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Review

# Membrane Fabrication, Characteristics and Filtration Process for the Removal of Aqueous-Electrolytes/Heavy Metal Ions from Wastewater: A Short Review

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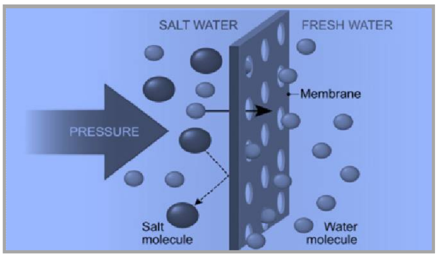
## ABSTRACT

*Membrane filtration (MF) is a pressure-driven separation process that employs a membrane for both mechanical and chemical sieving of particles, as well as also uses to remove particles from waste water. This process is very similar to conventional sand or media filters where the suspended solids are removed, but generally dissolved solids are not removed, but membrane is a material that separates substances, when a driving force is applied across the membrane. Membrane processes are increasingly used for removal of bacteria, microorganisms, particulates, and natural organic material, which can impart colour, tastes, and odours to water and react with disinfectants to form disinfection by-products. The basic technology behind MF is using a semi-permeable membrane to separate a liquid into two distinct streams. Filtration membranes are essentially micro porous barriers of polymeric, ceramic or metallic materials which are used to separate dissolved materials (solutes), colloids, or fine particulate from solutions. To remove aqueous-electrolytes/heavy metal ions from wastewater many conventional techniques such as membrane filtration, reverse osmosis, ion exchange, chemical precipitation, electro dialysis, electrochemical treatment, and adsorption technique have been employed. The membrane filtration for wastewater is a promising new avenue. With increasing pollution of water bodies as well as increasing complexities related to removal of heavy waste from water, membrane filtration can be a cost-effective, compact, and time-efficient solution.*

## Graphical Abstract



Indicated the Separation of electrolyte solution
through reverse osmosis membrane

**Keywords:** Membrane filtration, Conventional, Microporous barriers, Aqueous-electrolytes/ heavy metal ions, Sand filters,.

## INTRODUCTION

Nowadays membrane systems are used in many separation processes. Composite and asymmetric membranes are used in desalting processes under the pressure gradient such as nanofiltration and reverse osmosis due to their high salt rejection, volume flux, and mechanical stability. These membranes can be considered as multilayer systems coupled in series by infinitely thin layers of aqueous solutions in local equilibrium with both adjacent layers. Membrane-based chemical separations constitute an emerging research area and industrial technology [**1**]. The objective is to develop membranes that selectively transport a particular targeted molecule which are having definite sizes and discard (or transport at much lower rates) other molecules that might be present in the feed solution or gas [**2**].

The membrane separation techniques like nanofiltration, ultrafiltration, microfiltration, gas separation, reverse osmosis, pervaporation, and liquid membranes etc, have been studied and industrially applicable. The ion-exchange membrane is one of the most sophisticated separation techniques among these above membrane separation. The important property of the cation and anion-exchange membrane is to selectively permeate cations or anions through the membrane [**3**]. Membrane- based technologies are potentially less energy intensive than other types of competing separations technologies and, as such, can be viewed as an example of “green chemistry.” However, materials with higher chemical selectivity for the desired target molecule that can be incorporated into geometries that required high flux of this particular molecule [**4**]. A charged membrane transforms the ions due to the differences in their concentrations, pore sizes of the membrane and electrolyte interaction with the membrane. In addition to this, a charged membrane can separate electrolyte ions according to the charge of the membrane. Recently it has become necessary to analyze the ion transport phenomena specifically in aqueous, organic, electrolyte solution systems across a charged membrane from the view point of industrial and medical applications [**5, 6**].

As the membrane begins to capture particles that larger than the pore size, it begins to “ripen.” As a membrane ripens, the pore size available for filtering decreases and smaller particles are captured. The main disadvantages of barrier-based filtration are: Replacement and disposal costs. When this type of filter becomes blocked by waste particles, it needs to be replaced [**7**].

Application of extraction techniques for removal and recovery of heavy metals is of immensely growing importance from the viewpoint of environmental protection problems [**8**]. During the second half of the last century ion-exchange membranes and their practical utilization in electro-membrane processes have gained significant technical and commercial importance in water deionization and purification as well as in electrochemical synthesis and in energy conversion and energy storage, while other processes such as capacitive electro-deionization and electro-dialysis with bipolar membranes or the use of ion-exchange membranes in fuel cells and energy conversion are more recent developments which show a large number of interesting applications. Removal of heavy metal ions from wastewater is of prime importance for a clean environment and human health. Different reported methods were devoted to heavy metal ions removal from various wastewater sources. These methods could be classified into adsorption, membrane, chemical, electric, and photocatalytic-based treatments [**9, 10**]. The chemical and membrane methods are pre dominantly used, through which the large-volume sludge formation and post-treatment requirements are vital issues that need to be solved for chemical techniques. Fouling and scaling inhibition could lead to further improvement in membrane separation. However, pre-treatment and periodic cleaning of membranes incurs additional costs. Following figure 1 are the various methods which are used for the filtration of waste water as well as heavy metal ions [**11**].

**Composite membrane fabrications and their characteristics:** The synthesis of ion-exchange inorganic-organic hybrid membranes can be done by several processes like sol-gel, co precipitation, intercalation, blending, in situ polymerization, molecular self-assembling etc, but among them the sol-gel process is one of the most common and qualitative method of material synthesis. Many researchers used the sol-gel or liquid coupling process of silane coupling agents to prepare a hybrid anion exchange membrane [12].

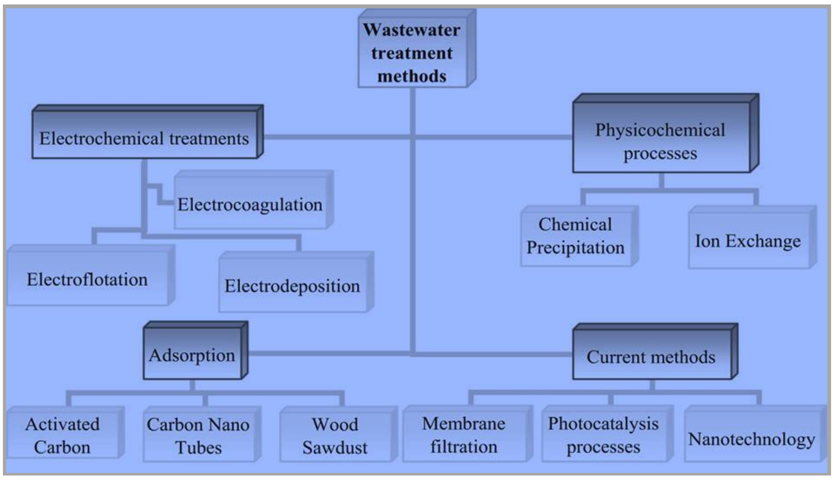


**Figure 1.** The methods used for the filtration of waste water as well as heavy metal ions.

The organic-inorganic or polymeric-inorganic composite materials which are used to make the membrane, have been widely studied for a long time due to their combined characteristic of both the used materials, and these may be micro or nano composites about 200-800 mesh size. Such type of micro and nano composite membranes generally have the organic polymer materials with inorganic nano scale building blocks which results to show the combine advantages of inorganic materials rigidity, thermal stability ion exchange property and organic polymers flexibility, dielectric property, ductility and easy binding ability. Therefore such membranes are confirmed to be useful for the molecular separations such as bimolecular purification, seawater desalination, environmental remediation as well as petroleum, chemicals and fuels production. These molecular separations are classically used for distinguished technologies like distillation, filtration, absorption and adsorption, which otherwise involve extreme energy and capital. Recently the selective permeations through the membranes have become much attractive because these are economical therefore categorized as green technology [13-15].

The extensive use of such membranes is due to the low operating costs with a desirable combination of high selectivity and high permeability. Presently, polymers are still the main materials in membrane technology with the advantages of good binding ability, flexibility and low cost criteria, however some limitations in their chemical, mechanical and thermal resistance restrict the applications of polymeric materials [16]. The inorganic materials used in membranes although have longer lifetime· and higher thermal and chemical stabilities but they are expensive and brittle in nature with poor membrane forming ability. Therefore, the organic-inorganic composite materials are used to make the membranes and these have attracted more attention due to combining the basic properties of both the materials and these give advantage in designing the membranes with excellent separation performances, good thermal plus chemical resistance and adaptability for insensitive environments [17-19]. So the composite membranes find interest in analytical chemistry as these can be used for the direct measurement of ion concentration, precipitation reaction and titration analysis which provides the information means that it may easily provide the fundamental knowledge of precipitation processes.

It has been observed that the mechanical, chemical and thermal stabilities of the membranes make it applicable for the water filtration and purification processes like industrial wastewater as well as hazardous waste treatment, oil-water separations etc [20, 21] through it. Such membranes are more easily recovered after fouling the flux process as these can sustain very harsh chemical condition [22].

These membranes are more expensive for the large scale applications like drinking water production as well as wastewater treatment etc. So the applications of such membranes are relatively limited and these are mostly used for the separation purposes in small scale industries [23].

**Process of ions separation through membrane technology:** The separation process occurs at the thin side of membranes whereas the support layer provides a nearly resistance free path for water to exit through the membrane. The highly selective MF and UF membranes have the pore size ranging from -0.01-0.2 µm. A thin sheet of MF and UF membranes are formed by an induced phase inversion of preformed polymers over a support fabric which provides the mechanical stability for the membranes, whereas the alternative of phase inversion reaction can be completed to form a hollow fiber forms of MF and UF membranes. The phase inversion technique has been completed by a controlled interaction of solvent and non solvent solutions to induce a phase separation transition which means a polymer forms a liquid dispersion into a solid state. A recent review has indicated that the uniform polymer solution contains the polymer as well as solvent immersed into a non solvent coagulation bath which results the solidification of polymer during the exchange of miscible solvent and non solvent [24, 25]. The overall characteristics of membrane can vary according to the conditions like casting condition, polymer selection, polymer concentration, solvent and non solvent system and additives and coagulation bath condition etc. Separation of electrolyte solution through reverse osmosis membrane shows by the following figure 2.

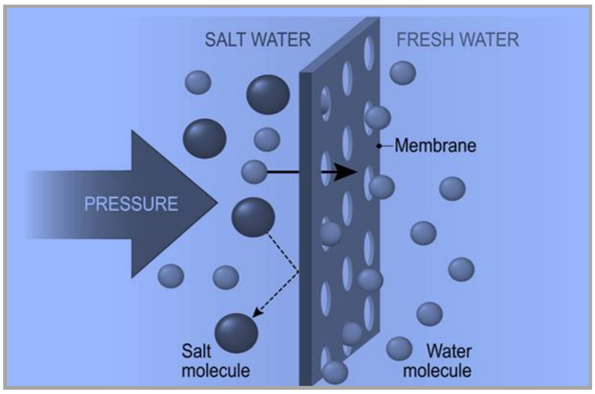


**Figure 2.** Indicated the Separation of electrolyte solution through reverse osmosis membrane.

**Ionic conductivity and porosity:** The ionic conductivity of membrane is an important characteristic which is the major deciding factor for the application point of views in any ion exchange membranes. It depends on the type of functional groups like strong ionic phosphonic, sulfonics acids and quaternary ammonium salts and the weak ionic like hydroxyls, carboxylic acids and primary secondary and tertiary amine groups etc. It has been analyzed that the porosity of membranes also affects the ionic conductivity, which suggest that a highly porous membrane always follow high ionic conductivity and vice versa. So the porosity in hybrid composite membrane can easily be modified by using the suitable organic and inorganic materials as well as the synthesis processes [26, 27]. Water content property of hybrid membrane has also indicated the effect for ionic conductivity, which means that the high water uptake leads to high ionic conductivity or ionic migration. So, the well and appropriate applications in different industrial fields demand the low water content with high ionic conductivity. Therefore, the designing of new composite membrane for the commercial purposes, the required criteria that must be followed is the lower water content as well as higher ionic conductivity. Perm selectivity is also an important phenomenon which governs the performances as well as applications of membranes and it is essential that the membrane should have impermeable to co-ions but be permeable for the counter ions. It mainly depends on the type of ion-exchange charges present on membranes as well as the surface porosity of membrane [28].

**Separation of aqueous electrolyte/heavy metal ions through membrane:** In the separation of electrolyte ions through membrane, many authors suggested that there are membranes with characteristic fixed surface charge and that the mechanism of separation of ions is by the differences in the valences of ions. A membrane is a barrier that allows certain substances to pass through while blocking others. Water treatment facilities use various types of membranes and processes to clean surface water, groundwater, and wastewater to produce water for industry and for drinking [29, 30]. There are mainly four main types of these membrane filtration processes. These are microfiltration (MF), ultrafiltration (UF), nano filtration (NF), and reverse osmosis (RO). The main difference exhibited by these processes, apart from their pressure requirements, is their membrane pore sizes. Therefore it is very clear that membrane technology is a generic term for a number of different, very characteristic separation processes. These processes are of the same kind, because in each of them a membrane is used. Membranes are used more and more often for the creation of process water from groundwater, surface water or wastewater. It is an important characteristic that the composition of membrane has cation or anion exchangers [31, 32].

**Cation and anion exchangers:** In most of the industrial processes ion-exchange membranes are used to complete the process of purification, separation and decontamination of aqueous and other ion containing solutions. Typical ion exchangers which are used to make the ion exchange membranes are ion exchange resins, zeolites, montmorillonite, clay, soil humus etc. Wide use of ion exchange membranes for fuel cell storage batteries, electrochemical separation, electro dialysis, electro deionization etc have drawn the attention of the researchers in making ion selective membrane using ion exchange materials. Cation exchange materials and cation exchange membranes have been widely explored by researchers over the past few years because of their commercial applications [33, 34]. However, anion exchangers have been poorly reported and need proper investigations because of their importance in the field of environmental science for separation, identification and determination of toxic anions from industrial waste and drinking water. There are also amphoteric exchangers which are able to exchange both the cations as well as anions simultaneously. These ion exchangers may be selective or nonselective which are used to bind certain ions or classes of ions depending on their physical and chemical properties [35].

**Pore size of membrane for ion filtration:** The separation of particles by membrane mainly depends on the pore size distribution. If size of the particles is larger than the pore size of membrane then these are rejected, while the smaller particles can easily pass through the membrane barrier. Hence, the membrane filtration is entirely based on the membranes pore size distributions [36]. The resistance 'of mass transfer in such type of membranes is totally determined by their thickness and porosity which shows that the membrane thickness is inversely proportional to the permeation rate of transferable particles. Membranes often respond to gradients that they experience on either sides of them. If concentration is a gradient, the dialysis results, if pressure is a gradient then reverse osmosis, ultra filtration, micro filtration or nano filtration result. If potential is a gradient then electro dialysis and electrophoresis result. All these processes differ from each other depending on the pore diameter of the membrane [37, 38].

**Electrochemical studies of composite membrane for ionic filtration:** Membrane potential is defined as a potential difference arising between the solutions of an electrolyte or heavy metal ions with different concentrations at the constant temperature and pressure separated by a membrane with fixed ion exchange groups [39]. At the interface between membrane and electrolyte solutions, the donnan potential occurs due to the transfer of ions. donnan potential appears as a result of donnan equilibrium, which refers to the distribution of ionic species between two ionic solutions separated by a permeable membrane or boundary. The boundary layer maintains an unequal distribution of ionic solute concentration by acting as a selective barrier to ionic diffusion. Some species of ions may pass through the barrier while others may not. Electrical potential arising between two solutions is called donnan potential. Inside the membrane, the diffusion potential arises since ions would diffuse from the high concentration side to the low concentration side under a certain concentration gradient.

Diffusion potential is the potential difference generated across a membrane because of the concentration difference of an ion. It can be generated only if the membranes are permeable to the ions. The size of the diffusion potential depends on the size of the concentration gradient. The sign of diffusion potential depends on whether the diffusing ion is positively or negatively charged. Diffusion potentials are created by the diffusion of very few ions which do not result in changes in concentration of the diffusing ions. Membrane potential is the summation of the donnan potential and the diffusion potential, and it can also be named as the exclusion-diffusion potential [40]. Membrane potential can be measured directly or by determining the electrical properties of a membrane or the activities of ions inside the membrane. The earlier theoretical studies on membrane potential were almost based on the Teorell, Meyer and Sievers (TMS) model and developed by Kobatake et.al. [41, 42], Lakshminarayanaiah *et.al*. [43]. Kobatake *et. al*. derived an equation of membrane potential for uni-univalent electrolyte solutions and first time proved that the derived equation agreed well with typical corresponding experimental data. Nikonenko *et al*. [44] investigated the influence of the electrolyte/ heavy metal ions concentration, and the ratio of the diffusion boundary layer length and the counter-ions diffusion coefficient on the membrane potential of an ion-exchange membrane. The research work concluded that the membrane potential determined numerically by the TMS model were similar to those obtained experimentally by Dammak if the salt concentration was less than 100 mmol. Lefebvre *et al*. [45] derived the general equations of the membrane potential, and the filtration potential of a charged membrane in an arbitrary electrolyte solution using an analytical approach. The group limited their studies to the related aspects of the comparison of normalized filtration potential calculated numerically and analytically with no discussion on membrane potential. The above analysis demonstrates that most studies of membrane potential evaluated by the TMS model have been emphasized with the attention being given to the uni-univalent electrolytes. Nevertheless, there is not enough convincing theoretical investigation concerning the other kinds of electrolytes. It is worthwhile clarifying the fact whether the TMS model can be employed to evaluate membrane potential in multivalent electrolyte solutions [46]. In contact with external electrolyte solutions of low or moderate concentration the membrane excludes the co-ions (donnan exclusion) by electrostatic repulsion while the counter ions are admitted to the membrane and experience negligible resistance in passing from one side of solutions to the other. At higher concentration, the donnan exclusion becomes less effective and thus perm selectivity gets reduced. The perm selectivity [47] is reflected not only in the differences in permeability, but also in the electric potential difference which arises between the two solutions. Figure 3 shows the electrochemical setup used for observing the membrane potential through digital potentiometer.

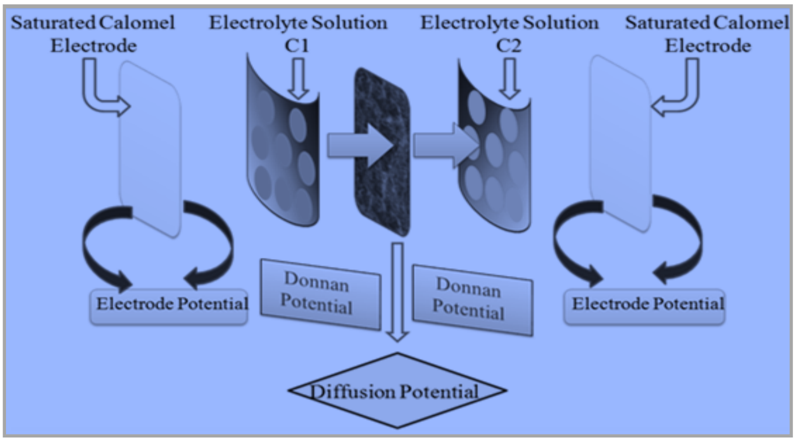


**Figure 3.** The electrochemical setup used for observing the membrane potential through digital potentiometer.

**Ionic transference in terms of water flux:** In the absence of an electric field, the migration of an ionic species across the membrane involves a transfer of electric charge and this charge transfer has been balanced by one or more other fluxes. The compensation of the fluxes is brought about by the electric potential gradient, called the diffusion potential, built up by the process of diffusion. These characteristics of the fluxes, the action of the diffusion in the membrane and the perm selectivity for counter ions are the key to the understanding of diffusion phenomena in membrane systems. When a membrane is between two solutions of the same electrolytes of different concentrations, the membrane potential is called concentration potential. In such a concentration cell, the counter ions diffuse more rapidly than the co ions, due to perm selectivity, resulting in a net transfer of electric charge. With cation selective membranes, the electric potential in the dilute solution thus is more positive than in the concentrated solution. With anion-selective membranes, the opposite is true [**48**].

**Charge density, ionic mobility and transport number:** The important parameters of membrane like ionic mobility, which is defined as the velocity attained by an ion moving through a medium under an electric field. The effective fixed charge density of membranes refers to the charge distribution over the volume of a particle, such as a molecule, atom or ion. Charge density is the central parameter that controls the membrane phenomenon, which calculated by using the observed potential values of different used electrolyte/heavy metal solutions as well as TMS theoretical potential values [**49, 50**]. The other important parameters of membrane which include the transport number, mobility ratio and charge effectiveness and distribution coefficient have been easily calculated by the above discussed TMS equations. The transport number is another very important factor of membrane defined as the mobility of the ion divided by the sum of mobilities of the two ions. It is also called as the transference number which is the fraction of the total current carried by an electrolyte/heavy metal ion. The transport number has been obtained by using the above Nernst-Planck equations [**51**].

So, the electrochemical studies of membrane have been done by observing the membrane potential throgh using the potentiometer. Different univalent and divalent electrolytes like KCl, NaCl, LiCl and $CaC1_2$, $MgCl_2$, $BeCl_2$ respectively may used to observe the membrane potential. The measurement of membrane potential is used to obtain the transport property of ions across an incubated charged membrane. Hypothetically the membrane potential for aqueous electrolytes or heavy metal ions solution system can determined by many theories like TMS, Altug and Hair, Kobatake *et.al*., as well as the most new one is Nagasawa and co-workers. Among these the TMS theory is most prominent and easily used, which can treated by the help of donnan equilibrium and Nernst Planck equation. The donnan potential totally depends on the membrane charge density which plays a significant role in the selectivity and applications of membrane [**52**]. The diffusion potential depends on the mobility of ions through membrane that affects the transport property of ions, through which the measurement of diffusion as well as donnan potential will be very easy and give the important parameters like ionic mobility and effective fixed charge density of membranes.

## APPLICATION

This review article may be helpful to understand the filtration of electrolytes/heavy metal ions from waste water by composite membrane, through which it must be easier to analyse the membrane application for waste water filtration.

## CONCLUSION

The preparation of membrane material is mostly done by the sol gel process while the membrane fabrication done by the die casting methods, which shows the uniform and novel characteristics like, there chemical, mechanical and thermal stabilities. The filtration of electrolytes/heavy metal ions through membranes are increasingly used, it can also used for removal of bacteria, microorganisms, particulates, and natural organic material, which can impart colour, tastes, and odours to water and react with disinfectants to form disinfection by-products. The basic technology behind membrane filtration is by using a porous membrane to separate a liquid into two distinct streams. It is amicro porous barriers of polymeric, ceramic or metallic materials which are used to separate dissolved materials (solutes), colloids, or fine particulate from solutions. To remove Aqueous-Electrolytes/Heavy metal ions from wastewater many techniques like ion exchange, chemical precipitation, electro dialysis, electrochemical treatment, and adsorption are mostly used but the membrane filtration is most prominent and cost effective among others. The widely used membrane processes include microfiltration, ultrafiltration, nanofiltration, reverse osmosis, electrolysis, dialysis, electrodialysis, gas separation, vapor permeation, pervaporation, membrane distillation, and membrane contactors.So the membrane technology is dominantly used in the process of waste water which mostly includes the heavy metals as well as electrolyte solutions of various ions.

**Conflict of Interest:** The authors declare that there is no conflict of interests regarding the publication of this paper.

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