta-potential and rejection rates of a polyethersulfone nanofiltration membrane in single salt solutions, *J. Membr. Sci.* 165, 251–259.
- [9] A.E. Childress, M. Elimelech, 1996, Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes, *J. Membr. Sci.* 119, 253–268.
- [10] A.E. Yaroshchuk, 1998. Rejection mechanisms of NF membranes, *Serono. Sym.* 9–12.
- [11] D.L. Oatley, L. Llenas, R. Pérez, P.M. Williams, X. Martínez-Lladó, M. Rovira, 2012, Review of the dielectric properties of nanofiltration membranes and verification of the single oriented layer approximation, *Adv. Colloid Interface* 173, 1–11.
- [12] A.W. Mohammad , Y.H. Teowa, W.L. Ang , Y.T. Chung , D.L. Oatley-Radcliffe , N. Hilal, 2015, Nanofiltration membranes review: Recent advances and future prospects *Desalination* 356, 226–254.
- [13] FILMTEC™ Membranes Tech Manual Excerpt ,Trademark of The Dow Chemical Company (“Dow”) or an affiliated company of Dow, Form No. 609-02003-1004 , 1-4.
- [14] N. Hilal, A.W. Mohammad, B. Atkin and N. Darwish, 2003, Using atomic force microscopy towards improvement in nanofiltration membrane properties for desalination pretreatment: a review, *Desalination*, 157, 137-144.
- [15] J. Marriott, E. Sorensen 2003, A general approach to modelling membrane modules, *Chemical Engineering Science*, 58, 4975 – 4990.
- [16] R. P. Feynman, R. B. Leighton, M. Sands, 1963, *Lectures on Physics*, Volume 1. Addison-Wesley, Reading MA.
- [17] R. Schlogl, 1966, Membrane permeation in system far from equilibrium, *Ber. Bunsenges. Phys. Chem.* 70, 400–414.
- [18] M. H. Friedman, 1986, *Principles and Models of Biological Transport*, Springer-Verlag, Berlin.
- [19] A. Katchalsky, P. F. Curran, 1965, *Nonequilibrium Thermodynamics in Biophysics*, Harvard Univ. Press, Cambridge.
- [20] P. Lauger, 1991, *Electrogenic Ion Pumps*, Sinauer Association, Sunderland, MA.

- [21] H. C. VanderHorst, J. M. K. Timmer, T. Robbertsen, J. Leenders, 1995, Use of nanofiltration for concentration and demineralization in the dairy industry: Model for mass transport, *Journal of Membrane Science*, 104, 205–218.
- [22] Y. Garba, S. Taha, J. Carbon, G. Dorange, 2003, Modeling of cadmium salts rejection through a nanofiltration membrane: relationship between solute concentration and transport parameters, *Journal of Membrane Sciences*, 211, 51–58.
- [23] A. W. Mohammad, R. Othaman, N. Hilal, 2004, Potential use of nanofiltration membranes in treatment of industrial wastewater from Ni-P electroless plating, *Desalination*, 168, 241–252.
- [24] D. L. O. Radcliffe, R. S. Williams, T. J. Ainscough, C. Lee, D. J. Johnson, P. M. Williams, 2015, Experimental determination of the hydrodynamic forces within nanofiltration membranes and evaluation of the current theoretical descriptions, *Separation and Purification Technology*, 149, 339–348.
- [25] G. Bargeman, J.B. Westerink, C.F.H. Manuhutu, A.T. Kate, 2015, The effect of membrane characteristics on nanofiltration membrane performance during processing of practically saturated salt solutions, *Journal of Membrane Science*, 485, 112–122.
- [26] C. Niewersch, A. L. B. Bloch, S. Y. T. Melinc, M. Wessling, 2014, Nanofiltration for the recovery of phosphorus — Development of a mass transport model, *Desalination*, 346, 70–78.
- [27] A. Efligenir, S. Deon, P. Fievet, C. Druart, N. M. Crini, G. Crini, 2014, Decontamination of polluted discharge waters from surface treatment industries by pressure-driven membranes: Removal performances and environmental impact, *Chemical Engineering Journal*, 258, 309–319.
- [28] P. C. Lee, S. M. C. P. Leo, T. Y. Wua, S. P. Chai, 2014, Phosphorus removal by NF90 membrane: Optimisation using central composite design, *Journal of the Taiwan Institute of Chemical Engineers*, 45, 1260–1269.
- [29] A. L. Ahmad, B. S. Ooi, 2006, Characterization of composite nanofiltration membrane using two-parameters model of Extended Nernst–Planck Equation, *Separation and Purification Technology*, 50, 300–309.
- [30] C. Diaper, V. Correia, S. Judd, 1998, Characterisation of zirconium/poly(acrylic acid) low pressure dynamically formed membranes by use of the extended Nernst–Planck equation, *Journal of Membrane Science*, 138, 135–140.
- [31] X. Hua, H. Z. R. Yang, W. Zhang, W. Zhao, 2010, Coupled model of extended Nernst–Planck equation and film theory in nanofiltration for xylo-oligosaccharide syrup, *Journal of Food Engineering*, 100, 302–309.
- [32] J. M. G. Zafrilla, A. S. Moros, 2008, Nanofiltration Modeling Based on the Extended Nernst–Planck Equation under Different Physical Modes, *Proceedings of the COMSOL Conference 2008*.
- [33] T. Chaabane, S. Tahab, M. Taleb Ahmeda, R. Maachib, G. Dorangeb, 2007, Coupled model of film theory and the Nernst–Planck equation in nanofiltration, *Desalination*, 206, 424–432.
- [34] X. Wang, B. Li, T. Zhang, X. Li, 2015, Performance of nanofiltration membrane in rejecting trace organic compounds: Experiment and model prediction, *Desalination*, 370, 7–16.
- [35] Y. Roy, M. H. Sharqawy, J. H. Lienhard, 2015, Modeling of Flat-Sheet and Spiral-Wound Nanofiltration Configurations and Its Application in Seawater Nanofiltration, *Journal of Membrane Science* accepted manuscript.
- [36] W. Liu, H. Xu, 2015, A complete analysis of a classical Poisson–Nernst–Planck model for ionic flow, *J. Differential Equations*, 258, 1192–1228.
- [37] G. Bargeman, J.B. Westerink, O. G. Miguez, M. Wessling, 2014, The effect of NaCl and glucose concentration on retentions for nanofiltration membranes processing concentrated solutions *Separation and Purification Technology*, 134, 46–57.