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Nanocomposite Membranes for the Separation of Emulsified Oily Wastewater

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Abstract

This chapter provides an overview on the membrane technology applied to the separation of emulsified oily wastewater as alternative to conventional methods, focusing mainly on the nanocomposite materials. These systems are capable to enhance the performance of the membranes reducing the incidence of fouling issues and low permeation fluxes. The more recent progresses in membrane research are discussed, evidencing the future directions and the main challenges to face.

Introduction

Nowadays, the actual situation of water shortage, according to a logic of sustainable growth, requires innovative or improved methods to purify oily-contaminated water. Indeed, water is one of the most precious natural resources and its quality has a big impact on human health and socio-economic development. Every year, large quantities of emulsified oily wastewater are generated in various industrial processes, ranging from petrochemical, oil and gas production industry to metal processing, passing for textile and leather industries, as well as domestic sewage. On the other hand, oil spill represents a serious issue because of frequent accidents. These streams present harmful effects on human health, aquatic and terrestrial ecosystems [1]. Therefore, the maximum allowable discharge concentration for oil is restricted (10 mg L^{-1} in China [2]).

The chemical composition of these wastewaters is complex and depend on the site. Many type of chemicals can be found: Linear chain and aromatic hydrocarbons as well as metals and additives (e.g., corrosion inhibitors and/or emulsion destabilizers).

Typically, conventional oily wastewater treatment methods, such as coagulation, de-emulsification and flocculation, air-flotation, gravity separation and skimming, suffer of low efficiency, high operation cost, corrosion and re-contamination problems. Most of these operations are not effective in removing oil droplets having micron or submicron size [3]. Indeed, conventional methods for oil removal are more appropriate for surfactant-free emulsions with oil droplet larger than 10μm [4]. Wastewaters with particles with size smaller than 20 µm as well as emulsified oily wastewater stabilized by surfactants remain highly stable making their purification very difficult [5].

Membrane technology is recognized as an environmentally friendly solution for the separation of gases or liquid mixtures, with an energy consumption lower than conventional separation methods, modularity, easy operation and maintenance [6,7]. For this reason, we present a concise outlook of the more recent developments in membranes for oily wastewater treatment by discussing the major progress, opportunities and challenges, mainly focusing on polymer-based nanocomposites.

Porous membranes

Porous membranes are the sole type of membranes used in the treatment of oily wastewaters. Numerous studies, reported in the open literature, focused on the filtration of oil-in-water emulsions using porous membranes [8]. Figure 1 shows the increasing number of scientific papers on wastewater treatment by membranes. The reason for this trend relies on the high efficiency, small footprint and easy scale-up that are achievable with membranes [9].

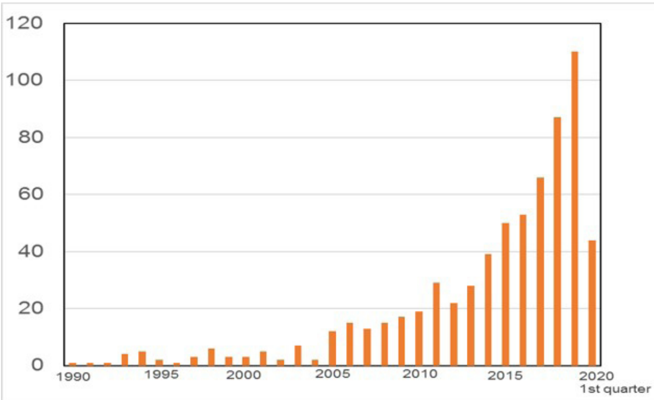

Figure 1: Number of yearly published scientific papers on wastewater treatment with membranes. Source: Scopus, Title-Abstract-Keywords containing the words 'oily', 'wastewater' and 'membranes'. Accessed 26 Feb 2020.

Essentially, on the basis of surface properties membranes can be distinguished in hydrophobic and hydrophilic. The former repel water and allow oil droplets to permeate freely, the latter allow water to permeate through the membrane and repel oil droplets. Porous membranes operate on size exclusion retaining almost all contaminants larger than their pore size. In particular, Ultrafiltration (UF) membranes present pore size in the range of 0.002–0.05 µm, whilst the size of the oil droplets in emulsion is usually in the range of 0.1–10 µm. Therefore, most of these oil droplets can be effectively removed, guaranteeing a good quality for the permeated water [10].

An important issue related to the treatment of emulsified oily wastewater is a highly polydisperse droplet distribution, from micron to nanosize [11]. In addition, the oil droplets being deformable can pass in the permeate effluent since the feed stream is under pressure [12]. Even though narrowing pore size can be considered, it would reduce the permeate flux and thus the system productivity.

Membrane fouling

The accumulation of macromolecules and microorganisms on the surface of membrane or inside the pores of membranes is referred to as membrane fouling. It is caused by various factors such as adsorption of organic molecules, particulate deposition and microbial adhesion on the membrane surface [2]. Membrane systems are negatively affected by fouling which reduces permeation flux and severely decreases the efficiency of filtration. These aspects are particularly important in the case of oily wastewater treatment. Indeed, the accumulation of oil droplets on the surface or within the membrane's pores requires a more frequent cleaning and, finally, replacement of the membrane, in order to operate in optimal conditions. The oil gel layer that builds up on the membrane surface has high compressibility and low porosity. Therefore, the related hydraulic resistance can be even 2–3 orders of magnitude higher than that associated to solid particles or undistorted spheres [13]. As a result, it is still a challenge for membranes to separate emulsified oily wastewater simultaneously meeting the requirements of high permeate flux, significant particle removal and adequate resistance to oil-fouling.

The hydrophilic membranes exhibit better antifouling properties as compared with the hydrophobic membranes. In order to cope with the fouling issues, a vast number of studies was devoted to the increase of the membrane hydrophilicity [14].

Oil repellency as well as the stability of Cassie-Baxter state can be improved by hierarchical structures or enhancing the surface roughness. In this context, bioinspired diatomite membranes, prepared by a freeze casting as hierarchically structures, were recently applied in oil/water separation [15]. On the other hand, electrospun nanofibers are suitable for combining tunable wettability, large surface area, high porosity, good connectivity, fine flexibility, and ease of scalable synthesis starting from various materials. In virtue of these properties, they hold great potential for many emerging environmental applications, including the separation of oily wastewater [16]. However, electrospinning is applied to small-scale production.

Inorganic membranes

Different studies are devoted to development of inorganic membranes (e.g., alumina-based) since they are suited to operate in severe conditions (high temperature and pH values) [17-19].

Alumina microfiltration membranes were modified by coating them with nanosized ZrO_2 to improve the hydrophilic properties and diminishing membrane fouling caused by oil droplets [20].

Zeolite-Coated Mesh Films (ZCMFs) with superhydrophilicity and underwater superoleophobicity were developed by a seeding process [21]. Various oils can be efficiently separated from water based on the gravity-driven separation process. Such films with low oil-adhesion properties are easily recyclable and residual trace oils can be simply removed by calcination while do not change the wettability of the films. The ZCMFs display an anti-corrosion behavior and could be applied as oil retention barrier of industrial outlet sewer pipes, oil fences for oil spill accidents, etc.

The high cost of inorganic membranes is their major limitation for industrial application when compared to polymeric membranes. Therefore, less expensive ceramic membranes as kaolin-based would promote the use of ceramic membranes for the treatment of oily wastewater [22].

Polymeric membranes

Currently, most oil–water separation membranes are made of polymeric materials. Polysulfone (PSf) and Polyvinylidene Fluoride (PVDF) are two of the most used polymers for the preparation of porous membranes, particularly for ultrafiltration processes [23]. However, both polymers are hydrophobic and thus present poor membrane performance for separating oil-containing streams [24]. A general strategy to confer a more hydrophilic character to a membrane involves its surface or bulk modification (Figure 2).

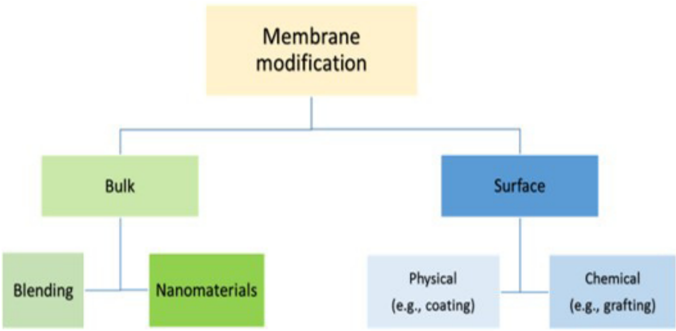

Figure 2: Strategies to improve membrane hydrophilicity.

Surface post-treatment is finalized to the formation of hydrophilic layer on membrane which prevents the contact between membrane surface and pollutants, thus diminishing fouling phenomena. This approach can be performed by direct coating or promoting the chemical grafting of hydrophilic polymers on the membrane surface. Stability and long-term resistance are the main drawbacks of the samples prepared according to these methods. In addition, the coating layer partially intrudes in the pores occluding them, reducing the permeation flux through the membrane and nullifying the containment effect on fouling. Bulk modification is the main alternative method to prevent the undesired adhesion of foulant agents on the membrane. Therefore, the blending with hydrophilic polymers (e.g., polyvinyl pyrrolidone, polyethylene glycol, polyvinyl alcohol) is considered to tailor micropores and enhance hydrophilicity [25,26]. Nevertheless, the mechanical strength, stability and selectivity of the composite membrane can decrease due to the addition of hydrophilic polymers [27].

Nanocomposite membranes

Recent studies have focused on the addition of inorganic nanoparticles in the membrane matrix, thus improving the polymer hydrophilicity in order to overcome fouling issues. The fouling mitigation maintains high permeate flux, reducing the necessity of physical and chemical cleaning which enhances the operating cost of treatment significantly. The loading of inorganic nanoparticles offers additional advantages, such as improved filtration selectivity, higher thermal and mechanical resistance [28].

Nanocomposite materials represent an attractive solution to take advantage of the exceptional properties of some innovative materials, such as graphene, keeping the easy handling, processability and low cost of the polymers [29]. Nanocomposite membranes exhibit excellent structural performance and multifunctional properties owing to their intrinsic capability to combine synergistically nanofiller and host matrix properties, achieved by a suitable interfacial organization [30]. In these nanostructured systems, both mechanical and physical (thermal, electrical, barrier and optical) properties can be finely modulated by processing conditions and interfacial interactions.

Different inorganic nanoparticles were considered for the specific wastewater treatment, including silica, titania and carbon-based materials. Silica (SiO_2) is widely used to increase the hydrophilicity of the membranes [31-33]. Zhang *et al*. incorporated titania (TiO_2) nanoparticles in PSf membranes, measuring water permeate flux, hydrophilicity, as well as mechanical strength and fouling resistance higher than unloaded polymer [34]. Nanocomposite UF membranes based on PVDF in which nanosized TiO_2/Al_2O_3 is dispersed displayed an increased antifouling resistance [35]. TiO_2/Al_2O_3 addition provides both higher hydrophilicity and required flux recovery. In another study, PSf-based membranes were prepared adding the phosphorylated TiO_2–SiO_2 (PTS) particles to the polymer matrix, specifically for oily wastewater treatment [36]. The PTS particles, uniformly dispersed in the composite membrane, resulted capable to improve significantly the original membrane hydrophilicity, antifouling capacity and mechanical strength. A 10 wt% of PTS is sufficient to lower the contact angle of the membrane from 78.0° to 45.5° with 92% oil rejection and a flux of 116 L/m^2 h measured at 0.1 MPa. Similarly, the effect of Sulfonated Zirconia Particles (SZP) in the treatment of oily wastewater was studied [37]. The oil concentration in permeate decreased from 80 to 0.67 mg/L in a PSf-based mixed matrix membrane containing 15 wt% of SZP, with satisfied recycling standards.

$CaCO_3$ nanoparticles have been attracted considerable attention in water and wastewater treatments owing to a high specific area, great biocompatibility and low cost [38,39]. Mixed-matrix membranes based on polyethersulfone and hydrophilic hydrous manganese dioxide nanoparticles improve membrane hydrophilicity and antifouling resistance against oil deposition and/or adsorption. These membranes were successfully applied to treat a synthetic oily solution containing 1000 ppm oil showing a significant improvement in water permeability and oil rejection [40].

An example of combined approach between the bulk and surface modification is represented by the bioinspired membranes having composite coatings based on polymer–nanoparticle–fluorosurfactant complex [41]. These structures show fast-switching oleophobic–hydrophilic and antibacterial properties. The nanoparticle enhanced surface roughening lead to improvement in hydrophilicity and oleophobicity resulting in a large difference between the equilibrium oil and water static contact angles (switching parameter). The presence of nanoparticles (silica) at low loading (< 5 wt%) in the coating layer also increases hardness and durability of the coatings.

Carbon-based nanocomposites

A special class of promising fillers that can be incorporated within a polymer matrix is constituted by carbon-based nanomaterials. They have the same chemical composition but differ for their configuration and dimensionality. In addition, the production methods involve deeply different syntheses. These nanomaterials incorporated in polymeric matrices are capable to modify significantly the performance of the original membrane for oil-water separation as regards the permeation flow, the self-cleaning and antifouling properties [42]. In the following, some representative applications are discussed for carbon-based nanocomposites.

Carbon nanotubes

Carbon Nanotubes (CNTs) are rolled single or multi walled graphene layers, folded in a cylindrical shape with a hexagonal lattice structure [5].

Nanocomposite membranes made of CNTs in polyvinyl alcohol were applied to the filtration of *n*-hexadecane-in-water emulsion, showing as the application of negative electric potential alleviates the permeation flux decline [43].

Since purified CNTs are intrinsically hydrophobic, it is necessary to functionalize their edges by specific chemical groups both to give a hydrophilic character to the particles and to prevent their tendency to agglomerate, generating preferential paths that reduce the selective action of the membrane. Accordingly, Multiwalled Carbon Nanotubes (MWCNTs) decorated with TiO_2 nanoparticles were dispersed in polyethersulfone resulting in mixed membranes successfully applied for antibiotic and photodegradation in oily wastewater treatment [44]. The membrane was designed to take advantage of the synergistic photocatalytic activity induced by incorporated nanoparticles. The membrane loaded with 0.1 wt% of a TiO_2-coated MWCNT, having the lowest surface roughness, revealed the best antibiofouling properties.

Aspects related to the alignment of the nanotubes within the matrix in order to improve further the permeation flow remain to be improved.

Graphene-nanocomposites

Graphene, a bidimensional carbon nanomaterial, has recently shown superior electrical, thermal and mechanical properties with interesting prospective as separation material [45,46]. The most immediate way to exploit these characteristics is its dispersion in a suitable matrix. Thus, graphene-based nanomaterials have been investigated increasingly, while other carbon-based nanomaterials such as fullerenes and carbon nanotubes were explored more intensely decades ago [47,48]. The addition of strong and flexible graphene-based nanomaterials into polymer matrices can produce a dramatic improvement in properties and reaching the percolation threshold at very low filler content [49]. Rafiee *et al*.comparing the mechanical properties of epoxy nanocomposites with graphene platelets, single-walled carbon nanotubes and multi-walled carbon nanotubes with a loading of 0.1 wt%, observed as the graphene platelets significantly outperform carbon nanotube additives [50]. Indeed, if the addition of graphene enhances of about 30% the elastic modulus of the nanocomposite with respect to the pristine epoxy, single-walled CNTs improve the same parameter only of the 3%. Correspondingly, graphene platelets and MWCNTs enhance the tensile strength of the neat epoxy matrix by 40% and 14%, respectively. In addition, the fracture toughness of the nanocomposite incorporating graphene platelets showed a 53% increase over the epoxy compared to 20% improvement for MWCNTs. This confirms a generalized superiority of graphene platelets over carbon nanotubes in terms of mechanical properties enhancement of the neat polymer. This is related to the high specific surface area, enhanced nanofiller-matrix adhesion/interlocking arising from their wrinkled (rough) surface, as well as the two-dimensional (planar) geometry of graphene platelets. However, also graphene has a hydrophobic nature, so there is chance for improvement in this specific application.

Graphene oxide

Graphene Oxide (GO) is the oxidized state of graphene and contains epoxide, hydroxyl and carboxylic acid groups, which both increase its compatibility with most polymers and confer a hydrophilic character.

Graphene oxide modification of commercial alumina ceramic filtration membranes showed enhanced flux and oil rejection in the oil–water emulsion microfiltration [51].

Nanocomposite membranes based on Copper Hydroxide Nanowires (CHNs)-graphene oxide were fabricated by a vacuum-assisted filtration self-assembly process [52]. The membranes, having a rough surface and nanostructure channels display hydrophilicity (water contact angles of 53°), under water superoleophobicity (oil contact angles of 155°) and ultralow oil adhesion. Anti-fouling properties of the membrane result in a high efficiency of >99% in the oil-water emulsion separation. These membranes combine a high oil rejection rate and ultra low membrane fouling, making them promising for practical emulsified oil-water separation.

Challenges

The treatment of the wastewater discharged from oil and shale gas fields (‘produced water’) is still challenging, owing to the contemporary presence of high contents of oils and salts [53]. Conventional pressure-driven membranes suffer either severe membrane fouling or incapability of desalination. For this purpose, a new nanocomposite Forward Osmosis (FO) membrane was specifically designed: an oil-repelling and salt-rejecting hydrogel selective layer was coated on top of a nanocomposite support (polymer loaded with GO nanosheets). These membranes are capable of a simultaneous oil/water separation and desalination. The hydrogel selective layer presents underwater oleophobicity resulting in superior anti-fouling capability, while the GO-based support is capable to diminish internal concentration polarization. In the case of simulated shale gas wastewater, this new type of FO membrane demonstrates more than three times higher water flux, higher removals for both oil and salts (>99.9% for oil and >99.7% for multivalent ions) and significantly lower fouling tendency with respect to commercial FO membranes.

Conclusions

The development of nanocomposites is steadily continuing, driven by the request of more performing systems in various areas. Membrane systems offer interesting solutions to cope with the water shortage, even for a demanding application such as the water-oil separation. Considerable progress has been made developing advanced membranes by incorporating different types of inorganic nanoparticles within polymeric matrices. Superior performance with respect to neat polymer membranes are reported for nanocomposite membranes in terms of reduced fouling tendency and high flux through the membrane. Typically, their enhanced hydrophilicity, induced by selected nanoparticles or by a modified surface roughness, prevents the foulant attachment. In addition, the mechanical and physical properties of these nanocomposites are enhanced owing to the synergistic action of nanofillers and host matrix.

Other efforts are needed to develop membranes suited for the purification of highly saline and oily wastewaters (e.g., ‘produced water’) and to move to a large-scale production of the nanocomposites.

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