American Journal of Energy Engineering
2020; 8(4): 34-39
http://www.sciencepublishinggroup.com/j/ajee
doi: 10.11648/j.ajee.20200804.11
ISSN: 2329-1648 (Print); ISSN: 2329-163X (Online)

Investigation of Polysulfone Based Aluminium Oxide Coated Membrane for Separation of Crude Oil Emulsion in the Niger Delta

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To cite this article:

Ngozi Claribelle Nwogu, Nkemakolam Chinedu Izuwa, Chioma Deborah Mbakaogu, Stanley Toochukwu Ekwueme. Investigation of Polysulfone Based Aluminium Oxide Coated Membrane for Separation of Crude Oil Emulsion in the Niger Delta. *American Journal of Energy Engineering*. Vol. 8, No. 4, 2020, pp. 34-39. doi: 10.11648/j.ajee.20200804.11

Received: October 1, 2020; **Accepted**: October 19, 2020; **Published**: December 16, 2020

Abstract: There is need for efficient separation of crude oil from its emulsion in oil and gas processes especially during production and refining activities. Among other methods used for crude oil emulsion demulsification, polymer membranes have attracted a lot of attention. The increasing interest in polymer membranes usage for ultrafiltration and micro filtration are mainly due to their versatility, efficiency and reduced operating cost when compared with conventional techniques such as use of chemical, flocculation etc. This paper illustrates experimental process for the separation of crude oil emulsion using Polysulfone membrane material coated with Aluminium oxide nanoparticle. The crude oil emulsion was prepared by mixing with distil water to obtain an oil in water emulsion. Because of the oleophilicity of Polysulfone membrane materials in oil/water separation, aluminum nanoparticles were used as metallic coatings to their Polysulfone membrane to improve efficiency and anti-fouling characteristics. Three parametres were investigated in the results, these include the separation efficiency in terms of oil rejection, the permeation flux, the filtrate volume for pressure application of 80% stroke and 60% stroke. The augmented membrane construction yields 98.5% and 97.6% efficiency in terms of oil rejection for a pressure application of 60% stroke and 80% stroke respectively while the permeation fluxes are 0.911 ml/cm^2-min and 1.024 ml/cm^2-min for 80% stroke and 60% stroke pressure application respectively.

Keywords: Polysulfone, Aluminium Oxide, Emulsion, Membrane, Nanoparticles

1. Introduction

The prevalence of emulsions have been extensively investigated with relevance to several technological operations such as oil and gas, food, chemicals, metal processing, pharmaceuticals etc. In oil and gas industry operation, emulsion occur between water and crude oil and its formation has been inevitably encountered in many stages of oil and gas activities such as drilling, production, transportation and processing of the crude. It has been revealed by researchers that crude oil emulsion is closely associated with the composition of the crude which contains natural emulsifiers like asphaltenes, acidic compounds (like naphthenic acid, fatty acid, aromatic acids) and resins [1]. Crude oil emulsion forms due to contact between crude oil and water in the presence of this emulsifiers provided there is sufficient agitation enough to disperse one phase of the liquid in the other as droplets. Use of membranes for oil/water emulsion separation has become more popular owing to its versatility and efficiency when compared to conventional techniques such as gravity settling, coagulation, flotation, flocculation, ozonation, and chemical methods. These conventional methods have become ineffective in treatment of oil/water emulsion due to high operational cost, higher energy consumption, lower efficiency and the problem of getting secondary pollutants as by-products [2].

Polymer membranes have been popular in use as filtration materials. Polymers such as polyvinylidene fluoride (PVDF), Polysulfone (PSf), Polyethersulfone (PES) etc. have been applied in separation of oil-water emulsions.

Liquid-Liquid phase inversion is the most popular membrane preparation technique. In this method, the exchange of the solvent in the homogeneous polymer solution with its non-solvent from the coagulation bath results in a porous polymer film [3]. Most polymeric membranes owing to their intrinsic properties are oleophilic which means that they attract oil to its surfaces. Oil retention to polymeric membrane surface have been shown to be the cause of membrane fouling. To improve the hydrophilicity and antifouling performance of polymeric membranes, the membrane can be blended with hydrophilic components or surface modification of the membrane surface can be done.

Blending is usually done during the phase inversion process of the membrane [4, 5]. This is achieved by blending the polymer matrix with hydrophilic components such as hydrophilic polymers, amphiphilic copolymers and inorganic nanoparticles. These are the three main types of additives used extensively to modify the porous filtration membrane. Although the effects of different additives on the membrane performance differ, the main objective of blending is to enhance the membrane permeability and antifouling property. However, the stability of the blending membranes remains a challenging issue [6].

On the other hand, surface modification can be achieved either by chemical reaction or physical absorption. Physical absorption methods include surface grafting and surface coating. In Surface grafting, hydrophilic polymer chains or nanoparticles are immobilized onto the membrane surface. To achieve this, reactive groups need to be first introduced on the membrane surface by either introducing initiator sites or exposing the membrane to low-temperature plasma, ultraviolet, g-ray or electron beam radiation [7]. In surface coating, various hydrophilic layers are constructed by dipping or spraying steps or by directly physical adsorption on the membrane surface. Most times the coated layers are unstable and may result to parting from the membrane. Therefore to improve stability of the coting, crosslinking can be done.

Aside polymeric additives, inorganic nanoparticles, such as Al_2O_3, TiO_2, ZrO_2, and SiO_2, have been used to improve membrane performance [8]. It has been shown that nanoparticles have large surface areas and abundant surface-active groups. Addition of inorganic nanoparticles to membranes has proven to be helpful in membrane permeability and fouling resistance by these two mechanisms i) changing the membrane pore structure ii) increasing the hydrophilicity of the membrane.

Li et al [9] blended Al_2O_3 nanoparticles with PVDF UF membranes. He observed upon addition of Al_2O_3 nanoparticles increased the hydrophilicity of the PVDF membrane but had no effect on the effective pore size and porosity of the membrane. Saththasivam et al [10] researched on flexible $Ti_3C_2T_x$ (MXene)/paper membrane for efficient oil/water separation. They developed $Ti_3C_2T_x$ (MXene) as the functional layer on conventional print paper which they used as the substrate. Using MXene ink and a simple coating process, they developed a highly hydrophilic and oleophobic membrane with an underwater oil contact angle of 137°. The membrane was observed to have high separation efficiency for oil/water emulsions, of over 99%, and a high water permeation flux of over 450 L per m^2 per h per bar and also showed excellent anti-fouling properties. Yang et al [11] researched on TiO_2 nanoparticles. They used the nanoparticle in blending with a polysulfone ultrafiltration membrane which was used with success in the separation of kerosene/water emulsion. Furthermore the membrane was observed to have improved anti-fouling properties. Matsuyama and Yoshioka [12] developed ultrathin durable membrane for efficient oil and water separation. The membrane was developed to have a fouling-resistant silica surface treatment to enable high performance separation of oil from water. The result of the experimentation show that the membrane was versatile; able to separate water from a wide range of emulsions. Liu et al [13] worked on efficient oil/water separation membrane derived from super-flexible and superhydrophilic core–shell organic/inorganic nanofibrous architectures. They synthesized superhydrophilic and underwater superoleophobic organic/inorganic nanofibrous membranes using a scale-up fabrication method. The membrane that was synthesized retains a delicate organic core of PVDF-HFP and an inorganic shell of a CuO nanosheet structure, this provides super-flexible characteristics owing to the merits of PVDF-HFP backbones, and superhydrophilic functions contributed by the extremely rough surface of a CuO nanosheet anchored on flexible PVDF-HFP. This organic core and inorganic shell architecture not only improves membrane performance in terms of antifouling, high flux, and low energy consumption, but also prolongs the lifespan by enhancing its mechanical strength and alkaline resistance to widen its applicability. The resultant membrane exhibits good oil/water separation efficiency in terms of oil rejection of more than 99.7%, together with excellent anti-fouling features for different oil/water emulsions. Borisov et al [14] worked on “Development of Polysulfone Hollow Fiber Porous Supports for High Flux Composite Membranes: Air Plasma and Piranha Etching”. They used Polysulfone (PSf) pellets, Ultrason 6010 and N-methylpyrrolidone (NMP 99% extra pure) base polymer and solvent, respectively, with no additional purification. The results reveal that the modified membranes have higher CO_2 permeation than that of the virgin PSf membranes. The average pore size of the air plasma treated membranes calculated based on the gas permeability data is 1.5 times greater than that of the virgin membrane. Oh et al [15] researched on “Performance Analysis of Gravity-Driven Oil-Water Separation Using Membranes with Special Wettability.” They focused on investigating three parameters of separation which are: separation efficiency, liquid intrusion pressure, and mass flux, as a function of pore geometry and liquid properties. They chose metallic meshes with surface wettability being modified by scalable spray coating. In their results they observed that their constructed membrane exhibits a separation efficiency in terms of oil rejection of more than 98%. Yu et al [16] worked on "A Simple, Green Method to Fabricate Composite Membranes for Effective Oil-in-Water Emulsion Separation" They fabricated a corn straw powder (CSP)-nylon 6,6 membrane (CSPNM) using a phase inversion process with no chemical modication. The CSPNM showed superhydrophilic and underwater superoleophobic properties. The CSPNM showed excellent separation ability after 20 cycles of separation with an oil rejection of more than 99.60%. In addition, the CSPNM showed excellent thermal and chemical stability under high temperature and varying pH conditions.

In this work, experimental evaluation of Polysulfone based polymeric membrane coated with Aluminium oxide nanoparticle is done to determine its applicability and efficiency in separation of crude oil emulsion

2. Materials and Methods

Crude oil sample used was sourced from Niger Delta flowing well. Iso-Hexane, sealant, Petroleum ether, silver nitrate and Aluminium oxide nanoparticle were purchased from the market. The Polysulfone membrane material which is used is purchased from the market.

2.1. Preparation of the Emulsion Solution

50ml of crude was put into a beaker. 500ml of deionized water was added to the crude oil. The resulting mixture was mixed thoroughly to obtain a homogenous oil/water emulsion (0.01% w/o emulsion). The Mixture was then blended in a high speed blender at 20,000rpm (high rotational speed) for 1 minute. The oil droplet size was then measured by an optical microcopy method.

Figure 1. *Polysulfone membrane material.*

2.2. Preparation of Nanoparticle Mixture and Coating of Membrane

5g of silicon sealant was dissolved in 10ml of iso-hexane. 20g of Aluminium oxide nanoparticle was put into 500ml beaker. Then 20g of the Aluminium oxide nanoparticle was added into the silicon sealant-iso-hexane solution at room temperature, this was stored for 1 minutes to form a paste like slurry. The whole mixture was then stirred consistently and cast on the top of the sample membrane based support. This was also done at room temperature and then left to settle for 10 minutes. The coated membrane sample was anchored to the membrane filtration apparatus with vacuum grease and then allowed to dry in open air for about 1 hour. A thickness of 3 mm was obtained.

The membrane filtration apparatus consist of the beaker, filtration apparatus and has a magnet on the bottom to fix tightly to the base. The base is connected to the stopper. In-between the base and the stopper is the nano-ultrafiltration membrane which is held tightly together with an external clip placed between the upper filtration beaker and the receiver conical flask where filtrate samples goes into.

2.3. Oil/Water Emulsion Separation

The prepared oil-water emulsion was stirred for 60minutes to achieve a homogenous mixture under ambient conditions. The membranes to be used were pre-wetted before used for the separation. The emulsion was poured into a measuring cylinder in the filtration apparatus. The procedure was carried out under 80% stroke and 60% strokes pressure using vacuum pump.

Figure 2. *Membrane Separation Process using vacuum pump.*

Figure 2 shows the actual emulsion separation process. The separation funnel is connected to the vacuum pump via the connecting pipe. The vacuum pump supplies pressure necessary to agitate the sample and create pressure differential that will induce separation. From the figure water tends to settle at the bottom while oil floats at the top because water is denser than oil. The separation is carried out by forcing the oily water at the bottom of the beaker in the filtration funnel to pass through the nanoparticle doped membrane substance where the oil part is retained and the water selectively allowed to pass through to the conical flask where it is stored.

Figure 3. *The Emulsified oil-water separated.*

Figure 3 shows the sample after separation. The first two black samples are oil recovered from the emulsified water after the filtration experiment while the last two samples are water that passed through the funnel as filtrate.

The membrane separation efficiency is calculated from the equation given below. This separation efficiency is given in terms of oil rejection.

$$S.E = \left(1 - \frac{C_f}{C_o}\right) x\ 100\% \quad (1)$$

Where

S.E = Separation efficiency in terms of oil rejection, %

C_o is the oil content in the original emulsion, ml

C_f is the oil content in the filtrate, ml

The permeation flux of the Polysulfone membrane is calculated using the equation given below

$$J = \frac{V}{PAt} \text{ (Units in ml/cm}^2\text{-min)}$$

J = Permeation flux, ml/cm^2-min (2)

V= Volume of Filtrate, ml

P = Separation Pressure, bar

A=Area of the Membrane, cm^2

t= separation time, min

3. Results and Discussion

The Result for the oil/water emulsion separation using Polysulfone membrane material for 80% stroke and 60% stroke is given in table 1 below. The efficiency of the separation is given in terms of oil rejection.

Table 1. *Result for Polysulfone membrane material for emulsion separation.*

Parameter	Raw sample	Polysulfone	
		80% stroke	60% stroke
pH	5.89	4.91	5.36
Conductivity, S/cm	33	50	44
Turbidity, NTU	15.7	11.6	18.7
Chemical Oxygen Demand (COD), mg/l	7800	1200	1200
Viscosity, mPa.s	19.9	19.41	19.34
Filtration time, min	-	18	22
Oil Content in filtrate, %	14	0.404	0.25
Volume of Filtrate, ml	-	165	170
Volume retained, ml	-	28	21
Total volume of emulsion used, ml	200	200	200
Volume absorbed by membrane	-	7	9
Volume of oil content in filtrate	-	0.67	0.43
Separation Efficiency	-	97.6	98.5
Permeation Flux, ml/cm^2-min	-	0.911	1.024
Filtrate Flowrate, ml/min	-	9.17	7.73

From table 1, the volume of liquid absorbed by the membrane material are 7ml and 9ml for 80% stroke and 60% stroke respectively. The volume of oil in the filtrate are 0.67ml and 0.43ml for 80% stroke and 60% stroke respectively; the separation efficiency of the separation process are 97.6% and 98.5% for 80% stroke and 60% stroke respectively. The permeation flux are 0.911 ml/cm^2-min and 1.024 ml/cm^2-min for 80% stroke and 60% stroke respectively. The average flowrate of the filtrate are 9.17ml/min and 7.73ml/min for the 80% stroke and 60% stroke respectively.

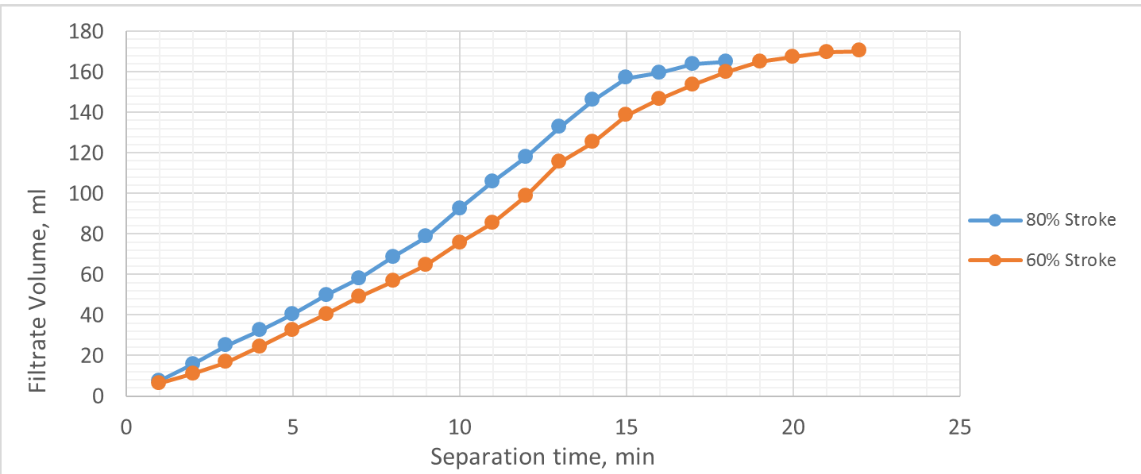

Figure 4. *Graph of Filtrate volume and separation time for Polysulfone membrane material.*

Analyzing the filtrate volume with time for Polysulfone membrane reveals that the 60% stroke yields more volume of filtrate than the 80% stroke, although by considering the closeness of the red and the blue line the difference is not profound meaning that the influence of pressure does not have appreciable effect on the filtrate volume for Polysulfone membrane material. Furthermore, from figure 4, more percentage water removal is realized from 60% stroke than 80% for the Polysulfone membrane material. The percentage water removal for 80% stroke is 95.5% while that of the 60% stroke is 98.6%.

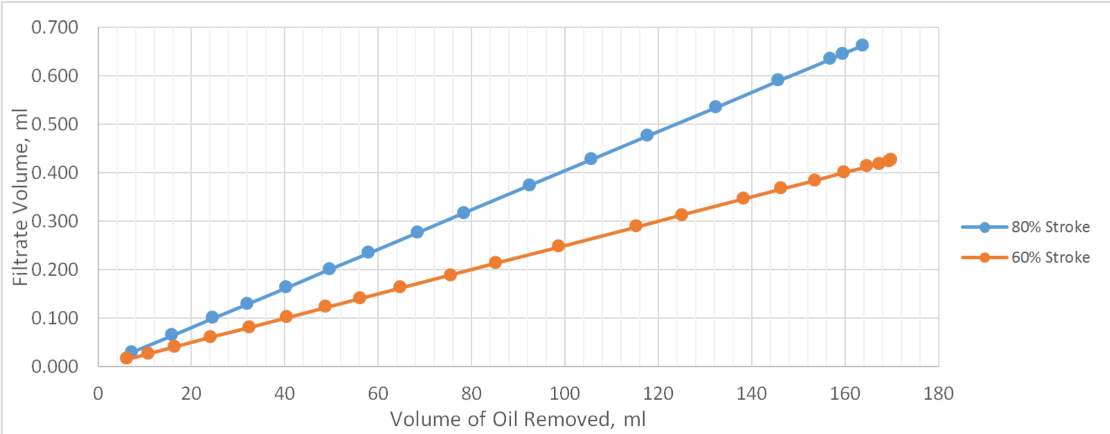

Figure 5. *Graph of Filtrate volume and volume of oil present in filtrate for Polysulfone membrane material.*

More oil is present in the filtrate volume for 80% stroke application than 60% stroke as seen in figure 5. This is because of increase in fluid velocity due to increase in pressure which forces the emulsion to pass through the pores without proper separation. This signifies that too high pressure is not good for membrane selectivity and separation as it damages the membrane surfaces and forces the sample down without proper separation.

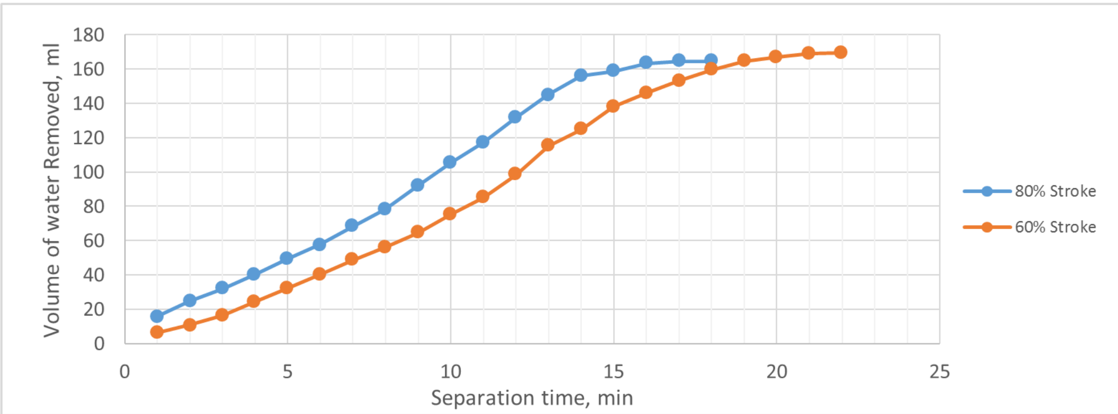

Figure 6. *Graph of water removal from the Polysulfone membrane material.*

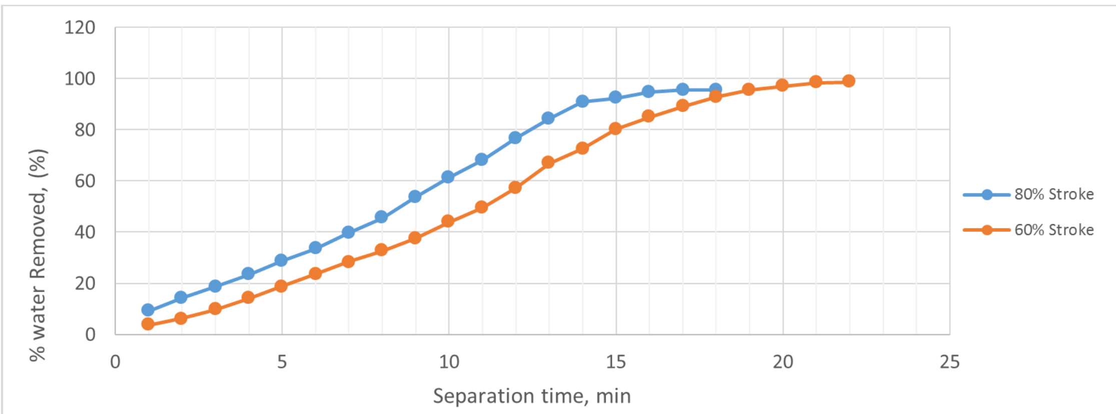

Figure 7. *Graph of Percentage water removal from the Polysulfone membrane material.*

The 60% stroke pressure application on the Polysulfone membrane material gave higher percentage of filtrate water from the emulsion solution than the 80% stroke pressure application.

The Polysulfone membrane material doped with Aluminium oxide nanoparticle shows high separation efficiency in terms of oil rejection. The efficiency of 98.5% for 60% stroke and 97.6% for 80% stoke pressure application indicates indicate that Polysulfone membrane is highly effective in use for treatment of oil/water emulsions.

4. Conclusion

Polysulfone membrane material coated with Aluminum oxide nanoparticles have been used in separation of crude oil emulsion. It has been observed that the addition of nanoparticle coating gives more mechanical stability and higher separation efficiency to the parent membrane material while improving its fouling resistance characteristics. The separation efficiency for the augmented membrane developed is 98.6% for a pressure application of 60% stroke and 97.6% for a pressure application of 80% stroke. Higher pressures applied signified faster rate of separation but at the expense of oil rejection efficiency. With higher pressures, the membrane pores are widened more allowing higher passage of the filtrate and thus giving more possibility of oil being retained in the filtrate. Thus, too low pressure increases the filtrate time and too high a pressure leads to reduction of separation efficiency with higher possibility of coating pull-out and membrane damage.

5. Recommendation

Polysulfone polymer membrane is recommended for use in separation of crude oil emulsion that frequently occur in oil gas activities in the Niger Delta. The membrane must be manufactured to be stable to withstand applied separation pressures. Furthermore, because of the oleophilic nature of Polysulfone membrane, coating with nanoparticles like aluminum oxide gives extra mechanical strength and anti-fouling resistance the membrane.

More research should focus on addition of a co-polymer to get a membrane-co-polymer-aluminum particle membrane construction for a higher efficient and durable membrane applicability for separation of a more varieties of oil emulsions.

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