POTENTIAL DEVELOPMENT METHODS OF MEMBRANE FILTRATION TO PURIFY OIL-CONTAMINATED WATERS

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Introduction

It is important to treat effectively the oil-contaminated waters, since they are produced in high amounts by several industrial activities [1], and their toxics compounds can significantly affect negatively the environment [2, 3]. To achieve excellent efficiency, the conventional techniques (such as flotation, centrifugation, skimming, *etc*.) are not enough because of the small emulsified oil droplets that cannot be removed by these methods [4]. The complementation of these techniques with membrane filtration can be a good solution to this problem, since, over the high achievable efficiency, it has other additional advantages, like the easy operation and integration. However, the generation of a hydrophobic cake layer – and the fouling of the pores – that reduce quickly and significantly the flux can make the utilization of this technology not feasible [5]. Thinking about this, many studies target to fix this problem by developing different promising solutions. One of them is the membrane modification, which can be achieved, for example, by using hydrophilic and photocatalytic nanomaterials. The present work shows a brief overview about the utilization of membrane filtration for treating oily wastewaters – explains the difficulties, the main problems and discusses promising solutions to improve this treatment method and to find feasible technologies, focusing on membrane modifications, mainly with hydrophilic and photocatalytic nanomaterials that can results in self-cleaning and antifouling properties.

Main pollutants of oil-contaminated waters and their harmful effects

Oils contain several harmful compounds: saturated straight and branched-chain hydrocarbons, cyclic hydrocarbons, olefins, aromatic hydrocarbons and others, such as sulfur compounds, nitrogen-oxygen compounds, and heavy metals. The harmfulness of the oil-contaminated waters depends on the type, volume, and quality of the polluting oil, but also on the place and conditions of the discharge. The oily wastewaters can cause harmful effects on organisms by coating, asphyxiation, poisoning or causing sublethal and stress effects, reducing the abundance and diversity of the fauna and flora [2]. The soils also can be affected by oil contaminations, reducing the bacteria activity, the life of earthworms and plant growth, by affecting the root elongation and germination [6]. In relation to animals and human beings, oil contaminations can be accumulated in the food chain, can damage the DNA, and can produce genotoxic, carcinogenic, mutagenic effects, and immune-suppression as well [3, 7].

Membrane technology to treat oil-contaminated waters

Membrane filtration technique became a promising purification method to treat oily wastewaters due to its' several advantages, *i.e.* no chemical addition, easy handling, low energy requirement, and high efficiency. The separation method consists of using a physical barrier (membrane) that allows the water to flow by the action of a driving force while the contaminants are retained by the barrier [8]. Both micro- and ultrafiltration can be used to remove efficiently the oils, however, ultrafiltration shows higher efficiency to remove smaller droplets and to reduce the total organic carbon (TOC) content and chemical organic demand (COD) [9, 10]. The technology faces several challenges *e.g.* the reduction of fouling, which is the major limitation in several cases [5]. During the filtration, various compounds can be deposited or adsorbed on the membrane surface, such as salts, hydroxides, surfactants and oil droplets [11], causing the fouling of the pores and the formation of hydrophobic cake layer. These problems cause significantly reduced flux, permeability, productivity, decreased life span, and increased energy consumption and treatment costs. The fouling layer can be affected by different reasons [5]:

i. characteristics of the feed water, *e.g.* concentrations and physicochemical properties;
ii. characteristics of the membrane, *e.g.*, surface roughness, charge properties, hydrophobicity;
iii. operational conditions, *e.g.* cross-flow velocity, applied pressure difference, recovery and temperature.

It is necessary to solve the major limitation and make the use of this technology feasible for treating oil-in-water emulsions.

Potential solutions for fouling problems

It is necessary to minimize the interaction between the wastewater's contaminants and the membrane surface to reduce fouling and, for this, there are some possible solutions, *i.e.*:

i. utilization of backflushing with air, water or permeate, to increase the efficiency and hydrophilicity [12];
ii. application of biological, physical or chemical pre-treatment for example, degasification, chemical softening, media filtration, ion-exchange softening, ozonation, *etc.* [13]–[15];
iii. Utilization of membrane modification by blending [16], by coating or by the deposition of nanomaterials onto the membrane surface [17].

The use of nanomaterials to modify the membrane has a huge potential to improve membrane efficiency due to its high surface area and high surface-active groups [8].

Membrane modification with photocatalytic nanomaterials

Photocatalytic nanomaterials can also be used to modify the membrane, since they have the ability to decompose several organic pollutants via their light-induced activation [18]. These UV and/or solar-light activated semiconductor materials can generate electron/hole pairs that can oxidize directly or indirectly the organic contaminants. Therefore, these photocatalytic nanoparticles can be used to prepare self-cleaning membrane, that can be activated and purified by photons regaining the permeability without shutdown the filtration, increasing costs or reducing the membrane life [19]. There are several well-known photocatalytic materials such as zinc oxide (ZnO), zinc sulfide (ZnS), tin oxide (SnO_2), copper oxide (CuO_2), cadmium sulfide (CdS), tungsten trioxide (WO_3), and the most investigated, titanium dioxide (TiO_2) due to its low cost, high chemical stability and photocatalytic activity, availability, *etc.* [18]. TiO_2 can improve hydrophilicity, stability and anti-fouling properties of membranes, however, it can be activated mostly with ultraviolet light, which is a small fraction of the solar spectrum – 3 to 8%. Therefore, efforts have to be done to develop visible-light sensitive photocatalytic material [20], [21], to form solar-light activable photocatalytic membrane. The addition of other nanomaterials to TiO_2 to modify the membrane has gaining attention because of the enhanced properties of the coupled materials. The use of WO_3, ZnO, $BiVO_4$ and noble metals such as Ag, Au, Pt, and Pd are showing good results in relation with visible-light-driven activities [20, 22–25], but their effects on filtration properties are also important, and not well investigated until now. It is possible to recognize the effort on research to find efficient photocatalytic composites that can be used to modify membrane used to the treatment of oily wastewater with higher efficiency and better anti-fouling properties, however, further investigations are necessary to be carried out for industrial utilization.

Conclusions

It is difficult, but necessary to find an excellent purification technology to treat oily wastewaters with high efficiency and economically friendly. Membrane filtration has been developed intensely in the last years, nevertheless, membrane fouling and flux reduction are still serious limiting factors in the case of oily contaminants. Membrane modification methods show good potential to further enhances because they can improve the hydrophilicity and anti-fouling properties of the membranes. Photocatalytic nanocomposites can be used to reduce the adhesion of these kinds of pollutants on the membrane surface and to decompose photocatalytically the yet adhered organic pollutants. TiO_2 has been widely investigated for membrane modification, but further investigations are necessary to be done in order to find photocatalytic nanocomposites that are able to combine the good filtration properties and high visible-light and solar-light activities to make the system more economical and efficient.

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