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Characterization and evaluation of nanoparticles ceramic membrane for the separation of oil-in-water emulsion.

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CHARACTERIZATION AND EVALUATION OF NANOPARTICLES CERAMIC MEMBRANE FOR THE SEPARATION OF OIL-IN-WATER EMULSION

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ABSTRACT

The mixture of oil with water from industrial activities creates an emulsion which is now termed as Oil-in-Water (O/W) emulsion. Several chemical and physical methods have been successfully used for the separation of O/W emulsions; however, the trace amounts of oil remain unfiltered in the separated water. This research aims at comparing two nanoparticles (Iron and Silver) coated ceramic membrane with self-cleaning ability for the effectively separation of low concentration (<250mg/L) of O/W Emulsion. Preliminary experiments have been done to determine the morphology and pure water flux of unmodified commercial ceramic membrane using Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Analysis (EDAX) and in-house installed separation rig respectively. An uneven pore size with a densely packed image from SEM indicates an increase in flux. Steady pure water permeate flux shows possibility of anti-fouling in ceramic membrane.

KEYWORDS: Oil-in-water emulsion, Nanoparticles, Ceramic membrane, Separation

1 INTRODUCTION

Oil refineries produced large quantity of oily wastewater which can also be termed as (O/W) emulsion with oil droplet of different sizes (oil in water or o water in oil emulsion). Offshore oil spillage produces huge amount of oily wastewater (Elanchezhiyan, Sivasurian and Meenakshi 2016). This O/W emulsion discharged into the environment directly will not only pollute the environment but reduce water resources especially drinking water. A way to address this problem is to separate oil from water and possibly reuse or recycle both components. Several promising methods have been reported so far by researchers for the separation of oil from O/W emulsions before discharge into the environment, which have their advantages and disadvantages (Wang, Wang and Geng 2018). Materials that can meet the challenging requirements of real-world applications are still in the process of development. Hence, there is a need for the advancement of a recyclable, cost -effective, environmentally friend, simple and efficient method that can separate big volumes of O/W emulsions into two phases with high flux and oil rejection rates. These several methods researched and reported for the separation of O/W emulsions are adsorption, electrocoagulation, flocculation, bioremediation, centrifugation, membrane etc (Shi et al. 2019).

These traditional methods are insufficient in the treatment of O/W emulsions due to the small size of oil droplets as well as lower concentrations of oil in water, because below 250mg/L separation is usually not possible (Huang et al. 2018). However, membrane technology has been recently most researched as a promising alternative for the separation of O/W emulsion. This may be because of merit features which includes an excellent combination of longer shelf life, better self-cleaning properties, mechanical, chemical, and thermal strength, survival in organic solvent, low cost, compact design, removal of secondary separation and superior separation factor (Suresh and Pugazhenthi 2016).

A major drawback in the use of membrane technology in the industrial separation of O/W emulsion is the issue of membrane fouling after few cycles of use (Guo, Xu and Qi 2016). Recently, there has been a growing interest of research on the use of nanoparticle in O/W emulsion separation. Nanoparticle has been reported that it has excellent oil adsorption, high surface area, and can be 30% less costly than other available techniques (Almomani et al. 2020). This research aims at coating nanoparticles especially iron and silver on commercial ceramic membrane for the separation of low concentration (<250Mg/L) O/W emulsions. The nanoparticles are to increase hydrophilicity on ceramic membrane and possibly high flux and oil rejection (>99%), creating two phases that can be reused.

A mixture of wastewater with oil from industrial activities in varying concentrations creates oily wastewater or in this context known as O/W emulsion. Various compounds like hydrocarbons, fats, diesel, gasoline kerosene etc. can form oily wastewater depending the on the products of different industries. The daily generation of O/W emulsion from industrial activities adversely affects the entire sector of the environment. For example, air pollution is achieved by the evaporation of oily substance released into the environment. Drinking water is affected by the peculation of this wastewater beneath the soil to underneath water resources (Jamaly, Giwa and Hasan 2015). Ground water and sea waters are not left out as they are the primary discharge sites. Humans and animals health are at great danger from the hazardous substance from O/W emulsion discharged into the environment (Ma et al. 2021). Therefore, the separation or treatment of O/W emulsion is required before discharge. (Padaki et al. 2015b) reported that the emulsified form of oil in wastewater is considered the most difficult to separate from oily wastewater. Compared with other conventional method for separation of O/W emulsion, membrane technology especially when coated with nanoparticles promises a good outcome due to the advantages associated with them. Following the drawbacks in most of the conventional techniques listed in table 1, this article adopts the membrane technology for O/W emulsion separation because of current breakthroughs such as low energy usage, low costs and its material durability, reusable, compact design and elimination of secondary treatment.

Table 1 shows different physical and chemical methods suitable for oily wastewater removal, advantages and disadvantages. Adopted from (Padaki et al. 2015a)

Methods for purification	**Advantages**	**Disadvantages**
Solvent extraction	Very fast and efficient method	High operational cost and environmentally unfriendly, no suitable to remove heavy metals
Centrifugation	Environmentally friendly and easy to process	Requires high energy usage, which makes it economically unfit.
Forth flotation	Less energy usage and easy to apply	The process cannot remove high viscous oily wastewater
Ultrasonic irradiation	Fast and effective, no need any chemicals	High cost of operation, not suitable to treat heavy metals
Surfactant EOR	Easy to process and limited application in heavy metals	Economically costly to use, requires alternate process to remove toxic surfactant
Freeze/thaw	Short treatment process and suitable for cold regions	Less effective and coastally process

Microwave irradiation	Very fast and efficient and no need of chemical addition	Economically costly, and not effective for large scale process
Electrokinetics	No need to chemical addition and fast process	Difficult operating process and less effective
Pyrolysis	Large treatment capacity, fast and effective	High capital, maintenance and operational cost
Incineration	Rapid and complete removal of PHCs in oily sludge	High capital cost of equipment and requires alternate process to remove ash
Stabilization/solidification	Fast and efficient to produce PHC stabilized compounds, low cost and capture the heavy metals	Loss of recyclable energy and less effective in process
Oxidation	Rapid and complete removal of PHCs in oily sludge.	Large amount of chemical required, high cost and environmentally unfit
Land farming	Low cost and do not need much maintenance and applicable to large quantity also	Underground water pollution and sand pollution
Landfill	Less cost and large treatment capacity	Very slow process and required more place
Biopile/compositing	Large treatment capacity, low cost, faster and less area required for the process	Applicable in cold condition
Bioslurry	Fastest degradation approach, great PHC removal	High cost and applicable to small scale

Membrane is a semipermeable and selective barrier that can separate phases limiting, totally or partially, the passage of one or more constituent contained in a solution. Membranes are fabricated from organic (polymers) and inorganic (carbons, alumina, and zeolites) materials. Comparisons are ongoing between polymeric membranes and ceramic membranes about the advantages one has over the other. It has been reported by several authors (Hendren, Brant and Wiesner 2009) (Phan et al. 2016) that ceramic membranes have more advantages in chemical, mechanical, and thermal stability, longer shelf life, high membrane flux and formidable corrosive resistance. Based on this, ceramic membrane is receiving recent attention in separation processes for water purification and will be used in this research. Membranes are further classified by pore size into Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and reverse osmosis (RO) as shown in figure 1. (Bolto et al. 2020).

Nanoparticles have drawn wide attention the treatment of wastewater. nanomaterials are generally known as materials whose components are in sizes between 1-100nm (Buzea, Pacheco and Robbie 2007).

Nanoparticles are very reactive and have strong adsorption capacities because of their sizes which gives large surface area (Lu et al. 2016). Based on these properties, nanoparticles iron and silver which are known for excellent adsorption and high toxicity against microorganisms respectively will be impregnated into the surface of micropore unmodified ceramic membrane for the purpose of this study**.**

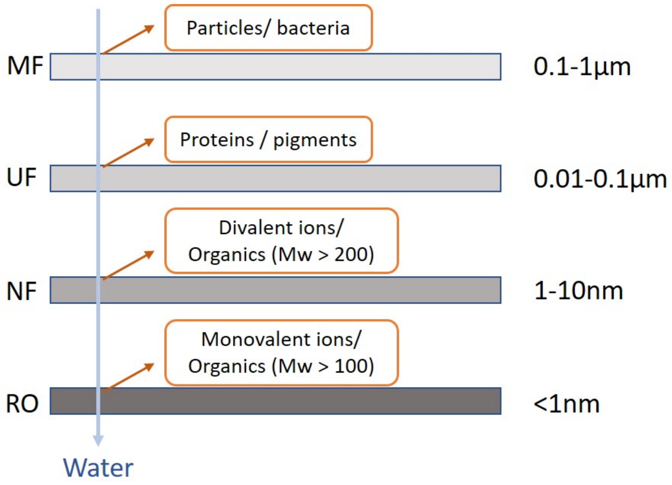

Figure 1: Pore size classification of membrane

2 EXPERIMENTALS

2.1 Characterization

The microstructure of the unmodified ceramic membrane was analyzed using Scanning Electron Microscope (SEM). Unmodified ceramic membrane samples were placed firmly on a stub and transferred to the sample carousel of the SEM for analysis. The SEM generated images of both outer and inner areas of the sample at 500X, 1000X and 3000X magnifications. The elemental structure of the ceramic membrane was analyzed using Energy dispersive Xray (EDAX). Header, footer and page numbering are not allowed.

2.2 Cross Flow Microfiltration

Experiment was conducted using a home-made cross flow setup rig at room temperature (250C) as shown in figure 2. Pure water flux of unmodified ceramic membrane was measured at different times (5 minutes interval) to determine the volumetric flowrate. The experimental rig consists of a feed tank to contain the O/W emulsion/ pure water which is connect via an inlet tubing to peristaltic pump and then the outlet tubing leading to the membrane module housing the membrane. A pressure gauge is attached to the membrane module to monitor the inside pressure of the membrane. The retentate (outlet tubing) was joined with adjustable valve and connected through a flowmeter measure the outlet flow velocity of retentate. The retentate is connected back to the feed tank for a continuous flow. At the bottom of the membrane module is a tubing receiving the permeate solution into a calibrated beaker placed on a weighing scale to measure the weight of permeate at a certain time interval. The amount of water collected through the permeate at every 5minutes was measured.

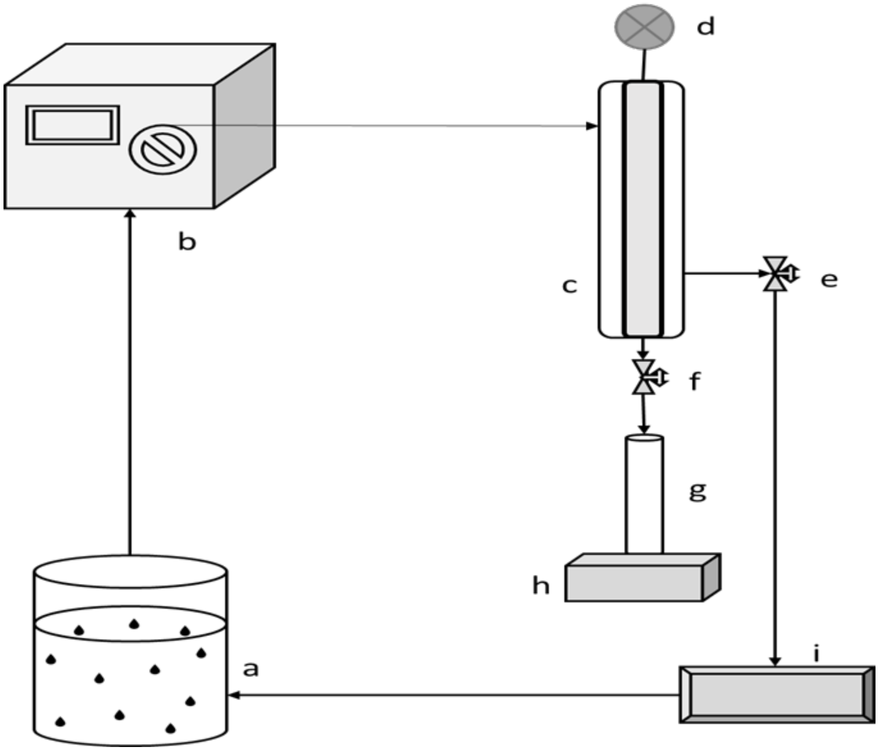

Figure 2: Picture of the in-house rig setup

3 RESULTS AND DISCUSSIONS

The microscopic analyses such as scanning electron microscopy (SEM) images of the outside surface of the ceramic membrane support displaying the pore structure are presented in Figure 3 for different magnifications. A closer look at the membrane in figure 3(c) indicates that the particles in the structure are densely packed and rough and that the pores are not evenly distributed. According to (Gupta et al. 2017) surface roughness in membranes can increase contact angles (Cas) which may increase flux for hydrophilic surface wetting membrane.

With respect to pore radius, it is frequently found that the membrane having the most open pores does not necessarily result in high permeate flux in filtration processes. This is so because porosity which is defined as the ratio of void space to total membrane volume in porous membrane and the distribution of pore size could have an influence on the apparent size of particles retained. Typical microporous membranes do have average porosities in the range of 30%–70%. Porosity was measured by analysing the processed images obtained from the SEM which was 20%. From Figure 3 it may be noted that the membrane has pores which are fine enough through which raw water can be filtered. The ceramic membrane elements are usually constructed from supported multiple ceramic layers that constitute an asymmetric porous structure as shown in Figure 4. Multiple layers emanate from residual spaces created in between ceramic particles during the sintering process and can give bottleneck geometry which is representative of pore formation due to sintering of near spherical particles, which is the case for our membranes since the porous structures are obtained with titania, zirconia as confirmed by the EDXA in Figure 5. The porous sites appear to have a uniform distribution in the membrane and effective diameter of 6000nm was determined by assuming pores are of circular dimension. However, another factor which is the pore geometry or tortuosity (τ) can also have an affect the retention of molecules by a membrane because it reflects the length of the average pore when compared to the membrane thickness.

The unmodified ceramic membrane was subjected to the evaluation of pure water flux in a crossflow microfiltration. The pure water flux from the permeate was calculated at atmospheric pressure for 30minutes at 5 minutes interval. Figure 6 depicts the effect of time on the pure water flux unmodified ceramic membrane. As can be seen, the flux stays the same with an increase in time without decline. Any variation in pure water flux in a ceramic membrane will rely on the physical properties of the membrane such as hydrophilicity, pore size and porosity. Similar result is noticed in the work of (Suresh and Pugazhenthi 2017) for support and TiO2 composite membrane.

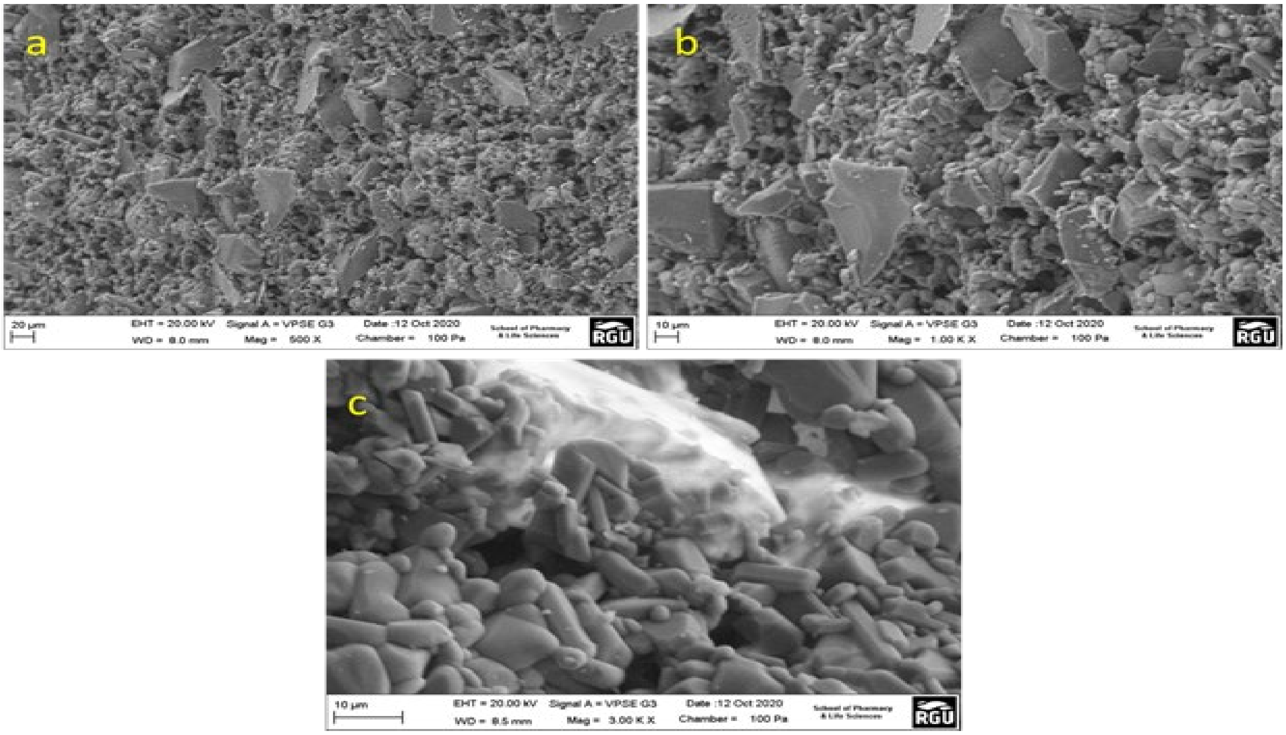

Figure 3: SEM images of support ceramic membrane magnification (a) outer surface view 500X, (b) 1000X, (c) 3000X

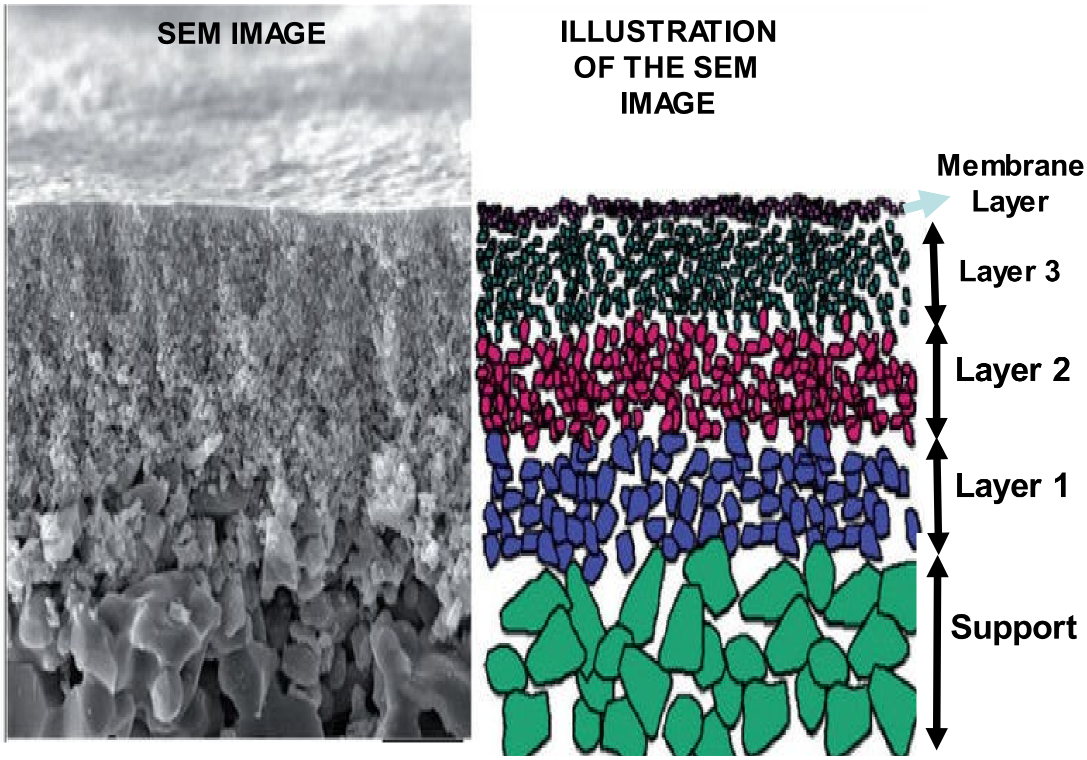

Figure 4: Supported multiple ceramic layers constituting an asymmetric porous structure.

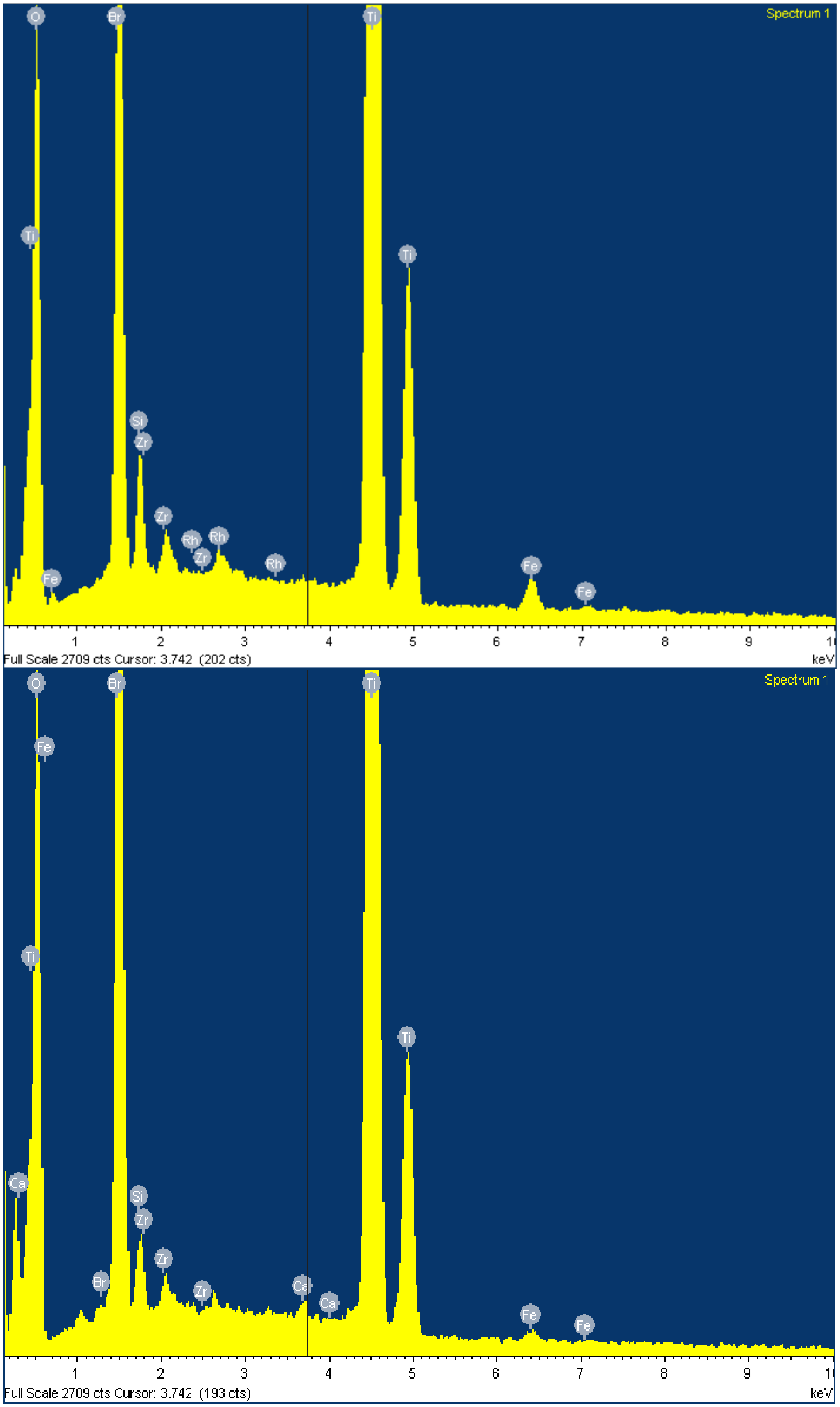

Figure 5: Energy dispersive x-ray analysis (EDXA) of membrane surface

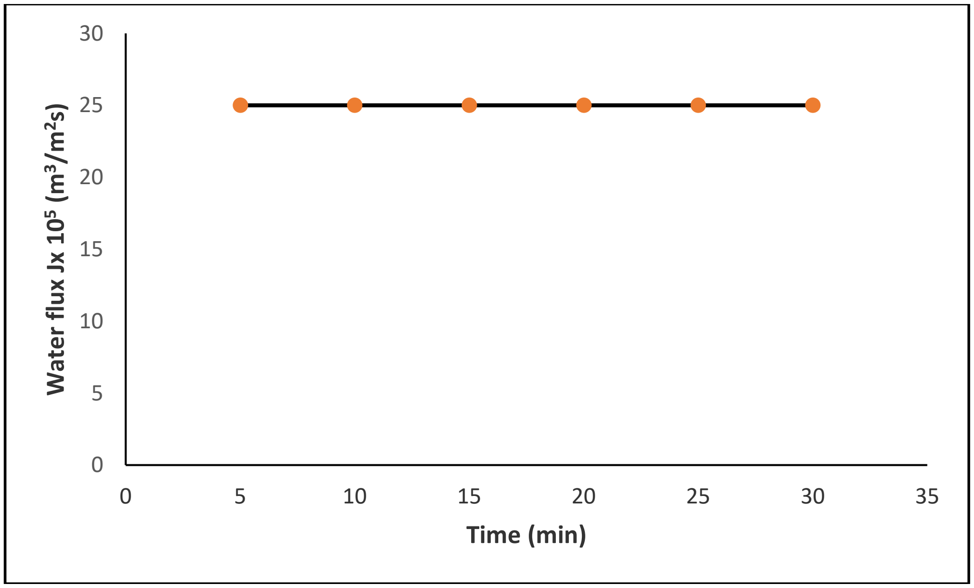

Figure 6 Pure water flux of unmodified ceramic membrane

4 CONCLUSION AND FURTHER WORK

From the experiment carried on pure water flux on unmodified ceramic membrane, it is evident that any variation in flux for ceramic membrane will be dependent on physical properties of the membrane such as hydrophilicity, pore size and porosity. The pure water flux on unmodified ceramic membrane remained stable with time. The next step involved in this research is the coating of ceramic membrane with Iron and Silver nanoparticles for surface modification using dip-coating method. Prepare modified anti-microbial nanoparticle ceramic membrane. Subsequently, characterization of the modified ceramic membrane to determine pore size, porosity, contact angle, morphology using Quantachrome Analyzer, ThetaLite Contact angle meter and Field Emission Scanning Electron Microscope (FESEM) respectively. Preparation and measurement of Oil-in-water (O/W) emulsion and characterize is required as well as the determination of flux, % oil rejection and anti-fouling in modified ceramic membrane.

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