Chapter-2

Literature Review

Commercial membranes were initially constructed of cellulose, ethyl cellulose and cellulose acetate. The materials for these membranes could be found in nature, and so were economical. Unfortunately, they had low chemical resistance but the industries require such membranes that could be used under stress and in difficult conditions. In the last 20 years, researchers have focused on preparation and large scale production of synthetic membranes for use in both the industrial and domestic environments. These membranes can be constructed using organic material e.g. polymers or inorganic material e.g. ceramics. Polymeric materials have the advantage of higher mechanical strength, chemical stability and flexibility. Regardless of the membrane materials used, the general aim of researchers and technology is to produce membranes with high permeability, low fouling, high flux recovery, stable flux and excellent rejection of foulant materials.

In this chapter, we have summarized the work of various researchers of recent years who have contributed significantly to improve membrane performance and antifouling nature by physical blending of modifiers to base polymer with surface segregation. Different types of modifiers are blended with membrane matrix during membrane preparation. These modifiers are of different categories and used for enhancement of specific property of membrane to improve overall membrane performance. The main three categories of modifiers viz. **nanofillers, copolymer** and **pore former** have been outlined in this chapter.

2.1 Membrane modification by nanofillers

Khakpour et al., 2019 prepared Polyvinyl chloride based composite membrane with graphene oxide-nanodiamond (GO-ND) by phase inversion method and characterized the membranes by XRD, FTIR, FESEM, AFM and Raman spectroscopy. Researchers also performed various tests for pure water flux, contact angle, abrasion, elongation and tensile strength. To counter the problem of agglomeration of nanodiamond particles in membrane, graphene oxide was introduced. It was found in results that addition of GO-ND improved the hydrophilicity and surface roughness and pure water flux was also increased. It was 2.2 times higher for 0.15 wt% composite membrane as compared to neat polyvinyl chloride membrane. Tensile strength and abrasion resistance were also improved because of uniform dispersion of inorganic nanoparticles throughout membrane matrix.membranes was further used to filter BSA solution and highest rejection was observed for 0.10 wt % of GO-ND composite membrane.

Mohammadnezhad et al., 2019 developed ntifouling PVC membranes with improved hydrophilicity by doping lignin into PVC by Yong et al. Lignin is usually a waste material from paper industries that possess valuable hydrophilic groups which attracted researchers to utilize it for increasing hydrophilicity of polymeric membranes. PVC/lignin composite membranes were prepared by phase inversion technique and characterized by XPS, XRD, FTIR, SEM and DSC. Membranes were used for separation of oily wastewater. Results obtained by SEM, DSC and XRD verified the compatibility between lignin and PVC. The contact angle of composite membranes decreased till 41.53^{O} and improved the hydrophilic nature of pure PVC membrane which had 106.73^{O} contact angle. Permeation flux through composite membrane was also observed very high almost 2.5 times of pure PVC membrane. Porosity was also increased by upto 84.9% for 0.5 wt % composite membrane. Fouling was also reported to be low for modified membranes with improved hydrophilicity (Yong et al., 2019)In another study, Mohammadnezhad et al. used nanocrystalline Ce (III) metal-organic framework $[Ce(tp)\ (NMP)_2(CH_3COO)]_n$ to modify polyethersulfone composite membrane. The composite PES membrane was fabricated using solution casting by phase inversion method and characterization techniques involved were SEM, AFM, powder XRD, FTIR, BET, water contact angle and porosity analysis was done to study the change in membrane properties. Membranes were used for removal of Direct Red 16 dye from aqueous solutions. Modification of membranes, improved the pure water flux, porosity and pore size of membrane. Surface hydrophilicity of composites was also increased which in turn enhanced the antifouling properties of membrane. Filtration experiments revealed that all the composite membrane showed better performance than pure PES membrane and membrane-embedded with 0.5 wt% nanoparticles had the highest porosity,water flux and good antifouling nature.

Lakhotia et al., 2019 investigated the effect of ferrous oxide (FeO) nanoparticles on the polyethersulfone (PES) based membrane. Membranes were prepared by pre-seeding interfacial polymerization. Two different concentrations of nanoparticles were used to fabricate composite membranes and then further characterized by different instrumental techniques like SEM, AFM, XRD and FTIR. Polyethylene glycol (PEG) with M.W. 1500 Da was used as a solute to check the separation performance of the modified membranes. The highest rejection of 90% was observed by nanofiltration experiments. Composite membranes were further used for the separation of various salt solutions of $CaCl_2$, $MgCl_2$, $C_6H_5Na_3O_7$, Na_2SO_4, NaCl. The increased concentration of nanoparticles in composite membranes showed improved surface charge (−6.27 to −14.21 mC/m^2) and hydrophilicity (84.7 to 49.6°). Flux was improved almost 1.33 times from 27.46 to 36.85 L/m^2h and rejection was reported more than 90% for modified membranes. Flux recovery ratio was calculated to define the antifouling nature of membranes and these values showed that fouling was reduced in nanoparticles embedded modified membranes.

El-Gendi et al., 2018 proposed a novel cellulose acetate based membrane that is modified with a composite of graphene, silver nanoparticles and copper nanorods and termed as CA/G/Ag–Cu membrane. The composite membranes were prepared by solvent casting method using acetone as a solvent and dispersing composite of graphene/silver/copper at 18°C. Characterization of membranes was further done by XRD, SEM and TEM. To study the performance of membranes, these were used for separation of aqueous salt solutions of sodium chloride. Gram +ve and Gram −ve bacterial test organisms technique were used to study the effect of nanoparticles on biofouling. Composite membranes showed antibacterial activity while pure membrane did not have any antibacterial activity and bacterial growth was found on membrane surface. Higher water flux and rejection were observed for composite membranes infiltration experiments. Composite membranes containing 0.03 (Ag + Cu:1:1) wt% showed best results at 25 bar.

Bagheripour et al., 2018 utilized graphene oxide/chitosan (GOC) nanoplates for the synthesis of polyethersulfone composite membranes with superior hydrophilicity and antifouling properties. Chitosan was modified by GO first using surface modification technique and then further used to change membrane structure. Membranes were further used to separate the sodium sulphate and chromous sulphate solutions. SEM analysis verified the proper distribution of nanoplates across membrane. Chitosan has higher hydrophilic active sites. Therefore a significant improvement was observed in water flux, hydrophilicity and rejection of GOC modified PES membranes. 1 wt % composite membrane showed best performance.

Mishra et al., 2018 have prepared halloysite nanotubes (HNTs) embedded poly(vinyl chloride) ultrafiltration (UF) membrane (PVC/HNTs) and examined the changes in membrane properties by SEM, EDX, FTIR, TEM and SPM. Non-solvent induced phase separation method was used for preparation of composite membranes and three different samples of 1, 2 and 3 wt% were prepared. Membranes were further used for separation of BSA solution and sewage water to study the performance. SEM results showed that nanofiller halloysite nanotubes were dispersed properly in membrane structure and finger-like pore structure was created across the membrane. Tensile strength and elongation at break were also increased for composite membranes. Pure water flux was increased by 70% for composite membranes as compared to pure membrane. Flux recovery was increased for composite membrane upto 92.1% and rejection rate was 93% for BSA filtration. EDX mapping also verified the proper dispersion of HNT into the membrane surface. SPM results showed that surface roughness was less for composite membranes.

Behboudi et al., 2018 used silver nanoparticles and silica modified silver nanoparticles as nanofillers for modification of polyvinyl chloride membrane. PVC based hollow fiber membranes were synthesized by the wet spinning method and silver/ silica nanoparticles were prepared by Stober method. Prepared membranes were characterized by FESEM, EDX and FTIR. Various tests were also conducted to study the change in properties like contact angle, pure water flux, mechanical strength and antifouling nature of composite membranes. SEM results revealed that there was no significant effect of different types of nanofillers on the morphology of hollow fiber membrane and all the membranes had similar asymmetric structures. The proper dispersion of nanofillers was verified by EDX analysis. Since hydrophilicity varies by hydroxyl groups present in the membrane structure, silver/silica-based membranes showed higher hydrophilicity than silver based composite membranes. In comparison to silver nanoparticle embedded membranes, modified silver nanoparticles based composite membranes showed better hydrophilicity, water flux and strength. Finally 1.5 wt% modified silver nanoparticles based composite membranes had shown the best performance and antifouling properties.

Zhang et al., 2018 employed a salt coagulation bath to increase the properties and morphological structure of PVC /Pluronic F127 membranes. The modified membranes had no macro voids. Porosity, hydrophilicity and permeate flux were significantly high for modified membranes. Prepared membranes were further characterized by FESEM, XPS, AFM, contact angle test to study the change in morphology, chemical compositions, roughness and hydrophilicity after modification.

Wu et al., 2018 used a simple approach to synthesize the quaternizated polyvinyl chloride (QPVC) membranes. For this, PVC hollow fiber membranes were soaked in trimethylamine solution and then further characterized by FTIR, NMR, TGA, XPS and zeta potential test. Grafting of quaternary ammonium group was verified by FTIR, NMR and TGA. By this reaction, the surface of membrane gets positively charged and thus, hydrophilicity of membrane surface was increased. Mean pore size got smaller which in turn results in improved rejection rate and permeability. After quaternization, antibacterial properties of membrane were also improved.

Nasseri et al., 2018 worked on developing a cost-effective method to remove Bisphenol A (BPA) contaminant from water sources. For this, a polysulfone based membrane was prepared using graphene oxide nanoparticles as surface modifiers. Membrane with 0, 0.4 and 1.0 wt % of graphene oxide were prepared by phase inversion method. To study the surface roughness, porosity, zeta potential and functional groups of composite membranes, these were characterized using FESEM, AFM, ATR-FTIR and streaming potential test. Incorporation of nanoparticles enhanced the hydrophilicity of membrane surface and improved the permeate flux. Pure water flux increased almost 2.5 times and had values of 512 L/m^2 h for 1.0 wt % composite membranes as compared to pure polysulfone membrane. Highest BPA rejection upto 93% was observed using 0.4 wt% composite membrane by optimizing operating conditions such as pressure, initial concentration of contaminant,operating time and pH by response surface methodology.

In another study Nasrollahi et al., 2018 prepared novel polyethersulfone (PES) based composite membranes by incorporating CuO/ZnO (CZN) nanocomposite within membrane structure by solvent-induced phase separation method. SEM, AFM, EDX techniques were applied to analyze the prepared membranes. SEM results showed asymmetric pore structure and composite membranes of nanoparticle upto 0.2 wt % had finger-like pore structure and as the nanoparticle concentration was increased, macro voids formation took place and due to agglomeration porosity of membranes decreased. The homogenous dispersion of nanoparticles was presented by EDX analysis. AFM images showed that roughness was decreased in composite membranes. Membranes were further used for separation of BSA solution and 0.2 wt% composite membranes showed best permeability and anti-fouling properties. BSA rejection was more than 95% and high flux recovery ratio of 50.1% was observed for composite membrane.

Kuvarega et al., 2018 prepared a hybrid multifunctional composite membrane which can be used for filtration as well as photocatalysis. Polysulfone based membranes were synthesized by phase inversion technique using N,Pd co-doped TiO_2 as nanofiller and utilized for degradation of eosin yellow dye under visible light irradiation. The prepared membranes were characterized by FTIR, NMR, SEM, EDX, XRD, AFM and contact angle test. TiO_2 embedded composite membranes showed improved porosity, hydrophilicity and visible light activity. 7 wt% composite membranes showed the best performance and degraded 92% eosin yellow dye during 180 min irradiation.

Demirel et al., 2017 synthesized a novel organic and inorganic mixed matrix membrane using polyvinyl chloride as base polymer and ferrous oxide nanoparticles as bulk modifiers by phase inversion technique. Different analytical and instrumental methods like SEM, AFM, contact angle goniometer, nanoindenter and dynamic mechanical analyzer (DMA) were utilized to study the changes in the surface. Membranes were further used to separate sodium alginate solution. SEM images revealed that composite membranes have more elongated finger-like structure and higher porosity. Nanoindentation experiments verified that hardness of membrane was enhanced with incorporation of nanomaterial. Nanomaterial loading higher to 1% caused nanoparticle agglomeration, which resulted in decline of membrane performance. 1% Fe_2O_3 composite membrane rejected more than 91% model foulant and showed improved antifouling properties.

Jhaveri et al., 2017 synthesized a low-cost anti-fouling membrane using polyvinyl chloride as base polymer, polyvinyl pyrrolidone as pore former and GO-TiO_2 nanosheets as nanofillers. Membranes were prepared by non-solvent induced phase separation method and characterized further by SEM, EDX, TEM, XRD and AFM. Humic acid was used as model foulant to study the performance of blended membranes.It was observed in filtration experiments that blending of nanosheets improved the permeate flux. However rejection of model foulant remained same for composite membranes and pure PVC membrane and it was above 98 % for 0.25 wt % nanofiller composite membranes. Membrane morphology was analyzed by SEM results. EDX and XRD analysis were done to confirm the presence of nanosheets in membrane structure. However experiments showed some rejection in flux recovery of composite membranes which is unexpected output in the study.

Behboudi et al., 2016 worked on preparing polyvinyl chloride based antifouling membranes by adding titanium dioxide nanoparticles to the membrane structure. Membranes were synthesized by non-solvent induced phase separation technique and further characterized by FESEM and contact angle test. Filtration experiments were performed using BSA solution to check the performance of membranes. FESEM results revealed that all the composite membranes had sponge-like pore shape and as the nanoparticles amount increased, pore numbers and size were also increased. However agglomeration was observed for composite membranes having 2% nanofiller. Hydrophilicity and water flux of composite membranes increased with presence of nanoparticles. Abrasion test with silicon carbide slurry was performed and it was observed that addition of TiO_2 had a negative effect on composite membranes. Membranes were used to filter BSA solution and it was found that flux recovery was higher for composite membranes and fouling was decreased. The rejection rate of BSA was low for composite membranes.

Zhao et al., 2016 used graphene oxide to modify polyvinyl chloride membranes. PVC/GO membranes were synthesized with phase inversion method. Membranes were characterized and used for filtration of BSA solution. 0.1 % GO composite membranes showed pure water flux 430.0 L/m^2h as compared to pure PVC membrane that showed 232.6 L/m^2h. Mechanical properties were found very much higher than pure PVC membranes. Graphene oxide has strong hydrophilicity which contributes in improvement of antifouling nature of PVC membrane. 0.15% GO composite membranes showed optimum results and flux recovery was 75.9 %.

Rabiee et al., 2016 used two non-ionic surfactants Tween-20 and Tween-80 to modify the morphology and increase hydrophilicity of polyvinyl chloride membrane. Phase inversion method was used to prepare membranes of different composition of Tween-20 and Tween-80 from 1-7 wt %. Membranes were characterized by SEM and contact angle tests. Pure water and BSA solution were used as foulant to study the performance of membranes. SEM results showed that composite membranes are more porous with macro voids in the sub layer. Hydrophilicity of membranes increased and contact angle test revealed that contact angle decreased to 55 and 58 for 7% Tween-20 and 7% Tween-80 composite membranes. Pure water flux increased with increasing amount of surfactants in the PVC structure. Composite membranes showed high flux recovery and low fouling. An increase of about 30% was observed in flux recovery of composite membranes compared to pure PVC membranes. However, BSA rejection was slightly reduced. Tween-20 composite membranes performed better than Tween-80 composite membranes and showed high water flux, and flux recovery.

Kumar et al., 2016 fabricated polysulfone based composite membranes by blending base polymer with PVP, P(VP-AN) and PVA-grafted bentonite particles. The wet phase inversion method was used for preparation of membranes. Synthesis of polymer grafted bentonite was verified by FTIR, EDX and TGA analysis. SEM analysis, water contact angle test and pure water flux experiments were performed to observe structural changes of membrane surface, hydrophilicity and water permeation through membranes. Filtration experiments were further done to separate oil wastewater. Composite membranes containing 92.0% PSF and 8.0% P(VP-AN)-g-bentonite showed best results. The contact angle was reduced by 47 % and pure water flux increased 6.6 times than pure polysulfone membrane.

Mukherjee et al., 2016 worked on in-situ photo-excitation assisted hollow fiber ultrafiltration for degradation of phenolic compounds. A mixed matrix membrane of polysulfone and titanium dioxide nanoparticles was developed. SEM results demonstrated that hollow fiber composite membranes had finger like pores. ARM analysis showed that surface roughness improved with the higher nanoparticle content. Hydrophilicity of composite membranes increased and contact angle was 45^O for 4 wt% composite membrane as compared to 83^O for pure polysulfone membrane and mean pore size increased from 87 Å to 172 Å. This property positively affected the permeability of membrane and permeate flux improved from 8.8×10^{-11} to 14.4×10^{-11} m/Pa.s, that was almost 70% more than the pure polysulfone membrane. Membranes were used for separation of orthochlorophenol, phenol and meta-nitrophenol and about 87%, 74% and 67% rejection was achieved for respective solutes. Membranes were then tested on steel industry effluent and rejected 75% phenols and showed 96% total solids, 73% TOC and 91% COD reduction.

Jafarzadeh et al., 2015 fabricated a composite antifouling polyethylene membrane by embedding TiO_2 nanoparticles to the membrane structure. Membranes were prepared by thermally induced phase separation (TIPS) method and characterized by DSC, XRD, DMA, TGA, FESEM and EDX to study the effect of nanoparticle on membrane properties. The presence of nanofillers was verified by EDX, XRD and TGA analysis while DSC results showed that with the increase of TiO_2 content, crystallinity and melting point of the membranes were also increased. Mechanical properties of composite membranes were also higher than pure polyethylene membrane. Performance of membranes was evaluated in terms of pure water permeation and humic acid rejection rate.

Yu et al., 2015 prepared a novel low-cost polyvinyl chloride based mixed matrix composite membrane using silicon dioxide nanoparticles (0–4 wt %) to improve antifouling properties of membrane. Membranes were characterized and used for separation of municipal wastewater. Membranes with 1.5 wt% nanoparticles showed the most optimum results. Composite membranes showed higher hydrophilicity, mechanical properties and pure water flux as compared to neat PVC membrane and during separation of municipal wastewater rejected 97.2 % suspended solids, decreased COD up to 82.9 % and total bacteria 93.6%.

Rabiee et al., 2015 modified polyvinyl chloride membrane by adding five different weights of zinc oxide nanoparticles. Membranes were further characterized by SEM, EDX and contact angle tests. SEM results revealed that morphology, porosity and mean pore size of membrane surface was improved. EDX analysis verified the proper dispersion of ZnO nanoparticles across membrane surface. Optimized results were observed for 3 wt% composite membrane. Pure water flux was 213 kg/m^2h for pure PVC membrane and it increased to 402 kg/m^2h for 3 wt% composite membrane. These showed flux recovery of 90% as compared to 69% of pure polymer membrane, indicating antifouling nature of composite membrane. BSA rejection was almost 97 % for 3 wt % membranes.

Rabiee et al., 2014 in another study worked on preparing polyvinyl chloride based composite ultrafiltration membranes and modifying it with titanium dioxide nanoparticles. The convectional phase inversion technique was used to prepare PVC membranes with different TiO_2 dosages. SEM, EDX and static water contact angle tests were performed to characterize the composite membranes. The performance and antifouling nature of membranes were investigated using BSA solution. Results showed that 2 % composite membrane was best among all samples. Higher dosage of nanoparticles caused agglomeration of nanoparticles in membrane and decreased the overall performance.

Maximous et al., 2009 prepared polyethersulfone based antifouling membranes using phase inversion technique and adding alumina nanoparticles as surface modifier. Membranes were further characterized by SEM to study surface morphology of composite membranes. Filtration experiments were done to evaluate membrane performance by separating activated sludge. Composite membranes showed lower flux decline as compared to pure PES membranes. 18 wt% polymer concentration and 0.05 alumina composite membranes showed the optimum results for optimum solvent evaporation time 15 sec. Porosity and hydrophilicity was increased with increasing nanoparticle concentration. Permeability increased 8-12 times in composite membranes as compared to neat PES membrane.

2.2 Membrane modification by copolymers

Wu et al., 2018b also worked on improving the performance and antifouling properties of PVC membranes. Composite membranes were prepared by copolymerization of PVC with amphiphilic copolymer PVC-graft-poly(ethylene glycol) methyl ether methacrylate (PVC-g-PEGMA) in different weight percentage from 5 to 20 % and termed as PVC/PVC-g-PEGMA membranes. NMR and FTIR were used to investigate the success of copolymerization. SEM verified that composite membranes had small pore size and porosity as compared to pure PVC membrane. Pure water flux was increased by 50% for 15 wt% PVC/PVC-g-PEGMA membrane and surface hydrophilicity was increased. Sodium alginate was used as solute to check the performance of membranes and more than 90% rejection was observed through experiments. Flux recovery was improved by 89% for 10 wt % PVC-g-PEGMA embedded composite membranes. All the results support the significant enhancement of antifouling properties and performance of composite membrane.

Wang et al., 2018 fabricated chlorine resistant membranes by using a polyvinyl chloride based copolymer. A novel polymer composite poly(vinylchloride-co-acrylonitrile-co-sodium 4-styrenesulfonate) (PVC-PAN-PSS) was developed by copolymerization and used for preparing membrane by phase inversion method. BSA, Sodium alginate and humic acid solutions were used for examining separation performance of membranes. Biofouling was very low in (PVC-PAN-PSS) membranes as compared to pure PVC and pure PAN membranes. As the amount of poly(sodium 4-styrene-sulfonate) (PSS) was increased in copolymer, the antifouling properties of membranes were also improved. The best performance and antifouling nature were exhibited by 2 wt% PSS membranes. For 2 wt % PSS membranes flux recovery was 86%, 95%, and 99% using different foulants BSA, sodium alginate and humic acid respectively. To check anti-chlorine nature of membranes, these were soaked in 1000 ppm sodium hypochlorite for 168 hours. No change was observed in pore structures and antifouling characteristics of membrane.

El-Gendi et al., 2017 investigated the performance of Polyvinylchloride/cellulose acetate composite membranes for the treatment of Red Sea water through reverse osmosis. PVC/CA blended membrane was synthesized by phase inversion technique using different concentrations of polyvinyl chloride and cellulose acetate. The prepared membranes were characterized using SEM, FTIR and tensile strength test. Prepared membrane showed excellent performance under high pressure up to 50 bar without any cracking issue. SEM results revealed that prepared membranes had an asymmetric structure with dense top layer and porous bottom layer. The composite membrane containing 3% CA and 16% PVC showed best results. Permeate flux and rejection was increased with increasing operating pressure.

Behboudi et al., 2017 worked on synthesizing a polyvinyl chloride based blend membrane after copolymerization with polycarbonate by non-solvent induced phase separation method. Characterization techniques such as FESEM, XRD and DSC were used to membrane analysis. Various tests like tensile strength test, abrasion test, contact angle tests were performed to study the change in physical properties of composite membranes. Membranes were used to separate BSA solution to investigate the effect of blending polycarbonate. The instrumental analysis confirmed the compatibility between PVC/PC polymers. SEM analysis showed that pore size of membranes decreased upto 50% by blending. Physical properties like tensile strength, abrasion resistance and hydrophilicity were enhanced in composite membranes. However, at higher PC concentrations, chemical stability of membranes against sodium hydroxide decreased. Higher pure water flux and BSA rejection were observed for composite membranes. Increasing PC content, antifouling properties were also improved. Polymer composite with 50-50% of both polymers showed best results for separation of BSA solution.

Fang et al., 2017 developed a novel phosphate-based zwitterionic polymer (methacryloyloxyethylphosphorylcholine-co-poly(propylene glycol) methacrylate, i.e., MPC-PPGMA) and blended that with polyvinyl chloride polymer to prepare membranes by phase inversion method. The zwitterionic copolymer has excellent compatibility with base polymer PVC and it was verified by FTIR results. Instrumental techniques SEM, EDS and contact angles tests were performed to see the porous structure, surface chemical composition and wettability of membranes. Since zwitterionic polymers have strong hydration ability, hydrophilicity and antifouling properties of membranes improved after blending with PVC. Composite membranes were used to filter the BSA solution. Composite membranes containing 1 wt% MPC-PPGMA showed the best performance and flux recovery was about 97% for this membrane.

Nayak et al., 2017 developed a novel membrane for separation of metal ions lead, cadmium and chromium. Amino benzoic acid (ABA) is copolymerized with polyvinyl chloride polymer to improve the hydrophilicity of PVC. Modified polyvinyl chloride is again blended with polysulfone in different compositions to prepare composite membranes. Composites are characterized by NMR and ATR-FTIR to check the compatibility and chemical modification of polymers. SEM and AFM techniques confirmed the morphological changes in membrane structure. Contact angle test and batch-wise filtration experiments were performed to observe the improvement in hydrophilicity and performance of the blended membrane. Metal ion solutions were filtered and effect of pressure, pH and interference of ions were studied. 0.5% PVC-ABA/PSF membrane showed a high rejection of metal ions at neutral pH. Composite membranes showed the highest rejection rate even more than 99% in acidic medium and permeated flux 2.56 L/m^{2}h.

Zhou et al., 2016 prepared antifouling microfiltration membranes by modifying polyvinyl chloride membrane with poly(ethyleneglycol)methylethermethacrylate by non-solvent induced phase separation method. Characterization techniques XPS, SEM and contact angle tests revealed that morphology, pore size, hydrophilicity and antifouling properties of membranes was increased. BSA solution was separated by composite membranes and it was found that biofouling was decreased in the membrane. 9.8 mol% of composite membranes showed the best performance.

Hosseini et al., 2012 developed a novel heterogeneous cation exchange membrane by blending polyvinyl chloride with cellulose acetate copolymer. Membranes were prepared by solution casting method. Cation resin powder was added to the solution as functional group agent. Instrumental characterization techniques SEM and contact angle tests were used to study the effect of blending cellulose acetate with polyvinyl chloride on the physicochemical properties of composite membranes. It was found in SEM results that composite membrane had uniform resin particle distribution and relatively less roughness on the surface. Surface hydrophilicity and membrane ion exchange capacity were increased by increasing cellulose acetate concentration in dope solution. Ionic permeability was also enhanced by adding cellulose acetate but only up to 20 % loading. Beyond 20% to 50% concentration, composite membranes showed a decline in the ion permeability but from 50 to 100% of cellulose acetate, ion permeability of composite membranes again increased. Membrane areal electric resistance decreased with increasing cellulose acetate amount in composite membranes. Thus these membranes were found very suitable for electrodialysis applications.

Liu et al., 2012 fabricated a low cost antifouling membrane by adding amphiphilic copolymer to base polymer. Polyvinyl chloride based hydrophilic membranes were developed by copolymerization with Pluronic F 127 copolymer. The change in characteristics of modified membranes was observed by XPS, SEM, AFM and contact angle test. Membranes of different Pluronic F 127 concentration from 0-10% were prepared. It was found in instrument analysis that oxygen content of membrane increased in modified membranes and pore size and pore density was higher in modified membranes. However, membranes with 8% and higher copolymer showed a decline in pore size. Hydrophilicity was highest in the 10 wt% composite membrane. Membranes with 8% copolymer showed optimum results.

2.3 Membrane modification by pore formers

Bhran et al., 2018 worked on enhancing performance and antifouling properties polyvinyl chloride based membrane by incorporating polyvinyl pyrrolidone as pore former. Nonsolvent induced phase separation technique was used to prepare membranes by dissolving polymers into a mixture of tetrahydrofuran and N-methyl-2-pyrrolidone solvents. Further membranes were characterized by such as SEM, EDX and FTIR. The membrane surface was smooth and pores were well distributed across the bulk body. The porosity of PVP modified PVC membranes were almost twice than pure membrane. This also results in higher permeation. Membranes were used for separating salt solution and modified membranes showed 98% salt rejection. This study also revealed that membranes prepared by mixture of THF and NMP performed better as compared to membranes prepared by THF only.

Sabzi Dizajikan et al., 2018. fabricated a polyvinylchloride based membrane using poly(vinyl pyrrolidone) as pore former and NMP as a solvent. They used Design Expert software for designing the experiments. Characterization techniques such as SEM, AFM contact angle test were used to study the change in properties of different membrane samples and membranes were used for separation of blue indigo dye. These PVC membranes were further used as a substrate for thin-film composite membranes of polyamide for reverse osmosis application for NaCl rejection. Results revealed that increasing the PVC concentration in dope solution resulted in lower water flux.

Moghadassi, 2016 prepared polyvinylchloride (PVC) membrane by casting solution technique using N, N Dimethylacetamide as solvent and porosity was improved by incorporating polyethylene glycol as pore former. In this study, researchers studied the effect of membrane thickness, amount of polyethylene glycol and solvent evaporation time on the antifouling properties and performance of the modified membrane. Filtration experiments were done using deionized water and salt solutions. It was found in results that flux decreased with increasing membrane thickness. As the evaporation time was increased, tensile strength of modified membranes also increased. PEG was added to membranes in different concentrations from 1-4 %, which affected flux and increased it from 1.04 to 13.62 (L/m^2h). Membranes with 3 wt % PEG showed the most optimum results.

Fan et al., 2014 synthesized polyvinyl chloride based membrane by blending with polyvinyl formal using non-solvent induced phase separation method. Membranes were then characterized by SEM, EDX, FTIR and XPS techniques. SEM results revealed that the porosity and mean pore size of membranes was increased with the addition of PVF. The contact angle test showed that hydrophilicity was remarkably improved by PVF addition. The rejection rate of the BSA model foulant was also higher in composite membranes.

A brief summary of literature related to membrane modification using nanofillers, copolymers and pore formers is shown in table 2.1. this table gives a bird eye view of the base polymer along with additives involved, the characterization techniques used and the applications.

Table 2.1: Literature review of membranes modification by nanofillers

Sr. No.	Base polymer	Additive Type/ Modification	Additive	Instrumental Characterization Techniques Used	Application	Reference
1	Polyvinylchloride	Nano filler	Graphene oxide-Nano diamond	XRD, FTIR FESEM, AFM and NMR	BSA Solution	Khakpour et al., 201)
2	Polyvinylchloride	Natural Fiber	Lignin	XPS, XRD, FTIR, SEM and DSC	Oily wastewater	Yong et al., 2019
3	Polyethersulfone	Nano filler	Nano crystalline ce(III) meta organic framework	SEM, AFM, powder XRD, FTIR and BET	Direct Red 16 dye	Mohammadnezhad et al., 2019
4	Polyethersulfone	Nano filler	Ferrous oxide nanoparticles	SEM, AFM, XRD and FTIR	Salt solution	Lakhotia et al., 2019
5	Cellulose acetate	Nano filler	Graphene, silver nanoparticles and copper nanorods composite	XRD, SEM and TEM	Salt solution	El-Gendi et al., 2018

6	Chitosan	Nano filler	Graphene oxide nano plates	SEM, EDX and FTIR	Sodium sulphate and chromous sulphate solutions	Bagheripour et al., 2018
7	Polyvinylchloride	Copolymer	PVC-graft-poly(ethylene glycol) methyl ether methacrylate	NMR, FTIR and SEM	Sodium alginate	Wu et al., 2018b
8	Polyvinylchloride	Nano filler	Halloysite nanotubes	SEM, EDX, FTIR, TEM and SPM	BSA Solution	Mishra et al., 2018
9	Polyvinylchloride	Nano filler	Silica modified silver nanoparticles	FESEM, EDX and FTIR	BSA Solution	Behboudi et al., 2018
10	Polyvinylchloride	Pore former	Polyvinyl pyrrolidone	SEM, EDX and FTIR	Salt solution	Bhran et al., 2018
11	Polyvinylchloride	Nano filler	Pluronic F127	FESEM, XPS and AFM	BSA Solution	Zhang et al., 2018
12	Polyvinyl chloride	Copolymer	Poly(acrylonitrile-co-sodium 4-styrenesulfonate)	NMR, FTIR and SEM	BSA Solution	Wang et al., 2018

13	Polyvinyl chloride	Quaternization	Quaternary ammonium group	FTIR, NMR, TGA, XPS and zeta potential test	BSA Solution	Wu et al., 2018a
14	Polyvinyl chloride	Pore former	Polyvinyl pyrrolidone	SEM, AFM	Sodium salt solution	Sabzi Dizajikan et al., 2018
15	Polysulfone	Nano filler	Graphene oxide nano particles	FESEM, AFM, ATR-FTIR and streaming potential test	Bisphenol A	Nasseri et al., 2018
16	Polyethersulfone	Nano filler	Copper oxide/Zinc oxide nano particles	SEM, AFM and EDX	BSA solution	Nasrollahi et al., 2018
17	Polysulfone	Nano filler	Titanium dioxide nanoparticles	FTIR, NMR, SEM, EDX, XRD and AFM	Eosin yellow dye	Kuvarega et al., 2018
18	Polyvinyl chloride	Copolymer	Cellulose acetate	SEM, FTIR and tensile strength test	Red Seawater	El-Gendi et al., 2017
19	Polyvinyl chloride	Copolymer	Polycarbonate	FESEM, XRD and DSC	BSA solution	Behboudi et al., 2017
20	Polyvinyl chloride	Copolymer	Methacryloyloxyethylphosphorylcholine-co-	SEM, EDX and FTIR	BSA solution	Fang et al., 2017

			poly(propylene glycol) methacrylate			
21	Polyvinyl chloride	Nano filler	Ferrous oxide nano particles	SEM, AFM, goniometer, nano indenter anddynamic mechanical analyzer (DMA)	Sodium alginate	Demirel et al., 2017
22	Polyvinyl chloride	Nano filler	Graphene Oxide/Titanium dioxideNano composite	SEM, EDX, TEM, XRD and AFM	Humic acid	Jhaveri et al., 2017
23	Polysulfone	Copolymer	Amino benzoic acid modified Polyvinyl chloride	NMR, ATR-FTIR, SEM and AFM	Lead, cadmium and chromium metal ions	Nayak et al., 2017
24	Polyvinyl chloride	Copolymer	Poly(ethyleneglycol)methylethermethacrylate	XPS, SEM and contact angle test	BSA solution	Zhou et al., 2016
25	Polyvinyl chloride	Pore former	Polyethylene glycol	Tensile strength test	Salt solution	Moghadassi, 2016
26	Polyvinyl chloride	Nano filler	Titanium dioxide	FESEM and contact angle	BSA solution	Behboudi et al.,

			Nano particles	test		2016
27	Polyvinyl chloride	Nano filler	Graphene Oxide	SEM, EDX and FTIR	BSA solution	Zhao et al., 2016
28	Polyvinyl chloride	Fillers	Tween-20 and Tween-80	SEM and contact angle test	BSA solution	Rabiee et al., 2016
29	Polysulfone	Fillers	PVP, P(VP-AN) and PVA-grafted bentonite particles	FTIR, SEM, EDX and TGA	Oil wastewater	Kumar et al., 2016
30	Polysulfone	Nano filler	Titanium dioxide nanoparticle	SEM, AFM and contact angle test	Orthochlorophenol, phenol and meta-nitrophenol and steel industry effluent	Mukherjee et al., 2016
31	Polyethylene	Nano filler	Titanium dioxide nanoparticle	DSC, XRD, DMA, TGA, FESEM and EDX	Humic acid solution	Jafarzadeh et al., 2015
32	Polyvinyl chloride	Nano filler	Silicon dioxide nanoparticle	SEM, EDX and contact angle test	Municipal wastewater	Yu et al., 2015
33	Polyvinyl chloride	Nano filler	Zinc oxide nanoparticle	SEM , EDX and contact	BSA solution	Rabiee et al.,

				angle test		2015
34	Polyvinyl chloride	Nano filler	Titanium dioxide nanoparticle	SEM ,EDX and contact angle test	BSA solution	Rabiee et al., 2014
35	Polyvinyl chloride	Pore former	Polyvinyl formal	SEM, EDX, FTIR and XPS	BSA solution	Fan et al., 2014
36	Polyvinyl chloride	Copolymer	Cellulose acetate	SEM and contact angle test	Electrodialysis	Hosseini et al., 2012
37	Polyvinyl chloride	Copolymer	Pluronic F 127	XPS, SEM, AFM and contact angle test	Municipal wastewater	Liu et al., 2012
38	Polyethersulfone	Nano filler	Alumina nanoparticles	SEM and contact angle test	Activated sludge	Maximous et al., 2009

2.4 Summary of literature review and research gap

From the literature review, it is summarized that continuous research and development work is going on these years for the preparation of composite polymeric membranes. Preparing new composites and finding their suitable application has always been an interesting area of work for material researchers. Developing composites is an easy way to enhance the properties of any particular material for the desired application. These formed composites have a combined effect of properties of the components used for composite development. Challenges of fouling in membrane processes have also attracted researchers to focus on the preparation of polymeric composites of better physicochemical properties for fabricating antifouling membranes. Polymeric composite membranes are developed by numerous researchers by surface and bulk modifications of base polymer using various additives like pore formers, copolymers, crosslinkers and inorganic nanoparticles. A well fabricated composite membrane should have advantages of high flux, permeability, rejection rate, less fouling, high mechanical strength, strong chemical resistance and low cost. Each polymer has some specific property that is suitable for various selective separation applications. Many researchers have focused their attention on polyvinyl chloride based membranes. Polyvinyl chloride is one of the widely used polymers worldwide for different applications because it is inexpensive, possesses excellent chemical properties such as acid and alkali resistance, great mechanical strength and good thermal properties (Zhang et al., 2009). Because of these properties, it is an excellent material for membrane preparation. Still, this excellent material has a drawback of higher hydrophobicity which is not accepted in the membrane separation process for water purification. This shortcoming of PVC polymer became the motivation for research studies. It was observed in the literature review that researchers have worked on developing polyvinyl chloride based antifouling composite membrane by using graphene oxide-nano diamond, lignin, halloysite nanotubes, silica modified silver nanoparticles, Ferrous oxide nanoparticles, titanium dioxide nanoparticles etc. as surface modifiers. However no significant work was found developing composite membranes by blending polyvinyl chloride with alumina and bentonite nanofillers. This research gap has given motivation for this research work.

2.5 Research objective

In this research work, composite polymeric membranes are prepared by non-solvent induced phase separation method using polyvinyl chloride as base polymer and inorganic nanoparticle (alumina and bentonite) are added as fillers. The PVC/Nanoparticles composite membrane showed higher hydrophilicity, mechanical strength improves flux and low fouling as compared to pure PVC membranes.

The objectives of this research work are summarised as

- Synthesis of polyvinyl chloride based porous membranes by adding following inorganic nanoparticles
    - Alumina
    - Bentonite
- Characterization of the composite membranes to study the changes in some selected properties.
- To study the performance of membranes using humic acid as foulant.