Oily wastewater treatment using a zirconia ceramic membrane – a literature review

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Abstract: The goal of this article was to review the literature which discusses the problem of oily wastewater purification by membrane filtration. The authors focused on membranes containing zirconium compounds, mainly ZrO_2, used in pressure driven membrane processes. The efficiency of the oil removal processes for various membranes (ceramic and composite), usually above 95% for the oil contaminated sewage, was compared. The influence of zirconium compounds on the properties of ceramic membranes was also discussed. The methods of producing ceramic membranes have been briefly characterized as well. Ceramic membranes are usually obtained by sol-gel technique but also by isostatic compression, reverse phase technique, or hydrothermal crystallization. Ceramic membranes are formed with zirconia, which cause an increase in filtration efficiency by improvement of hydrophilic properties of the membrane. Moreover, the addition of ZrO_2 results in increased chemical and hydrothermal membrane stability. The efficiency of the filtration processes using the presented membranes was high, suggesting that membrane filtration processes are highly effective purification methods.

Introduction

The wastewater containing oils is released from many industrial processes, and related among the others to petrochemical and metallurgical industries, as well as cosmetics and food production (Ankyu and Noguchi 2014), tanning and leather processing (Coca et al. 2011). Contained in such wastewater greases, oils and fats cause that they are often classified as hazardous waste (liquid waste). This type of waste must be treated before being discharged into the wastewater network or surface waters. Oils and greases introduced into the water will inhibit the self-purification processes and adversely affect the physico-chemical and organoleptic properties of water. These compounds are not biodegradable, so their presence in natural waters is a serious problem. Set emission limits for mineral and synthetic oils are 5–15 mg/dm³ (Law Gazette 2014 r. item 1800), whereas for vegetable and animal oils are 100–150 mg/dm³ (The World Bank Group 1999, Coca et al. 2011). Oil solubility in water is very low and is around few mg/dm³, therefore these agents are present in the water in the form of an oil-in-water emulsion (Coca et al. 2011). Permissible limits for the oil content are determined on the basis of changes of the dissolved oxygen content in water. When oil enters the water, living organisms consume organic matter as a food source. But this process involves a biochemical reaction resulting in the decrease of the dissolved oxygen content. The saturation value of the dissolved oxygen is 8–15 mg/dm³, depending on temperature and salinity. If the oxygen consumed is not replaced by artificial or natural methods, the dissolved oxygen level decreases, leading to the death of fish and other aquatic organisms (Coca et al. 2011).

According to the classification of oily wastewater, free oil (droplet diameter >150 μm), dispersed oil (droplet diameter – 20 to 150 μm), and emulsified oil (droplet diameter <20 μm), are distinguished (Coca et al. 2011, Kajitvichyanukul et al. 2011). There are different methods of oily wastewater treatment. The type of method depends primarily on the concentration and sizes of oil droplets, and on their physical properties (Coca et al. 2011). The oily wastewaters contain surfactants, corrosion inhibitors, biocides, stabilizers and antifoaming agents, therefore the purification process consists of several steps (Kajitvichyanukul et al. 2011). In the first stage the free oil is removed. Gravity separation, centrifugation, chemical treatment, flotation, filtration, membrane processes and adsorption techniques (Pintor et al. 2016, Pérez et al. 2016, Tong et al. 2016, Duan et al. 2016) and mixed techniques (Ankyu and Noguchi 2014, Coca et al. 2011, Pérez et al. 2016, Tong et al. 2013) are used to remove all oil contaminants. In the first stage, the gravity separation and centrifugation are most commonly used (Pintor et al. 2016). The chemical, electrical and physical methods that aim to removing emulsified oil, are employed in a second stage (Kajitvichyanukul et al. 2011). In the third step more efficient processes of purification are used. These processes are either based on advanced oxidation

processes or on membrane filtration with membranes of a smaller pore size (Pintor et al. 2016). Membrane techniques have found particular application in the oily wastewater purification, because they result in high-yield purification and purity of the permeate, low energy consumption, and the possibility of continuous separation. Among the drawbacks of membrane techniques the high susceptibility to contamination and high maintenance costs are emphasized (Pintor et al. 2015). Emulsion separation takes place through microfiltration, ultrafiltration, and nanofiltration (Del Colle et al. 2011), what is discussed later in the article. The membranes, in principle, can be used in most separation processes, and may be a supplement or alternative to the chemical processes (Koyuncu et al. 2015). Especially in the case when chemical methods are ineffective, or when the oil in water emulsions is stable, the oil droplets are highly dispersed and have a low concentration and a diameter less than 10 μm. Conventional methods allow for the removal of oil impurities down to 1% of the total volume of wastewater, when for a better purification a membrane techniques are used.

Generally, in processes using pressure membrane microfiltration, ultrafiltration, nanofiltration and reverse osmosis stand out. Division of these methods has been made depending on the size of particles that can pass through the pores of the membrane. Microfiltration processes correspond to particles ranging from 0.05–1.5 μm, ultrafiltration processes are used to particles with size of 0.002–0.05 μm, and for the particles of a size 0.0005–0.007 μm and 0.0001–0.003 μm nanofiltration and reverse osmosis are used, respectively (Kajitvichyanukul et al. 2011). Figure 1 shows a schematic diagram of the pressure filtration processes in which the aforementioned four processes are distinguished.

It should be stressed that although the membrane techniques have been greatly developed over the past 30 years, there is still no fully elaborated theoretical model for accurately quantifying the dynamics of the membrane process (Salahi et al. 2013). The parameters characterizing membranes are trans-membrane pressure (TMP), salt concentration, cross flow velocity (CFV), molecular size of solutes, pH and feed temperature. Quantification of the effects of these basic parameters on membrane processes is not completely understood, which further complicates the development of the aforementioned model. These parameters also apply to the performance characteristics of the membranes. In the microfiltration process, the greatest problem encountered during operation of the membranes is the fact that the permeate flow is reduced over time because concentration polarization and membrane contamination (fouling) occur. Therefore, microfiltration membranes require frequent regeneration by washing with suitable cleaning reagents and water. This action determines the choice of a suitable membrane material that will withstand chemical agents. As such material zirconium oxide is commonly used. Also during ultrafiltration and nanofiltration processes the problem of membrane pollution and concentration polarization occur. Nanofiltration is most commonly used to remove water hardness. Microfiltration and ultrafiltration are used for the removal of microorganisms, colloidal and macromolecular compounds and turbidity (Koyuncu et al. 2015).

Preparation of ceramic membranes

In the filtration process the ceramic membranes are widely used. This is due to their properties, among which mechanical strength, chemical and high temperature resistance, ease of cleaning (Koyuncu et al. 2015, Narong and James 2008) and also microbial resistance, resulting from a nanometric metal particles (silver) addition to a membrane (Lv et al. 2009, Azócar et al. 2012), can be distinguished. In these respects, ceramic membranes surpass polymeric membranes (Kumar et al. 2015, Narong and James 2008) which in order to improve their properties are modified by doping with nanometric, inorganic particles, such as ZrO_2, Al_2O_3, TiO_2 and SiO_2 (Zhang et al. 2014). As membranes timber zirconium compounds found a wide use, but also tin and aluminum oxides and silica are applied frequently (Narong and James 2008). Choice of the membrane type depends on economic factors, especially on price, durability, service life, frequency and cleaning method and power consumption (Mucha and Kurbiel-Swatek 2015).
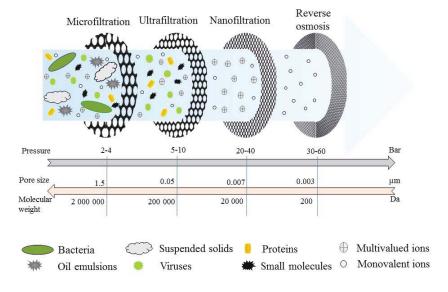

Fig. 1. Comparison of pressure filtration methods (own analysis)

Ceramic membranes are usually obtained by sol-gel technique, but also by isostatic compression, reverse phase technique or hydrothermal crystallization. In the all quoted methods, the common stage, the calcination of the membrane can be distinguished. It is also worth adding that the obtained results depend on the type of substrates used and the synthesis method.

Membrane preparation by sol-gel method

Most examples of the ceramic membranes preparation are based on the sol-gel method. Wu and Cheng (2000) received ultrafiltration zirconia membranes by the sol-gel method wherein as a substrate the zirconium butoxide was used. The resulting membranes were characterized by the presence of dense zirconia layer with thickness of 0.15 μm, which consisted of spherical nanoparticles. A second porous zirconium oxide layer consisted of two sub-layers, with pores of 1.5 nm diameter at the first one, and 3.6 nm at the second zone (Wu and Cheng 2000). Pan et al. (2010) obtained nanocomposite membranes based on Nafion and zirconium oxide for proton exchange membrane fuel cells (PEMFCs) operations. The membrane was formed as a result of conversion of the composite Nafion-zirconia. Nafion is a synthetic copolymer of tetrafluoroethane and perfluorinated oligovinyl ether terminated with strongly acidic sulphonic rest. The membrane formed is a result of conversion of the composite Nafion-zirconia which has been obtained based on a sol-gel technique. In the first step nanocrystalline zirconia particle size of 6.3 ± 0.5 nm was obtained by in situ sol-gel. Synthesis of nanometric zirconia took place after mixing together a solution of tetrabutyl zirconate in n-butanol and a solution of Nafion in N-methyl-2-pyrrolidone. Nafion particles have the capacity to accumulate on the ZrO_2 nanoparticles, due to electrostatic interaction, what effectively inhibits the growth of crystals. From the resulting composite a membrane was formed. This process took place in several steps and was described in (Pan et al. 2010). Pan et al. (2010) also showed that the addition of zirconium oxide nanoparticles did not significantly affect crystallinity and the structure of the Nafion membrane, while increasing the water retention capability.

Sol-gel method was used as well for the production of ceramic membranes by Araki et al. (2011). The porous membranes comprised of silica, wherein the hydrothermal stability was improved by the addition of 50 mol% zirconia. Uniform and defect-free membranes were formed by hydrolysis and condensation of tetraethoxysilane and zirconium n-butoxide. A high reaction rate of hydrolysis and condensation of n-butoxide zirconium was limited by the addition of a chelating agent (acetylacetone). Slowing down the hydrolysis and condensation reaction of a zirconium compound was necessary, since these reactions are faster than the reactions of hydrolysis and condensation of tetraethoxysilane. Such a phenomenon results in production of non-homogeneous structure (at the microscopic level), with lower chemical, thermal and mechanical stability. Such products are obtained when the content of zirconia in a mixture of zirconium and silicon oxide is high, above 40 mass%. Finally, membranes were formed on the microporous support as aluminum oxide. Araki et al. (2011) showed that during membrane formation, the creation of an intermediate layer between α-alumina and composite of silica and zirconium oxide was important. This

layer has been called γ-alumina. Its formation was necessary because the membrane formed directly on the α-alumina had numerous cracks. This was caused by the difference between the size of silica and zirconia sol particles and the volume of pores in the supportive layer. The intermediate layer consisting of γ-alumina with a pore size of 2–5 nm was coated on the surface of α-alumina. On such layer, silica and zirconia sol were deposited. This process was performed in three cycles, the so-called coating-calcination cycles. Araki et al. (2011) showed that in such membrane structural connections, heteroatom bonds type Si-O-M were formed, and the increase in the number of the coating-calcination cycles caused an increase in separation factor, which results in higher productivity and efficiency of the filtration process (Araki et al. 2011).

Zhu et al. (2015) also used a sol-gel method for the synthesis of membrane-containing zirconia. The aim of this study was to demonstrate the relationship between the size of the sol and the structure of the membrane, which directly affects the performance of the nanofiltration process. Zhu's et al. (2015) studies and the obtained results are consistent with the results of Araki et al. (2011). Whereas Van Gestel et al. (2008) showed that in the case of the sol, whose particle diameter was about 6 nm, the resulting membrane was dense and did not allow to pass water molecules, even with high pressure, e.g., 1.0 MPa. This is in line with Zhu's et al. (2015) findings. Zhu et al. (2015) showed that for the nanofiltration process, the most preferred sol was the one with the particle size of about 8 nm. The size of the particles in the sol depends on the process parameters, such as time, temperature and the degree of hydrolysis, as well as the size of a chelating agent dopant. The last is described as the molar ratio of a chelating agent to the zirconium compound used as a substrate. Qi et al. (2012) demonstrated that increasing the degree of hydrolysis results in a higher number of particles having larger diameters. Then, it was found that when conducting hydrolysis in the ice bath, the duration of the hydrolysis differed. The period of hydrolysis depended on the particle size and volume percentage of particles of a given diameter in the product. For example, when conducting hydrolysis for 10 min. the average particle size was 1.8 nm, but the particles occupied less than 30% of the sample volume. Whereas, after 30 min hydrolysis the average particle size was 1.5 nm, but the volume of these particles was approximately 60% of the sample volume. After next 30 min. an increase of particles' size, but also a decrease of their volume in the sample was observed. Whereas after 360 minutes, authors (Qi et al. 2012) reported particle size reduction while maintaining the volume occupied by the sample at the level of about 45%. The increased temperature resulted in smaller number of grains, however with a bigger size. The resulting product was also less homogeneous in terms of particle size distribution (Qi et al. 2012). In this experiment, a zirconium n-propoxide and diethanolamine were used as a substrate and the chelating agent, respectively.

Hove et al. (2015) also received the membrane for gas-separation applications, containing zirconium oxide. In this case, the membrane was obtained in the form of the organic-inorganic hybrid connections of silica doped with zirconia. Araki et al. (2011) and Hove et al. (2015) used the addition of zirconia to silica in order to improve the hydrothermal stability. Zhang et al. (2011) also used zirconium oxide, but

in order to improve the hydrophilic properties and to reduce vulnerability of polysulfone membranes for contamination. Polysulfone membranes due to the good physicochemical stability, resistance to oxidation and chlorine are used in water treatment processes in oil removal, but because of their hydrophilicity, were contaminated relatively rapidly, resulting in a decline of the filtration rate and decreased efficiency of the process. Zhang et al. (2011) proposed a solution to this problem, synthetizing nanometric particles of sulfated zirconia doped with yttrium oxide ($SO_4^{2-}/ZrO_2-Y_2O_3$) and then doping them with the polysulfone to form the new hybrid membranes. Polysulfone membranes were obtained according to the procedure set forth in Zhang et al. (2009).

Khajavi and Babaluo (2015) also proposed the method for preparation of membranes based on sulfated zirconium oxide, using the sol-gel technique. The resulting catalytic membranes can be used as a non-permselective membrane in a catalytic membrane reactor configuration. As substrates for the sol synthesis, aluminum triisopropoxide and nano-silica (average particle diameter approximately 35 nm) in powder form and sulfated zirconia (average particle diameter approximately 45 nm) were used. Sol layer was applied onto the support membrane, which was the α-alumina. Khajavi and Babaluo (2015) have found, also as Araki et al. (2011) and Zhu et al. (2015), that in order to obtain membranes free from defects, it is necessary to modify the surface of α-alumina. Such a modification can reduce the pore size and the support surface roughness, and also reduce migration of the sol particles into the interior of the α-alumina structure. In this case, the surface modification consisted of α-alumina coating by immersion in a sol containing boehmite. This resulted in a thin layer of γ-alumina with thickness of 2 µm and a suitable morphology, with no cracks and defects in the microstructure. The catalytic layer of the membrane was obtained by immersion in sol containing sulfated zirconia. Khajavi and Babaluo (2015) demonstrated that it is necessary to adjust pH of the sol during the process of membrane formation. At pH less than 2, the damage of the intermediate layer structure and penetration of sol particles into the interior of the membrane support was observed. In contrast, the coating prepared from sol of pH 3.5, was completely stable. The goal of this study was to obtain a catalytic membrane which is characterized by the presence of tetragonal phase zirconia. This resulted from the creation of a composite structure, that is a sulfated zirconium oxide-Al_2O_3-SiO_2 (Khajavi and Babaluo 2015).

The ceramic membranes prepared by sol-gel method were also used in the removal of high salinity from wastewater by nanofiltration (Da et al. 2016). Da et al. (2016) used ceramic membranes based on zirconium oxide. Membranes were prepared by sol-gel method, and as substrates zirconyl chloride and oxalic acid were used. An important role in the process of membranes preparation was played by glycerol, whose suitable addition contributed to the stabilization of the tetragonal phase of ZrO_2 in the calcination process, and also limited the growth of particles and regulated the sol viscosity. The glycerol was also responsible for the reduction of excessive agglomeration of the zirconia particles. Glycerol functions as blocking agent which generates bonds at the surface of particles and thereby prevents their over-aggregation due to their steric stabilization. Thus, the ceramic membranes

formed on a support comprising an ultrafiltration layer in the form of α-alumina. Depending on the glycerol content in sol, membranes with different pore sizes and specific surfaces were obtained. With the increase of glycerol content (from 0–50 wt.%) there was an increase of membranes surface area of 62.5 to 82.5 m^2/g, and reduced pore diameter from 3.9 to 1.0 nm. Initially, the pore volume of the membrane increased with increasing content of glycerol, but when its content reached 50 wt.%, a pore volume intensely decreased, reaching a value close to the initial one, when the addition of glycerol was 0% (Da et al. 2016).

Sol-gel method is quite commonly used for the preparation of membranes, as confirmed by the multiple examples. According to Zhu et al. (2015) this method can be considered as the most appropriate technique for the preparation of microporous ceramic membranes.

Other methods of obtaining ceramic membranes

Ceramic membranes are also obtained by isostatic compression, reverse phase technique or hydrothermal crystallization. Del Colle et al. (2011) receive membranes based on zirconium dioxide, but using isostatic pressing. Arthanareeswaran and Thanikaivelan (2010) obtained hybrid membranes, which consisted of cellulose acetate and zirconium oxide. The resulting membranes have been used in ultrafiltration and characterized by high mechanical stability and resistance to abrasion. Arthanareeswaran and Thanikaivelan (2010) showed that with the addition of zirconium oxide, tensile strength decreased from 2 to 1.4 N/mm^2. The addition of the zirconia contributed to a greater filtration performance. This effect was due to the increase of the filter affective area by accumulation of zirconia particles on the surface of membranes. Yin et al. (2009) were focused on obtaining highly asymmetric fiber membranes in the shape of hollow capillaries which contained yttria-stabilized zirconia. The membranes were formed on the basis of a reverse phase and sintering modified technique. This synthesis resulted in membranes of a double structure: the outer – formed by crystalline and dense zirconium oxide layer, and the inner – thicker layer of 28.8%surface porosity.

Kumar et al. (2015) received ceramic membranes based on the in situ hydrothermal crystallization technique. For this purpose, the support membrane in form of inexpensive raw materials, e.g. various types of clays, including feldspar, ball clay, kaolin, pyrophyllite and quartz was used. Zirconyl chloride and ammonia aqueous solution were also used as substrates. Such membranes were also studied by Monash and Pugazhenthi (2011a). Membranes containing zirconium oxide have been also obtained by Lv et al. (2016) who received the organic-inorganic composite thin-film nano-filtration membranes. The membranes were prepared by modification of the ultrafiltration membrane and then through mineralization processes. The authors showed that the resulting membranes had high retention (> 90%) for divalent cations and high structure stability for long term nanofiltration.

Based on the discussed methods it can be stated that ceramic membranes molded with zirconia are more effective and increase filtration efficiency. The addition of zirconium dioxide improves the hydrophilic properties of the membrane. But above all, the use of ZrO_2 results in increased chemical and hydrothermal membrane stability.

Separation of o/w emulsions using ceramic zirconium membranes

Ceramic zirconium membranes are used in the process of oil-in-water emulsion separation (Del Colle et al. 2011, Kajitvichyanukul et al. 2011, Wu and Cheng 2000, Zhang et al. 2014, 2011, Jamshidi Gohari et al. 2015, Yeom et al. 2016, Kumar et al. 2016). Emulsion separation takes place through microfiltration, ultrafiltration and nanofiltration (Del Colle et al. 2011).

Oily wastewater treatment using zirconium membranes

Ceramic polysulfone membranes doped with sulfated zirconium oxide developed by Zhang et al. (2011) were used for purification of wastewater containing oil, at the level of 80 mg/dm^3. After purification, the concentration in the permeate dropped to 0.67 mg/dm^3. Thus, it can be concluded that the use of developed membranes resulted in approx. 99%, oil pollution removal. This is a high degree of purification, comparable to the effect achieved by, e.g., membrane based on a polyvinylidene fluoride doped with titanium oxide obtained by Yuliwati and Ismail (2011). Polysulfone membranes were also used in the oily wastewater ultrafiltration process by Kumar et al. (2016). Polysulfone membranes were formed from polymer (polyvinyl pyrrolidone or polyvinyl acetate) and bentonite. The degree of oil removal for prepared membranes ranged from 90–98%, depending on the composition of a membrane. Table 1 shows selected examples of membranes used in deoilization of wastewater. The effectiveness of the membrane filtration process ranged from 85–99.9%, depending on the membrane used.

The membranes based on alumina doped with nanometric zirconia, used to separate oil at the concentration of 1,000 mg/dm^3 were highly efficient, which was 97.8% (Zhou et al. 2010). Also, the removal of oils at the same concentrations was achieved with use of the nano-sized TiO_2-coated Al_2O_3 membranes, with efficiency of 99.7% (Chang et al. 2014). Yeom et al. (2016) presented the composition and characteristics of membranes, based on less expensive materials. The purification efficiency of these membranes, depending on their composition, ranged from 85–99.9%. For example, zirconia-containing clay-based membranes have enabled the purification of oil wastewater with an oil concentration of 100 mg/dm^3 at 85% efficiency (Eom et al. 2014). For comparison, the clay-based membranes (Vasanth et al. 2013)

used to purify effluent with the same oil concentration, achieved efficiency of 97%. Higher purification efficiency (99.9%) at 600 mg/dm^3 oil concentration was obtained by Yeom et al. (2016) who used membranes comprising clay and diatomite, but doped with alumina. Monash and Pugazhenthi (2011b) and Emani et al. (2014) also achieved a high removal efficiency of 97–99% using kaolin-based membranes. But Monash and coworkers prepared titanium oxide-doped membranes, which contributed to increased efficiency of the process (Monash and Pugazhenthi 2011b). In contrast, Mittal et al. (2011) using a low-cost, hydrophilic ceramic – polymeric composite membrane composed from clay, kaolin and a small amount of binding materials, received a degree of oil removal, which amounted to 93%. Mullite membranes have also been found to be effective in the treatment of oily wastewaters. The oil remove level was 93.8% at oil concentration of 1,000 mg/dm^3 (Abbasi et al. 2010). Yang et al. (2011) received a kaolin-based membrane but coated with MnO_2, which was also used for the separation of oil from water.

Oily wastewater treatment using non-zirconium membranes

As another example of membranes used in the separation of oil pollutants from water a tubular UF module equipped with polyvinylidene fluoride membranes modified by inorganic nano-sized alumina particles can be presented (Yu et al. 2006). The efficiency of the membrane was considered high because the permeate oil concentration was 1 mg/dm^3. The authors have shown that the addition of alumina nanoparticles improves the antifouling performance of the membrane and increases its efficiency.

Song et al. (2006) received a carbon membrane with pore size of 1.0 μm. The efficiency of filtration process under specific conditions: operating through pressure of 0.10 MPa, flow rate of 0.1 m/s was 97%. Ceramic microfiltration (MF) membranes based on α-Al_2O_3 were also used to purify wastewater of a lower oil concentration up of 26 mg/dm^3, with the efficacy of 95% (Abadi et al. 2011). Cui et al. (2008) prepared NaA zeolite MF membranes on α-Al_2O_3 tube by in situ hydrothermal synthesis method. Membranes were used in the purification process with the oil removal yield of 99%. Hua et al. (2007) also used α-Al_2O_3-based ceramic membranes in the cross-flow microfiltration (MF) processes of oily wastewater. The pore size of the membrane was 50 nm. In this case, the efficiency of the sewage treatment process was not related to the degree of

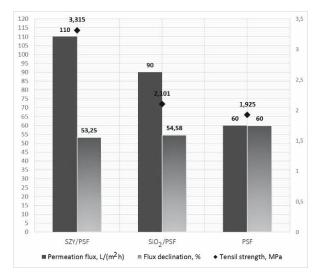**Table 1.** Effectiveness of oil wastewater membrane filtration processes

Membrane	Oil concentration in sewage (mg/dm³)	Degree of removal (%)	Ref.
Polysulfone doped with sulphated zirconium oxide	80	≈99	Zhang et al. (2011)
Based on clay doped with ZrO_2	100	85–99.9	Eom et al. (2014)
Based on Al_2O_3 doped with nanometric ZrO_2	1000	97.8	Zhou et al. (2010)
Based on Al_2O_3 doped with nanometric Al_2O_3	1000	98.5	Chang et al. (2010)
Mulit	1000	93.8	Abbasi et al. (2010)
Based on clay and diatomite doped with Al_2O_3	600	99.9	Yeom et al. (2016)

oil removal, but to the total organic carbon (TOC) content. The microfiltration process resulted in the TOC decrease of 92.4%. Sarfaraz et al. (2012) also used TOC to determine the filtration efficiency using nano-porous membrane-powdered activated carbon. TOC removal rate was 71.5%. In contrast, Salahi et al. (2013) determined the filtration efficiency based on chemical oxygen demand (COD). The authors used polyacrylonitrile nano--porous membrane and the effect was COD reduction of 76.9%.

The efficiency of filtration processes using the presented membranes was high, suggesting that membrane filtration processes are highly effective purification methods. To fully compare the effectiveness of the membranes used, it is not enough to compare only the obtained results by describing the degree of oil contaminant removal, especially when their initial concentrations are different. Larger initial oil concentrations contribute to more effective clogging of the membrane pores and will require different filtration conditions than in the case of diluted solutions. Therefore, it is also necessary to compare the conditions of the filtration process, which is difficult because the authors give different parameters. Narong and James (2008) studied the ultrafiltration process using ZrO_2 with $Al_2(SO_4)_3$ + CTAB membrane and found that better results were obtained at lower pH. They conducted filtration using trans-membrane pressure (TMP) and permeation flux of 250 kPa, 21.5×10^{-6} $m^3 \cdot m^{-2} \cdot s^{-1}$, respectively. At pH 6.2, the TOC was reduced by 22.1%, and for pH 3, the TOC reduction was 28.1%. Turbidity reduction in this process was 98%, up to NTU 4.2. For comparison, Yeom et al. (2016) used trans--membrane pressure (TMP) and permeation flux of 101 kPa, 6.91×10^{-6} $m^3 \cdot m^{-2} \cdot s^{-1}$, respectively. The functional properties of the membranes are particularly important and vary depending on the chemical composition of the membrane, as shown in Figure 2. Polysulfone doped with sulphated zirconium oxide (SZY/PSF) membranes exhibited higher tensile strength and were less susceptible to dirt than conventional polysulfon (PSF) and SiO_2 containing membranes (SiO_2/PSF).

Ceramic membranes are increasingly used, especially in the industrial micro and ultrafiltration processes, due to their mechanical properties and resistance to the high temperatures or pH limits. Ceramic-polymer hybrid membranes, with the addition of zirconium compounds to improve mechanical properties, including tensile strength and anti-compaction properties, are also used.

Conclusions

Oily wastewaters are purified by various methods which can generally be divided into mechanical, physical and chemical methods. The choice of treatment depends on the concentration and occurrence of oil form in water. Pressure filtration methods: microfiltration, ultrafiltration and nanofiltration, belong to the final stages of oily wastewaters treatment, when the oil is dispersed in water and forms oil-in-water emulsions. These methods represent high efficiency wastewater treatment methods, as they result in approximately 99% removal of oil from water. The increase of consumerism society, expansion and development of world economies make the amount of produced sewage, also industrial wastewater, grow. As a result, there is an increasing demand for wastewater treatment processes. In the case of membrane filtration, the focus is on improving the operational parameters of the membranes used. In the area of pressure filtration processes, new hybrid membranes are created that rely on polymers to which ceramic material such as ZrO_2 is attached, to improve their performance. In addition, ceramic membranes based on raw materials of natural origin are created, which also achieve high levels of purification as hybrid membranes. Such materials are also used to produce composite membranes, made of two different substances and obtained by coating. The use of natural raw materials in the molding process of membranes is a particularly advantageous solution that improves production costs. This serves to strengthen the "environmentally friendly" approach to research. The ZrO_2 ceramic membranes discussed in this paper are successfully used for the separation of oil-in-water emulsions and achieve a high purity (about 99%). The most common method of obtaining them is the sol-gel method, which is also constantly being improved and developed. The sol-gel method is used to obtain membranes used in the micro, ultra and nanofiltration processes.

Oily wastewater treatment technology should focus on study of oily wastewater degradation mechanism, to improve oily wastewater treatment efficiency and reduce processing costs. It seems that the most important issue is to maximize the advantages of membrane methods in order to avoid restrictions on their use. Since membrane methods are the last stage of oil wastewater treatment, when the oil is in the form of oil-in-water microemulsion, the efficiency of pre-filtration processes should be improved. At the same time, the operational parameters of the membranes used should be improved. Ceramic membranes should better withstand elevated temperatures, extreme pH values and high transmembrane pressures without fear of membrane tamping, delamination or swelling of system components.

Fig. 2. Utility parameters of polysulfon membranes (PSF), on the basis of (Zhang et al. 2011)

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Oczyszczanie ścieków olejowych przy zastosowaniu membran ceramicznych zawierających tlenek cyrkonu – przegląd literaturowy

Streszczenie: Artykuł stanowi przegląd literatury, w którym omówiono problem oczyszczania ścieków olejowych w oparciu o filtrację membranową. Skupiono się na membranach ciśnieniowych zawierających związki cyrkonu, głównie ZrO_2. Porównano skuteczność procesów oczyszczania dla różnych membran (ceramicznych i kompozytowych). Omówiono wpływ związków cyrkonu na właściwości użytkowe membran ciśnieniowych. Membrany ceramiczne są zwykle uzyskiwane za pomocą techniki zol-żel, ale również przez prasowanie izostatyczne, technikę odwróconej fazy lub krystalizację hydrotermiczną. Membrany ceramiczne są formowane z tlenkiem cyrkonu, co skutkuje wzrostem skuteczności filtracji.