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A novel method: mixed matrix membrane – An overview

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The development of India into a modern country is slow but the population growth is rapid. Pure air, water and soil are the three important things for a day to day life in the current scenario. Pure form of these three is must. Nowadays many water resources, soils and air in the environment are polluted due to massive increase in population growth, industrialization and modern Urbanization. The heavy metals, dyes, pesticides etc., are mainly polluting the water bodies. In current scenario the world is in the need of treating water bodies, wastewater and sea water to reduce the water scarcity level. All wastewater and water treatment processes possess at least one separation process in the treatment units. Membrane separation process is playing a main role in the treatment process. In this study, the different types of conventional and advanced treatment processes were discussed. Membrane treatment techniques, Types of membranes, materials which can be used for membrane preparation, advantages and disadvantages of each materials, performance of organic membrane (polymeric membrane), performance of inorganic membrane (ceramic membrane) and membrane fabrication methods were also discussed in this study. To overcome the drawbacks, the new innovative idea was derived and discussed.

Key words: Polymeric membrane, Inorganic membrane, Mixed matrix membrane.

Introduction

General

Population growth rate of the world was reported as a 75 million annually [1]. The world population was reported as 3.4 billion in 2009 and it was grown by 30% approximately between the year 1990 and 2010 according to the UN population statistics. If this situation continues, there is the possibility of having the population as 6.3 billion in 2050 [1]. In this, India's growth rate was reported as 350 million. Parallel to this population growth, the world is moving with rapid industrialization and urbanization too. Apart from the basic requirements (Food, Cloth and Shelter), pure air, water and soil are also added in the basic requirements due to this rapid growth of world. In most of the cases the air and water purification are considered as a major problem. The need of deriving pure fresh water from different water sources and domestic and industrial effluent is increased due to this growth. This paper discusses the new innovative membrane process for treating the water and suggests new material and method for the membrane preparation.

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Water and wastewater Treatment

Due to the water scarcity and pollution, the water and wastewater should be treated and reused. The treatment generally consists of the following conventional treatment methods [2].

1. Primary Treatment (Mixing, Equalization, Screening and Clarification)
2. Secondary Treatment (Sedimentation or Clariflocculation, Filtration and Advanced treatment methods like adsorption, Ion exchange, and membrane filtration).
3. Tertiary treatment (Nitrogen and phosphorous removal treatment methods and disinfection, etc.)

Initially the wastewater is mixed and equalized to get a homogeneous solution. The water from the equalizer is fed to the screen chamber for removing large size materials and followed by oil trap for removing oil, fat and grease. This water is then subjected to sedimentation tank or flash mixing chamber based on the intensity of the solids. Coagulants (such as lime, alum, polyelectrolyte, etc.) are added with the water in the flash mixing tank. Then it is processed through Clariflocculator to create high densed flocs. This floc contained water is sent to a settling tank for the settlement of the impurities (suspended matters) present [2].

Most of the processes in chemical industry involve at least one separation or purification to remove foreign matters or to recover the water [3]. The separation

Table 1. Types of filtration and its sizes.

Types of filtration	Particle Capture Size in µm	Contaminants removed	Operating pressure ranges in bar
Microfiltration	0.1-10	Suspended Solids, Bacteria and Protozoa	0.1-2
Ultrafiltration	0.003-0.1	Colloids, Proteins, Polysaccharides, Bacteria, Viruses (partially)	1.5
Nanofiltration	0.001	Viruses, Natural organic matter, multivalent ions.	5-20
Reverse osmosis	0.0001	All impurities	10-100

process is generally divided into as equilibrium governed process and rate governed process. Equilibrium governed process includes distillation, absorption, Adsorption, drying etc., Most of the membrane-based processes are rate governed process. It includes Osmosis, Reverse Osmosis, Dialysis, etc., These processes are carried over by the gradient of chemical potential (i.e., concentration gradient, pressure gradient, temperature gradient and electrochemical potential gradient) [3]. In this paper particularly membrane filtration was discussed.

Membrane Filtration

Initially the membrane separation process was started in laboratory scale. Later it started growing to the industrial pilot plant level with proper technical and commercial requirements. The reasons to choose for membrane technology are: fast process with short residence time, less component specific [4]. The basic principle of Membrane processes are the mechanisms of impaction, diffusion, electrostatic interaction, hydrophobic property, and adsorption [5]. The transport selectivity of the membrane, high efficiency, Low capital cost and operating cost, ease of operation and lower energy requirements and low time for the completion of processes are also the main advantages of the membrane separation processes. The gas separation and liquid separation by membranes is a growing field in the current scenario [4, 5].

The wide research spectrum subjects to modulation and improvement in search of better prototypes development.

Types of membrane filtration

The main part or heart of the membrane process is nothing but the membrane itself. To get the best efficiency in the removal, the identification of the new membrane materials that can be with the expected requirements is strongly growing in the current research field. Generally, the criteria for selecting materials for membrane separation are too difficult. Based on the purpose of utilization, the materials and pore size of the membranes will be selected. Fig. 1 represents the average pore size requirement for membranes for different water treatment processes [6].

There are four main types of membrane system commonly used in industry [7] based on pore size: (a) Microfiltration (MF) is widely applied in particulate removal process and maintains degreasing. (b) Ultra filtration (UF) is generally used for oil, water and emulsion separations; paint recovery; and the separation of fats, oils or greases in the food industry. (c) Reverse osmosis (RO) and (d) nanofiltration (NF) are used extensively for water purification and desalination. Membrane Distillation is one of the developing techniques to treat saline water [8, 9]. Fig. 2 shows the differences of membrane system.

Materials of membrane

Two types of materials are used generally in the membrane preparation. First one is organic membrane

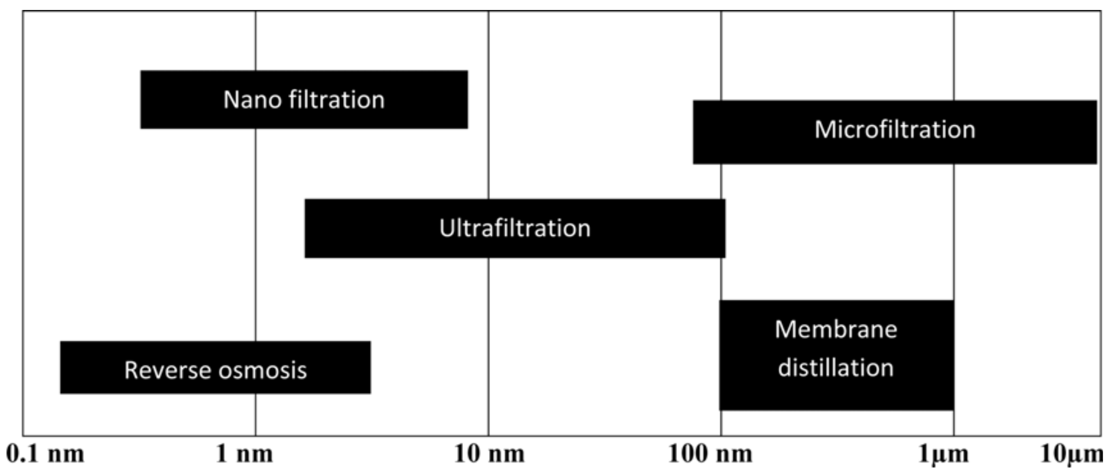

Fig. 1. Average pore size of the membranes used in different membrane process.

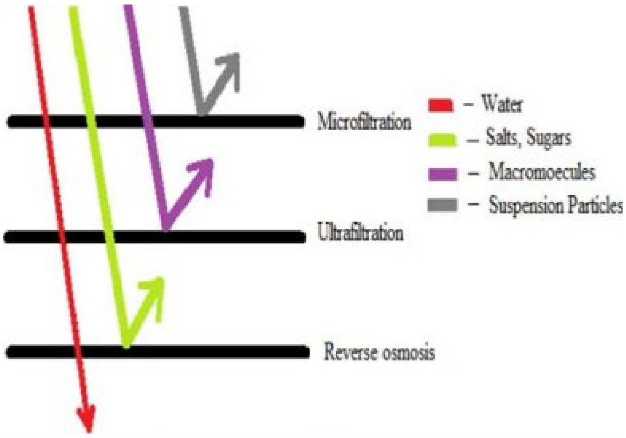

Fig. 2. Use of membrane systems to separate of different sized molecules

(polymeric membrane) and the other one is inorganic membrane (ceramic membrane). Membranes are made from different materials based on the application. They are manufactured in different forms to produce optimal hydrodynamic conditions for separation. Complete systems comprise arrangements of modules and control systems needed to integrate them into the various process configurations.

Polymeric membranes

Polymeric membranes are drawn the attention for its use in many applications such as wastewater treatment, food industries, etc., Due to its pore forming mechanism in a straightforward manner, higher flexibility, low installation cost and low manufacturing cost, the polymeric membrane turned the attention. Some important criteria (good filtration flux, low energy consumption) are considered in a selection of membrane to get a high quality [10]. Though, polymeric membrane has many advantages, it has some challenges such as relationship between selectivity and permeability and its resistance for the membrane fouling [10].

Polymeric membranes are very competitive in both performance and cost wise. The polymers must exhibit appropriate properties for specific applications. They offer low binding affinity in case of biotechnology applications. They show good fabrication properties for that fabricating process. The polymeric materials used for making into membrane are cellulose acetate, cellulose nitrate, polyamide, polysulfone, polycarbonate, poly (ether sulfone), polyimide, poly (vinylidene fluoride), polyacrylonitrile (PAN), polyphenols, polytetrafluoro-ethylene, etc., These membranes have many applications such as effluent filtration, dialysis, pervaporation, gas separation, etc., [11].

Advantages of polymeric membranes:

- They have excellent heat resistance and chemical compatibility [12],
- They have good mechanical properties and high modifying abilities [73-78]. Disadvantages of polymeric membranes
- It suffers from biofouling, mineral scaling, abrasion, metal oxide fouling,
- It has low stability and low rejection [6, 13].
- They have low surface hydrophilicity, low porosity and low permeability [73].

Ceramic membranes

Ceramic membranes are used in water treatment, fermentation industries, food industries, dairy industries, paper industries and petrochemical industries. The out promising advantages of ceramic membranes are extended lifetime, constant quality, excellent separation ability, reduced energy requirements, high permselectivities. The disadvantages of ceramic membranes are higher density, higher production cost, lower surface area per unit volume, complicated synthesis process [16].

The materials used for the preparation of ceramic membranes are alumina, zirconia, silica and titania [24]. Ceramic membranes consist of three layers.

Inner porous support layer-provides good mechanical strength. Intermediate layer-coated upon support layer and has lower pore size. Top layer-separation takes place Based on structure. Ceramic membranes can be classified as porous and dense membranes. The porous membranes may be symmetric or asymmetric. Asymmetric configuration gives high permeability property [23]. Ceramic membranes are prepared in various geometric configurations – plate and frame, tubular, capillary, hollow fibre [19].

Advantages of ceramic membranes [14]

1) They possess extremely high chemical, thermal, mechanical and physical stability.
2) Long working life.
3) Good separation characteristics.
4) Ecologically friendly
5) No additives are required
6) No phase transformation
7) Running costs can is less
8) They have high abrasion resistance.

Disadvantages of ceramic membrane [14]

1) Production cost is little high.
2) Low membrane surface area.
3) High density when compared with polymers.
4) Fabrication process is complicated

Mixed matrix membranes

To overcome the drawbacks of polymeric membranes, the novel technique with high stability and high ions rejection was developed. Mixed Matrix Membranes (MMM) consist of organic and inorganic particle phases. In this continuous phase is polymeric phase and dispersed phase is inorganic particles.

Mixed matrix membranes have higher selectivity, permeability. MMMs improve the mechanical [51], thermal [52], magnetic [53], and electrostatic [54]. So generally, to improve hydrophilicity in the polymeric membrane surface modification, hydrophilic polymer coatings, grafting, composite structure formations can be done. In the recent days the MMM is widely used in the gas separation process, textile effluent treatment, oil removal, desalination, etc..

Membrane Fabrication Methods

Polymeric membrane

The selection of method for the fabrication of membrane is highly dependent on the type of polymer and the geometry of the membrane to be designed. The methods commonly used for fabrication are [6]

- Phase inversion
- Interfacial polymerisation
- Stretching
- Track – etching
- Electrospinning

Phase inversion

This process is also known as de-mixing process. Here, the homogeneous polymer solution is transformed from liquid state into solid state in a controlled manner [13]. This transformation involves five ways [55]:

a) Immersion precipitation
b) Thermally induced phase separation
c) Evaporation induced phase separation
d) Vapour induced phase separation

Among these immersion precipitation and thermally induced phase separation methods are the most commonly used methods [11, [56].

Interfacial polymerization

It is a common method for the fabrication of thin-film composite (TFC) membranes for nano-filtration and reverse osmosis. The first interfacially polymerised thin-film composite membrane was developed by Cadotte et al. [57] and they are used for many RO and NF applications [58].

Stretching

This method is suitable to produce microporous membranes which are commonly used in applications such as microfiltration, ultrafiltration, etc., This process is first developed in 1970s. This process does not use any solvent. The polymer is heated above its melting point and extruded into thin films. Then it is stretched to make it porous [59-61].

Track-Etching

Here, irradiation of a nonporous polymeric membrane using energetic heavy ions. This leads to the formation of damaged tracks linearly in the irradiated polymeric film. This technique is more advantageous for its control on the pore size distribution [62].

Electrospinning

It is a new technique where a drop of polymer is made into a liquid jet by applying a high potential between the droplet and the ground collector. The droplet gets converted into liquid jet when the potential becomes greater than the surface tension of the droplet [63-65].

Ceramic membrane

The steps involved in the synthesis of ceramic membranes are, suspension preparation, forming and heat treatment.

There are various methods available for ceramic membrane synthesis. They are slip casting, sol gel, dip coating, extrusion, pressing, anodic oxidation, solid state process, pressing, tape casting and freeze casting [16]. The required membrane structures and the application are the major considerations for the selection of appropriate membrane preparation method.

Slip casting method

The most common method for ceramic membrane fabrication is the slip casting method. Fig. 3 shows the schematic diagram of slip casting method. The major disadvantages of this method are that the control of wall thickness is difficult, and it requires long time. The mold is filled with powder suspension and the diffusion of solvent into pore takes place. Hence gel formation occurs by precipitation followed by rapid condensation to prevent the penetration of particles into pores [17, 18]. Some of the membranes prepared by this method are alumina [19], zirconia [20], and perovskite [21], $BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ [22].

Sol gel

Sol gel is an important method for synthesis of ceramic membranes. This method gives a good control over the pore size and pore size distribution. They are of two categories – colloidal route and polymer route [16].

In colloidal route, the hydrolysis of dissolved metal alkoxide in alcohol is done by addition of acid or water. Maintaining the precipitate formed as a hot solution for long time results in stable colloidal solutions. It is then cooled and coated on the support surface followed by sintering process [23, 24]. His route is mainly used for the synthesis of silica [25, 26] and alumina membranes [27].

In the polymeric route, partial hydrolysis of metal alkoxides dissolved in alcohol is done by addition of excess of water to for inorganic polymer. The polymer formed is coated on the surface, dried and sintered [28]. This procedure is adopted for the manufacturing of titania [29] and zirconia membranes [30].

Dip coating

Thin membranes can be obtained by this method [16].

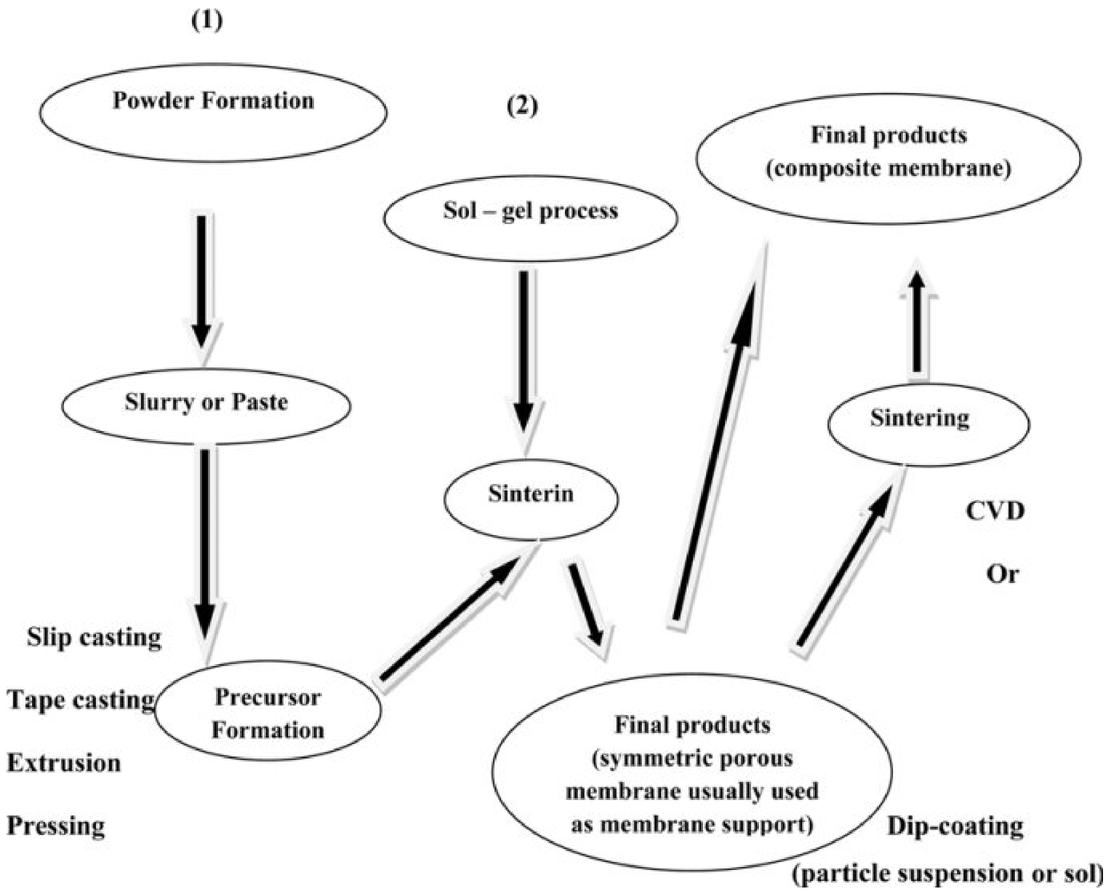

Fig. 3. Slip casting method.

This method involves the dipping of the supports in the sols followed by drying and calcining. This method is utilized in the preparation of silica membranes [25], alumina membranes [33, 34], titania [30], zirconia [35].

Extrusion

It is importantly used for production of ceramic tubes. A paste is formed by mixing raw materials. A mould is extruded from the paste, dried, calcined and sintered. The preparation of porous alumina ceramics by extrusion method is carried out using poly vinyl acetate as pore former. The remaining solvent is evaporated [36]. Usually, the diameter of the membrane formed is greater than 2 mm and the thickness is greater than 0.5 mm [16]. $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d}$ hollow fibre membrane synthesis by extrusion method involves EDTA –citrate complex as starting powders [37].

Freeze casting

This process involves the formation of slurry with ceramic powders, dispersant and deionised water. Then, it is poured in the mould and solidified. After complete solidification, specimens are lyophilized and dried. Finally, they are sintered. This procedure was adopted for the synthesis of yttria – stabilized zirconia membranes [38]. Freeze casting method is also employed to fabricate porous tubular mullite membranes [39]. Maintenance of constant cooling rate in this method produces porous alumina membrane with improved mechanical properties [22].

Mixed matrix membranes

According to recent study, wet phase inversion method was suggested to prepare the MMM [73, 74, 78]. Common procedure for preparing MMM is:

1. Polymer solution was prepared by dissolving the required amount of polymer in N- methyl-2-pyrrolidone (NMP) solvent.
2. Mixture should be stirred for 24 h at 60 °C to get a homogeneous polymer solution.
3. Desired amount of Inorganic material dispersed in NMP will be added.
4. Mixture should be stirred for 24 h at 60 °C to get a uniform dispersion of inorganic material in polymer solution.
5. This casting solution will be deposited on a clean glass plate pasted with adhesive material on both sides.
6. Glass plate will be allowed at room temperature for 30s and then it will be immersed in the non solvent bath until the complete phase inversion.
7. After complete phase inversion, the membrane will

be peeled, washed thoroughly with water.
8. Clean membrane will be stored in slightly chlorinated distilled water.

Polymeric, Ceramic and Mixed Matrix Membranes – An Overview

Polymeric membrane

Polyamide membranes being hydrophilic material do not require a wetting agent. This membrane is mainly used for microfiltration and reverse osmosis [66].

Polyimide has excellent heat resistance; chemical compatibility and resistance over wide range of pH are widely used in high temperature fuel cells and separation membranes [74].

Polysulphone membranes were more commonly used in the process of ultrafiltration of wastewater because of its mechanical robustness and chemical and structural stability. Since it is a low hydrophilic in nature, it is modified by blending it with SiO_2, ZrO_2, and TiO_2 which are hydrophilic nanoparticles to increase its hydrophilic properties. This blending process improved the separation performance of the membrane, its thermal and chemical resistance and its adaptability to wastewater environments [67].

PVDF (Polyvinylidene fluoride) membranes were used in wastewater purification and desalination in many trials. It has the advantage of good separation performance and mechanical stability. Qi Zhang et al. [68], fabricated membrane with PVDF and PVC (Polyvinyl Chloride) by phase inversion method. The polymer ratios were varied as 1%, 5%, 10%, 20%, and 50% and its influence on the structure and performance of the membranes were investigated. Among these, the membrane with 5% of PVC had high porosity, high break strength and water flux. The membrane with small wt% of PVC had better performance and increased the applications of PVDF [68].

Cellulose acetate is one of the first polymer membrane used for separation process and is used in both RO and UF applications. This material is generally used because it is naturally available, has high mechanical strength and it has high hydrophilic property. R. Saranya et al. [93], used the composite membrane of chitosan and cellulose acetate membrane for the removal of copper ions from the wastewater. It showed a retention of 81.03% for copper ions. The results of the studies carried out with Cellulose acetate is the one of the most important polymeric material [69]. It is having high hydrophilicity and easy processability. But it was having excessive fouling, lower pH, and thermal stability.

Ceramic membranes

Silica membranes

Silica membranes showed higher permeability with small molecules. Silica membranes can be prepared with low defect concentrations [31, 32]. They were employed for energy efficient separation processes under industrial conditions. They were also used for dehydration and hydrogen process [40]. When compared to other oxides such as alumina, zirconia and titania, silica involves easier preparation as ultra or microporous thin layers. Unsupported silica membranes prepared from the sol obtained by hydrolysis with acid catalyst and condensation of tetra ethyl ortho silicate followed by calcination is microporous in nature and showed a significant permeability to helium and hydrogen. At the same time, the permeability of N_2, Ar, O_2, C_3H_6, C_3H_8, nC_4H_{10}, $i\text{-}C_4H_{10}$ was very small. At 303 K, hydrocarbon permeation was 2 times that of helium [26]. Hydrophobic nature is being observed from the silica membrane prepared by the repeated dip coating of supported γ-alumina membranes in silica sol solution followed by drying and calcining. Hydrophobicity was due to the added methyl tri ethyl silicate. The obtained membrane has a pore diameter of 0.7 nm and a thickness of 60 nm. The hydrophobicity was 10 times more than that of ordinary silica membrane [31]. A double layered silicate coated membrane on γ-alumina was synthesized by sol gel dip coating using surfactant template silica as intermediate layer. Cheong et al., 1999 stated that the dual layered membrane showed improvement in flux and stability [25]. Sols were prepared from tetra ethoxy silane and octyl$^-$, dodecyl$^-$ and octadecyltriethoxysilane to fabricate silica membranes on γ-alumina coated α-alumina tube. Micropores were obtained in size range of 0.3-0.4 nm when calcined at 600 °C. Mesopores formed during the gelation step [42].

Alumina membranes

Alumina membranes have been used for both liquid and gaseous separations [43]. The alumina membranes had high resistance to temperature, pressure, oxidation, solvents, hot acids and caustic solutions [44]. They are back flushable and can be sterilized by steam [19]. It has an excellent thermal, chemical and mechanical strength [17]. Non supported mesoporous γ-alumina membrane prepared from boehmite sols were with a pore radius of 2.2. nm when calcined at 600 °C. Membranes with α-alumina support were with a pore radius of 2.5 nm [27]. Supported -alumina membrane were prepared by dipping into boehmite sols also observed that the layer thickness decreased with increase in the pore size of the support [33]. Mesoporous γ-alumina membranes on cordierite honeycombs were prepared by the method of dip coating into boehmite with addition of HNO_3 to bring the pH to 4.0 [34]. Preparation of alumina membranes from aluminium secondary butoxide reveals that the transition of 7-AlOOH to 7-Al_2O_3 takes place at 390 °C [33]. γ-alumina nanofiltration membranes with pore diameter greater than 5 nm were prepared from boehmite at low sintering temperature of about 540 °C. Boehmite can be obtained by the precipitation of complete hydrolysis of aluminium alkoxide [45].

Titania membranes

Titania membranes have unique structure and surface properties. Titania membranes show high resistance towards corrosion at strong acidic pH [46]. Titania membranes when calcined at high temperatures results in phase transformation to anatase and hence the structure collapses. Sekulic et al., 2004 reported that the membranes were of high chemical stability at wide pH ranges [29]. Titania membranes exhibit higher permeability to propylene. Asymmetric titania membranes were prepared by wang et al., 2008 from stable titania suspensions with a pore size in the range of 0.1-0.12 microns [46]. He used sol gel technique for the synthesis of titania nanofiltration membranes. Membrane with top layer of anatase – TiO_2 fired at 300 °C is with low crystallinity and at a pH of 2, the molecular weight cut off increased to 800 from 200 [35]. Microporous titanic membranes layers of pore size lesser than or equal to 0.8 nm are synthesized on mesoporous γ-alumina and titania/zirconia coated substrates by polymeric sol gel route [29]. Non supported titania membranes were prepared by dip coating in colloidal dispersions of titania. Supported titania membranes are prepared by slip casting with the same solution. The membrane is of 3-6 micron thick and with an average pore diameter of 3-4 nm [30].

Zirconia membranes

Zirconia membranes show higher rejection rates towards polyvalent ions and lower rejection rates towards monovalent ions [47]. Zirconia membranes possess superior stability in aqueous solutions [48]. At low and high pH values, zirconia membranes were preferred due to its chemical stability under these conditions [35]. Yttria stabilized the zirconia membranes prepared from polymeric sol gel method with zirconium tetra-n-propoxide and yttrium nitrate. The chelating agent used here is acetylacetone [49]. Yttria stabilized zirconnia membranes prepared by freeze casting method has a compressive strength of 23.57 to 63.86 MPa and they exhibit non catastrophic failures [38]. Nanofiltration zirconia membranes prepared by sol gel technique from synthesized zirconia sols were having average particle size of about 8.6 nm [50]. Membranes with molecular weight cut off less than or equal to 300 for nanofiltration and per evaporation purposes were produced with α-alumina support prepared by slip casting method, yttria doped zirconia interlayer and zirconia top layer prepared by dip coating method [35].

Mixed Matrix Membrane (MMM) – A Novel Separation Technique - Application

MMM-desalination

The freshwater resources are getting dried. Water desalination has been increased and got an important role in supplying freshwater [70-72]. In the todays trend, the polymeric membrane is preferred for the filtration more than the conventional treatment to get better salt rejection and high-water flux. But in all the polymeric membrane processes the water flux was stated as low due to low permeability. Currently, polymeric, ceramic and mixed matrix membranes are used in desalination. Polymeric membranes are widely used in this field. Bio-fouling, poor thermal and chemical stability are the main challenges for the polymeric membrane. Ceramic membranes show excellent thermal and chemical stability that make them a possible alternative to be used in water desalination process.

Combination of polymer with inorganic such as Graphene, carbon nanotubes and various nano particles such as silica, titania and zirconia MMM were produced to improve the performance of membrane. Low loading rate, poor dispensability, hydrophilicity are the major issues in the MMM. In the membrane filtration polysulfone based membranes were used. It had good resistance over the wide range of pH. But it was having the hydrophobic nature. By improving the hydrophilic nature of the membrane, the productivity will be increased. The blending of the polymer with hydrolysed poly isobutylene-alt-maleic anhydride is the promising method to improve the hydrophilicity [3]. High salt rejection and good hydrophilicity can be achieved by blended polymer membrane with surface midified poly isobutylene-alt-maleic anhydride [4]. Functionalised inorganic material in the membrane preparation also gives the increased hrdrophilicity [5, 6]. Mainly polysulfone (Psf), polyether sulfones, poyimides, polyamides were used in the MMM preparation [74].

Graphene oxide, Titania, silica and zirconia nanoparticles Iron III oxides were used with polymeric membrane to improve the hydrophilicity [2-5]. Ionic strength and pH of the solution also can induce agglomeration between nanoparticles. These materials absorb very easily the hydroxyl groups (OH^-) and they have high surface area and a very good antifungal and antibacterial materials.

Bo Feng et al., 2017 used nanohybrid graphene oxide (GO) and polyimide (PI) in the MMM preparation [74]. B.M Ganesh et al., 2013 used the GO and Psf (polysulfone) for the MMM preparation [73]. Javed aslam et al., 2013 used polyether sulfone with iron oxide nanoparticles [78]. A derivative of graphene containing oxygen rich functional groups leads the high hydrophilicity and high water permeability in the membrane. In this GO has the strong interaction with polymer chain. Mechanical strength, stability, water permeability, antifouling and salt rejection can be improved. Wet phase inversion method was used for the MMM preparation in this work.

B.M Ganesh et al., 2013 [73] used the GO and Psf in the MMM to enhance the hydrophilic nature of the membrane. Wet phase inversion method is used for the membrane preparation. He mentioned that the salt rejection depends on pH. If the pH increases, the salt rejection will be increased. Polysulfone based membranes are used because of its excellent heat resistance, Chemical compatability and have good resistance over the wide range of pH. Blending Psf with hydrolysed poly isobutylene-alt-maleic anhydride increases the hydrophilicity. GO is preferred due to its high surface area. GO is used due to its outstanding electron transport and mechanical properties, hydrophilic and pH sensitive behavior. In this after GO doping the salt rejection was increased.

Polyether sulfone is used by javed aslam et al., 2013 for the MMM preparation for desalination processes [78]. PES has high glass transition temperature, thermal and chemical stability. In this he doped the PES with iron III oxide nanoparticles. 15% Fe_3O_4 membrane gives the highest pure water flux, 10% Fe_3O_4 provides 10% salt rejection.

MMM – Dye removal from textile industry effluent

Among the several separation techniques (impaction, diffusion, adsorption and electrostatic interaction) [5], the dye component of the textile effluent can be removed by adsorption. The combination of adsorption and membrane filtration is generally suggested for the textile effluent treatment to enhance the membrane filtration. More number of research works are carried out with activated carbon as an adsorbent material [85-88] due to its large surface area [89] surface chemical deposition. The effect of Activated Carbon on polysulfone and Polyether sulfone has been studied thoroughly by Kusworo T.D. et al., 2010 [91] and Ballinas et al., 2004 [90] in their studies. With this Nanoparticles are also used to improve the hrdophilic nature, filtration efficiency of polymeric membrane. Nanoparticles of Iron oxide and Zero valent iron (ZVI) has high surface area [92]. R.saranya et al., 2013 carried out the experiment with Cellulose acetate+Activated carbon and Cellulose Acetate+Iron Oxide combination [93]. They synthesised the different membranes and tested the filtration efficiency. High pure water flux was achieved with the addition of 2.5%Activated Carbon and 0.5% Iron oxide addition. They concluded that the addition of Activated carbon Activated carbon influences the membrane permeability and Iron oxide not. High rejection efficiency was obtained with no compromise in membrane permeability.

R.saranya et al., 2015 [94] used green synthesized zero valent iron for the textile effluent treatment. They used ZVI for polymeric membrane modification. The synergistic effect of permeation and adsorption increases the use of ZVI/CA mixed matrix membrane for the textile effluent treatment. Cellulose Acetate membrane was prepared with different mass fractions of 0.5, 1.5 and 2.5 wt% of ZVI. Pure water permeability was increased with 0.5% of ZVI nanoparticles addition. Physisorption was happened with this filtration.

MMM – Phenol and phenolic compounds removal

Most of the chemical industries particularly petro-chemical industries produce phenol and phenolic compounds which is very toxic and carcinogenic [79, 80]. Continuous exposure to phenol gives eye irritation, skin allergies, Mucous, headache, high blood pressure, liver and kidney damage. Mixed matrix membrane is the better option to remove Phenol from the effluent. RO membrane [81], Ultra filtration [82] and nanofiltration are generally used in the phenol removal. A novel technique, Nanoparticles doped MMM was nowadays suggested as a better option to improve the removal percentage. Mixed matrix membrane of granular alumina and Cellulose Acetate shows flux enhancement [83]. Raka mukherjee 2014 [84] used doped alumina with Cellulose Acetate Pthalate by phase inversion method. Various concentrations membranes are prepared. 20 wt% alumina concentration membrane increases the porosity and permeability.

MMM – Proteins removal

Generally polymeric membrane with sulfone polymer [75, 76], polysulfone, poly phenyl sulfone is used in the separation processes. Polyethyl sulfone has the better properties than the polysulfone and polyether sulfone [77]. Lawrence Arokiasamy dass et al., 2017 [78] fabricated the sulfonated polyphenyl sulfone and Titania nanoparticles by phase inversion method. With the 25.5% wt% the attained flux rate was high. Thermal and mechanical properties also increased. Antifouling properties of MMMs were enhanced. They concluded that fuctionalised nanocomposite hollow fiber MMM will be the better promising membrane for the proteins removal.

MMM – Oilfield wastewater removal

Large quantities of oilfield wastewater are produced in onshore and offshore exploitation. According to API 18bbl of produced water were generated by US onshore operations in 1995 [96]. Oilfield produced wastewater creates major environmental iisues [97]. Oil drilling produces large quantity of wastewater. Skimmer is the general conventional treatment [98]. Polymeric and Ceramic membrane are used in the removal of oil [99].

Conclusion

The necessity of the treatment of water was discussed in this paper. In this paper, conventional treatment methods were discussed. Also, particularly different types of membranes based on materials and pore size and the factors affecting the Membrane processes were discussed. The mixed matrix membranes are the combination of polymeric and ceramic membranes. This MMM's hydrophilicity improving techniques were reviewed. Application of Mixed Matrix Membrane was also thoroughly investigated. So that Mixed Matrix

Membrane can be suggested as the novel technique in the water and wastewater treatment. The future work can be carried over with different material composition and with different inorganic particle size composition to study the performance behavior and other characteristics. Also, the work can be carried over with the derived inorganic and organic materials from waste material so that the cost of the membrane will be reduced. The wastes can also be recycled and reused.

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