PREPARATION OF CERAMIC MEMBRANES FOR EFFLUENT TREATMENT

Thesis submitted

by

DEBESH KUMAR RANJAN

(109CH0542)

In partial fulfillment of the requirements for the degree in

Bachelor of Technology in Chemical Engineering

Under supervision of

Dr. PradipChowdhury

Department Of Chemical Engineering
National Institute Of Technology
Rourkela, Odisha, India

CERTIFICATE

*Certified that this Project entitled "***Preparation of Ceramic Membranes for effluent treatment***" by* ***Debesh Kumar Ranjan (109CH0542)*** *during the academic year 2012 - 2013 in partial fulfillment of the requirements for the award of the Degree of Bachelor of Technology in Chemical Engineering at National Institute of Technology, Rourkela has been carried out under my supervision.*

Date:

Place: **Thesis Supervisor:**

Dr. PradipChowdhury

Assistant Professor
Department of Chemical Engineering
National Institute of Technology
Rourkela

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Debesh Kumar Ranjan

109CH0542

ABSTRACT

This work highlights the fabrication of ceramic microfiltration membranes using *drill mud* as the raw material. The raw material was pre-processed and paste casting method was used for fabrication. Three different membranes were successfully fabricated (keeping a standard stoichiometric composition of raw materials and binders) at three different sintering temperatures e.g. 500, 800 and 900°C. Comprehensive characterization techniques *viz.* scanning electron microscopy (SEM), powder X-ray diffraction (PXRD), BET surface area and Mercury porosimetry were followed to ascertain the nature of the membrane fabrication. The membrane sintered at 900°C, having an average pore size of 18μm was found best suited for oil-water emulsion studies. A rejection of *ca*. 38% was observed for this membrane. Another variant of ceramic membrane was fabricated at 900°C with an addition of 25% kaolin. A better rejection of *ca*. 49% was found for this case which can be attributed to better structural properties of the membrane surface and uniformity in pore size distribution. All the membranes were studied for their regeneration and reusability. A detailed cost analysis was also performed and it was seen that the membranes fabricated were much cheaper than the similar products reported in literature.

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Ci - Concentration of solute in feed

Cf - Concentration of solute in permeate

R - Rejection of solute

K - Permeability

ΔP_h - Hydrostatic pressure difference across membrane

ΔP_i - Osmotic pressure difference

L - Membrane thickness

r_p - Mercury intrusion pore radius

γ - Surface tension of mercury

θ - Contact angle of mercury

V_{total} - Total pore volume (*Using Hg porosity analysis*)

$D_v (d)$ - Volume pore size distribution

D_{eff} - Effective diffusivity

D_b - Bulk diffusivity

θ_c - Pore volume fraction

τ - Tortuosity factor

Lh - Hydraulic permeability

rl - Average pore radius *(Using hydraulic permeability studies)*

J - Liquid Flux across membrane

μ - Viscosity of water

P - Porosity

mD - Dry membrane support mass

mw - Mass of the support with pores filled with water

mA - Mass of the water saturated support measured in water

CHAPTER 1

INTRODUCTION

1.1 Prelude

Separation processes are considered to be an integral part of field of Chemical Engineering and it mainly refers to separation of mixture into two different products rather than two products with different composition. A variety of unit operations are used for separating mixtures depending upon the purity of desired product, type of mixture, chemical properties of mixtures and scale of production, which includes conventional techniques like distillation, adsorption, absorption, stripping, extraction and membranes. However among the mentioned technologies, membrane science has emerged recently as very attractive option for the inherent advantages it possesses like high energy efficiency, ease of scale up, ability to tune up according to process variables and availability of variety of materials.

The sturdy research carried out in material sciences and related area has largely contributed to development of porous solids particularly on ceramic membranes owing to its application in purification and separation applications. The growing trend towards clubbing one or more relevant unit operations so as to use properties and advantages of both techniques has marked new beginning in development of membranes with specific properties for specialty applications**.**Owing to this, exploring and developing new ceramic membranes has generated huge interest among research community and quickly developed into field of fruitful research. The performance of thesematerials in separation and purification applications has been promising and a truly interdisciplinary research field comprising of chemical engineering, materials science and others is requisite for its development from infancy.

1.2 Background of Present Research Work

Uses of ceramic membranes have been increased now days because of their excellent chemical, thermal and mechanical stability and higher separation efficiency [1]. Alumina based membranes are used in industries but with them is high cost and sinteringtemperature [2]. Therefore lowcost clay membranes will find its way in industries in coming years. Many researchers have used low cost clays like Moroccan clay, Tunisian clay,sepioliteclay, Algerianclay, dolomite and kaolin [3].

Large quantities of oily waste water generated by various process industries, especially refineries and metallurgical industries need to be treated before discharge to the river or any other sewage system. Discharging the effluents reduces oil yield and also pollutes the environment. Among the various treatments of oily effluents, membrane separation process appearsto be a most competent process. It has many advantages like resistance to corrosive feed, high temperature applicability, consistency in high pressure application and long life [4]. Many researchers have reported the oily wastewater treatment using ultra filtration (UF) and microfiltration (MF) with polymeric and ceramic membranes.

In drinking water and medical field removal of microorganism is a major concern. Membrane separation processes including microfiltration and ultra filtration, have received a great deal of attention for the removal of microbes. Kobayashi et. al have reported the cutoff performance of E.coli using charged and unchanged polyacrylonitrile(PAN) ultra filtrationmembranes with a feed concentration of 10^7 (CFU/ml). Karim et al. have used the polysulfone membrane possessing an average pore size of 0.1micron for the separation of E.coli lysate by flocculation enhanced microfiltration and achieved complete removal of E.coli.Marov et al. studied the removal of microorganism for the production of drinking water using different types of UF and MF membrane having different pore sizes and the results indicated a significant reduction in microbes [5].

1.3ResearchObjective:-

The main objectives my present research work is:

Synthesis, characterization and selection of a suitable ceramic membrane (using local mud), good enough (thermally and under organic and aqueous medium) for membrane based separation applications in treatment of industrial effluents: oil water emulsion, bacterial separation and fruit juice concentration.

CHAPTER 2

LITERATURE REVIEW

A comprehensive literature review on various types of membranes and a membranes material, a step by step procedure on ceramic membrane fabrication is also highlighted. Recent developments in the field of ceramic membranes are also highlighted. Finally, working details of various instruments used for characterizing membrane surfaces are briefly explained.

2.1General Theory and Classification of Membranes:-

2.1.1 Fundamentals of Membrane Technology

Membrane is defined as a semi permeable barrier, which separates two phases and restricts transport of various chemical in a selective manner. A membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid; can carry a positive or negative charge or be neutral or bipolar. Transport through a membrane can be affected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient. The membrane thickness may vary from as small as 10 μm to few hundred micrometers [6].

The main driving force in most of the membrane processes is pressure difference or concentration gradient across the membrane depending upon the type of process and membrane used. Parameters such as pressure, concentration and even temperature may be considered as one of parameters. If an electric potential is applied for any membrane separation, the electric potential difference also influences the transport of charged particles.

General terms and concepts of used in any kind of filtration process are enlisted below in brief.

Permeate: The part of feed stream, which can pass through the pores of the membrane.

Retentate: The part of feed stream, which is rejected by membrane on account of factors like high molecular weight compounds.

Rejection (R) %: The rejection % for any molecule, *i* is given by the equation

$$\text{Rejection \%} = \frac{(Ci - Cf)}{Ci} \times 100 \qquad (2.1)$$

Where C_f is concentration in the permeate while $C_i$is concentration of feed.

Flux: Flux may be defined as the total volumetric flow rate per area of membrane given by the equation

$$\text{Flux} = \frac{(\Delta \mathrm{Ph} - \Delta \mathrm{Pi})}{l} \times K \qquad (2.2)$$

Where K is permeability, $\Delta P_h$is hydrostatic pressure difference, $\Delta P_i$is osmotic pressure difference and l is the membrane thickness.

Molecular weight cut off: This term is particularly associated with polymeric membranes and generally expressed as MWCO. It refers to molecular weight (in Daltons) of species, which would be giving at least 90% rejection during process.

Concentration polarization: This is a phenomenon commonly encountered in most of membrane process which results in flux reduction drastically. When large colloids, macromolecules such as proteins are filtered, membrane largely rejects these molecules and forms a viscous and gelatinous layer on the surface of membrane. This adds to total resistance to flow in addition to those offered by boundary layer and membrane. Major impact of this problem is felt in ultra-filtration technique where flux reduces due to increased solute concentration on membrane surface resulting in higher osmotic pressure.

2.1.2Classification of Membrane Materials

With the advent of various synthesis strategies and development of specialized field like material sciences and ceramics, the research has proven fruitful in development of materials suitable for membrane fabrication. Based on the type of structure, membranes are classified into several classes indicated below [7].

2.1.2.1**Symmetric and Asymmetric membranes:** A synthetic membrane may have a symmetric or an asymmetric structure. A symmetric membrane refers to type of membranes which has identical structural and the transport properties over the entire cross-section and the thickness of the entire membrane determines its flux. Symmetric membranes are mainly used in applications like dialysis, electro-dialysis and microfiltration. Asymmetric membranes in contrast, the structural as well as transport properties vary over the membrane cross-section. Most of the membranes utilized in a pressure driven separation processes are sophisticated asymmetric structures requiring two major properties, i.e. high mass transport rates for certain components and good mechanical strength. An asymmetric membrane consists of a very thin (0.1 to 1 µm) "skin" layer on a highly porous 100 to 200 µm thick substructure. The thin skin on top of the asymmetric porous structure represents the actual selective membrane whose separation characteristics are determined by nature of membrane material and pore size of skin layer. Asymmetric membranes are used primarily in pressure driven membrane processes such as reverse osmosis, ultra-filtration, or gas and vapor separation, since the unique properties of asymmetric membranes, i.e. high fluxes and good mechanical stability can be best utilized.

2.1.2.2**Porous membranes:** These classes of membrane are the simplest kind of membrane possessing simplest of structures. These membranes consist of a solid matrix with defined holes or pores which have diameters ranging from less than 1 nm to more than 10 µm. Separation of the various components is achieved strictly by a sieving mechanism with the pore diameters and the particle sizes being the determining parameters. Porous membranes can be made from various materials such as ceramics, graphite, metal or metal oxides, and various polymers. The techniques for the preparation of porous membranes can be rather different and include simple sintering processes, irradiation, and etching techniques as well as phase inversion and polymer precipitation procedures. Porous membranes are used to separate components that differ markedly in size or molecular weight in processes such as microfiltration and ultra filtration or dialysis.

2.1.2.3**Homogeneous membranes:** A homogeneous membrane possesses a dense film through which a mixture of molecules is transported by pressure, concentration, or electrical potential gradient. The separation of various components of a mixture is directly related to their transport rates within the membrane phase, which is determined mainly by their diffusivities and concentrations in the membrane matrix. Homogeneous membranes are prepared from polymers or in some cases from metals and metal alloys by various film-forming techniques. Homogeneous membranes are used mainly to separate components which are similar in size but have different chemical nature; mostly in processes such as reverse osmosis, gas and vapor separation, and evaporation.

2.1.2.4 **Liquid membranes:** Liquid membranes have gained attention with new theory so called facilitated transport which utilizes "carriers", transporting certain components e.g. metal-ions selectively and at a relatively high rate. Two different techniques are used today for the preparation of liquid membranes. In the first case, the selective liquid barrier material is stabilized as a thin film by a surfactant in an emulsion-type mixture. In the second technique a porous structure is filled with the liquid membrane phase. Both types of membranes are used today on a pilot-plant stage for the selective removal of heavy metal ions or certain organic solvents from industrial waste stream. They have also been used rather effectively for the separation of oxygen and nitrogen.

2.1.2.5 **Ceramic membranes:** This kind of membranes refers mainly to those prepared with porous ceramics like alumina, silica, clay or substrates like titania and zirconia. These membranes find applications predominantly in the fields of solid-liquid separation and solid-gas separation. However, gas based separations also do exists with ceramic membranes. The structure of these membranes are unique with largest pore size are found at bottom as support and pore size decreases gradually towards the surface where the actual separation takes place. However these structures are highly amenable to modifications depending upon the selection of synthesis routes: from inner structures to top surface of membranes. The membrane is also available in different configurations like tubular, multi-channel monolith membrane etc. As indicated earlier, manufacturing method have an impact on membrane configuration and structural properties and some of methods are described.

Slip casting: This is the traditional method for membrane preparation where well mixed powder suspension are introduced, poured into a porous mould where solvent present is extracted into the pores of the mould via the capillary driving force. During this, the slip particles are consolidated on the surface of the mould to form a layer of particles which will not penetrate into mould as formation of this layer is ensured quiet quickly. The pore size of the membrane is mainly dependent on the particle size of the powders used in the slip.

***Tape Casting**:* This method is primarily used for synthesis of flat sheet ceramic membranes. Here, a powdered suspension is poured into a reservoir behind a casting knife. The carrier to be cast is set in motion and gap between the knife blade and carrier determines the thickness of the membrane formed. The important process variables are reservoir depth, speed of carrier and velocity of the powder suspension.

***Pressing**:* This is most widely used method for the preparation of disc inorganic membranes. Here, the particle mix is subjected to high pressure force for consolidation into single mass and later on if required, sintered. Method finds application in screening new ionic and mixed conducting materials for development of oxygen or hydrogen permeable ceramic membranes.

***Extrusion**:* This method is widely preferred for large scale manufacturing of membranes as well as bench scale. Here a stiff composite paste is compacted and shaped by forcing it through a nozzle. The required condition is that, the precursor should exhibit plastic behavior.

***Sol-gel process**:* Sol-gel process for fabrication of membrane is opted when the pore size of the membrane has to be controlled at lowest levels. Two main routes for the preparation of membrane using this method:

- *Colloidal route*- a metal salt is mixed with water to form a sol, which is coated on the membrane support to form a colloidal gel.

- *Polymer route*- A metal-organic precursors are mixed with organic solvent to form a sol. It is then coated on the membrane support, where it forms a polymer gel.

***Dip coating**:* Herein, a viscous suspension is coated on a suitable base and the critical factors are suspension viscosity, coating speed and time. Drying process starts simultaneously with the dip coating. To carry out multistep process, complete drying of initial coat is mandatory.

***Chemical vapor deposition**:* The method takes help of chemical reactions to deposit a layer of the same or different compound. Reaction takes place mainly in gaseous medium surrounding the component. The experimental system consists of a system of a mixture of reactive and carrier gas, a heated reaction chamber, and a system for the disposal and treatment of exhaust gases. The products of a CVD system contain various hazardous components and particles. Thus, reaction side products are required to be treated before exhausting to the atmosphere.

2.2 Characterization Techniques – An Overview

2.2.1Scanning Electron Microscopy (SEM) & Energy Dispersive X-Ray Spectroscopy

Scanning Electron Microscopy (SEM), is an electron microscopy technique which provides the detailed information regarding sample's surface morphology, composition and other surface properties such as electrical conductivity. A high energy electron beam is directed towards the sample surface which interacts with the atoms that make up sample, and produce secondary electrons, back scattered electrons, characteristic X-rays, light, specimen current and transmitted electrons which is detected with the help of special sensors to give high resolution images of sample surface morphology. When the high energy electron beam interacts with the electrons present in the sample, X-rays are emitted in this process, and these are used to identify the composition. It also measures the abundance of elements in the sample; characteristic feature of X-ray emitted depending up on the sample composition. The X-rays generated are mainly concentrated from a region 2 μm depth and hence EDX cannot be termed as purely a surface science technique.

The physical working of SEM involves, an electron beam being emitted from an electron gun, which is fitted with a tungsten filament cathode. Tungsten is used because of its highest melting point and low cost. The electron beam is condensed by one or two condenser lenses. When primary electron beam interacts with the sample, electron loses energy by repeated random scattering. The energy exchange between the electron beam and the sample, results in the reflection of high energy electrons, emission of secondary electrons and the emission of electromagnetic radiation, which can be detected, and so also the beam current absorbed by the specimen. This is used to create images of the specimen surface.

Sample Preparation: For the surface morphology analysis of all membrane, samples should be dried to remove moisture content and also ensured that sample size and thickness suited well to fit in the specimen chamber of equipment. Specimens were also coated with platinum by low vacuum sputter coating in order to increase the conductivity of the sample and to obtain superior image quality. The coated samples of membrane should be simply placed over the specimen slot and locked into the chamber.

Scanning Electron Microscope in operation for this entire project purpose was SEM, JEOL JSM-6480 LV facility.

2.2.2X-Ray Diffraction

X-ray diffraction (XRD) is a rapid analytical technique primarily used for phase detection of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.. In this technique, the scattered intensity of an X-ray beam generated upon hitting the sample is measured as a function of incident angle, scattered angle, polarization, and wavelength and as pointed out by A. W Hull in paper titled “A New Method of Chemical Analysis” that “Every substance produces a pattern, same substance produces always same pattern and in a mixture of substances each produces its pattern independently of the others”. Thus XRD patterns serves as a finger print of the each material.

In a typical analysis procedure of XRD machine, the sample is mounted on a goniometer and is gradually rotated with simultaneous bombardment of X-rays which after hitting the sample diffracts into different angles to generate two dimensional images at different positions. This data is integrated to obtain three dimensional data using mathematical method of Fourier transform, combined with the chemical data of the sample.

Although scattering of beams from the sample leads to destructive interference, there are specific directions in which they add up to give diffraction pattern governed by Bragg’s Law given by

$$2d \sin\theta = n\lambda \tag{2.3}$$

whereθ is the incident angle, d is the spacing between the planes, n is any integer and λ is the wavelength of incident beam.

Sample Preparation: For the analysis, membrane particles should be carefully placed in a sample slot to make powder bed and surface of powder was smoothened. The synthesized samples should be subjected to X-ray diffraction in 2θ angles ranging from 5^o to 75^o with a step size of 0.05 degrees and scanning rate 3^o per minute.

X-ray diffraction machine utilized for this entire project purpose was XRD, Philips Analytical, PW-3040 equipped with the graphite monochromatizedCuKα radiation (λ=1.5406Å).

2.2.3BET Surface Area Analysis

BET analysis provides precise specific surface area evaluation of materials by multilayer adsorption of gases measured as a function of relative pressure using a fully automatic analyzer. The technique include external area and pore area evaluations to determine the total specific surface area in m^2/g yielding important information in studying the effects of surface porosity and particle size in many applications.. This theory was later exploited to estimate the total surface area of material and is given by equation

$$\frac{x}{v(1-x)} = \frac{1}{cvmon} + \frac{x(c-1)}{cvmon} \qquad (2.4)$$

Where *x* is relative pressure P/P0, v is the STP volume of adsorbate, c*vmon*is STP volume of the amount of adsorbate required to form a monolayer, *c*is the equilibrium constant.

A key assumptions used in development of BET equation is that the formation of multi adsorption layers unlike Langmuir theory (assumes monolayer adsorption of gases) and that successive heats of adsorption for all layers except the first are equal to the heats of condensation of the adsorbate. It also assumes that no multilayer formation occurs until monolayer adsorption of entire sample is completed. Another critical assumption is that there are no lateral interactions between adsorbed molecules. Hence, BET model describes the process of physisorption better than the Langmuir theory although it is generally still not a good model for adsorption on micro porous materials. Micro pores are not covered under this model as BET equation over estimates the surface area of micro porous materials.

In a typical experiment, the sample to be analyzed is pre heated to remove maximum moisture. A known weight of dried sample is first known in the sample tube of known volume for a process called out gassing. Out gassing is performed in outgasser port of equipment prior to analysis in order to completely remove the moisture and gases already adsorbed in the micro and nano pores present sample. This out gassed sample is weighed and then employed for analysis in analysis port. Nitrogen gas is often used for analysis because of its well established molecular size, inert nature, availability in high purity and reasonable cost. The entire sample tube isimmersed in a coolant bath of liquid nitrogen exposing it to lower temperature. At this point, a purge of nitrogen gas is introduced into the sample tube, which slowly gets adsorbed on the sample surface. The relative pressure of nitrogen is recorded against the volume of adsorbate and finally surface area of sample is estimated. All the operations are computer programmed using software supplied with equipment.

Sample preparation: Membrane samples for surface area analysis should be dried initially at 100^{o}C for 3 hours prior out gassing.Well dried membrane should be analyzed by taking a small chunk of sample of suitable size to fit into the tube and directly analyzing without powdering.

The made of BET surface area analyzer employed during the studies of this project was Quantachrome - Autosorb-1.

2.2.4 Thermal Gravimetric Analysis

Thermal Gravimetric Analysis or Thermo gravimetric Analysis (TGA) is a laboratory technique which is used to estimate the thermal stability of material by measuring the change of weight with respect to increase in temperature in controlled atmosphere. Based on the data obtained like weight loss, temperature and rate of temperature change, the information on absorbed moisture, proportion of organic and inorganic materials in sample, and solvent residue apart from degradation temperature is obtained after performing required transformation of the results for interpretation. Normally TGA can be conducted either in atmospheric environment or inert environment using nitrogen gas in pre-programmed gas flow rate. The heat flow change is also monitored to obtain differential scanning calorimetery data used for calculating enthalpy of reaction.

The experimental procedure involves placing a known weight of sample in a crucible kept on high precision sample which resides in a furnace. The temperature is gradually raised to our requirement and cooled down to room temperature and .the data acquisition system automatically plots the relation between temperature and weight loss which is finally smoothened to find the exact point of inflection. Derivative weight loss curve can identify the exact point of maximum weight loss and the temperature which indirectly provides degradation profile of the sample.

Sample preparation: Samples should be subjected to maximum of $600^{o}C$ at gas flow rate of 45 ml min-1 and a consistent temperature ramp of $5^{o}C$ min^{-1}.

Thermo gravimetric analyzer employed for this project was from Shimadzu (DTG 60 H).

2.2.5Mercury Intrusion Porosimetry

Mercury porosimetry is a powerful technique utilized for the evaluation of porosity, pore size distribution, and pore volume (among others) to characterize a wide variety of solid and powder materials. A instrument, known as a porosimeter, uses a pressurized chamber to force mercury to intrude into the voids in a porous sample. As pressure is applied, mercury fills the larger pores first. As pressure increases, the filling proceeds to smaller and smaller pores. Both the inter-particle pores and the intra-particle pores can be characterized using this method.The working principle is based on Washburn equation which gives simple relationship between applied pressure and pore size given by

$$2\gamma cos\ \theta = r_p \qquad (2.5)$$

where$r_p$is the radius of pore which mercury intrudes, γ is the surface tension of the mercury and θ is the contact angle of mercury with the surface. Generally values of surface tension and contact angle are 480 mNm^{-1} and 140°.

Total pore volume is the total volume of mercury intruded at the highest pressure and mean pore diameter is calculated using the equation based on assumptions of cylindrical pores opened at ends.

$$D_{mean} = \frac{4 \times V total}{S} \qquad (2.6)$$

Volume pore size distribution is defined as the pore volume per unit pore diameter based on assumption of cylindrical pore shape and given by equation

$$\mathrm{Dv(d)} = \frac{p}{d} \times \frac{dV}{dp} \tag{2.7}$$

Conventionally while modeling the diffusion characteristics through porous solids, its reported that effective diffusivity (D_{eff}) differs from the theoretical diffusivity or bulk diffusivity (Db) related by a factor to structure of sample as follows:

$$D_{eff} = (Db\theta_c) / \tau \tag{2.8}$$

Where$\theta_c$is the pore volume fraction and τ is the tortuosity factor. This effective tortuosity factor accounts for all the deviations from straight diffusion paths into a single dimensionless parameter value of which usually falls between about 1 and 7, with a value of 2 being associated with nonintersecting cylindrical pores.

A typical experimental procedure involves placing the sample in a special sample cup from which gas is evacuated and mercury is transferred to sample cell under vacuum. Then pressure is applied to force mercury through the sample during which pressure and volume of mercury intruded is measured. As mercury is non-wetting liquid for most surfaces, it resists entering the voids and finally resulting in an intrusion-extrusion curve. Parameters required for describing pore structure of sample can be calculated from data obtained.

Sample preparation: Moisture free sample should be prepared by drying the samples for 10 hours at 100^{o}C. Moisture removal is very crucial since the presence of other liquids may interfere with the intrusion of mercury through the sample. Total weight and bulk density of sample is also determined prior the analysis.

CHAPTER 3

EXPERIMENTAL WORKS

This chapter describe the various experimental procedure followed, materials and resources used and a short report of logic behind the idea of pursuing the experiments wherever found essential.

3.1Raw materials

Clay: Taken raw drill mud from Ranchi, Jharkhand, dry the mud at 120 °C, it was then grinded in a ball mill and passed through BSS36 mesh screen. All the membranes were prepared with BSS36 mesh clay powder.

Kaolin: It provides low plasticity and high refractor properties to the membrane. Major constituents of kaolin are alumina silicates with the following chemical compositions (by wt %) SiO_2:46.5%, Al_2O_3:39.5% and H_2O:14%.

Crude oil:crude oil obtained from the Indian oil corporation Ltd. Located at Rajahmundry Andhra Pradesh India.

3.2Chemicals Utilized

All the chemicals were obtained from commercial sources and utilized without any purification. All the chemicals with their molecular formula and manufacturer are listed below:

Chemicals utilized for fabrication of membrane are:

(i) Sodium carbonate [Na_2CO_3, *Merck Specialities Private Limited, India*],
(ii) Sodium metasilicate [Na_2O_3Si, *Merck Specialities Private Limited, India*],
(iii) Boric acid [H_3BO_3].

3.3 Experimental Works

Synthesis of membranes using the locally available clay and finding application for filtration and purification studies was described by Jana et al. Following is a similar procedure followed in synthesis of ceramic membrane. Naturally available soilwas collected from Ranchi region of Jharkhand, India. It was sub-layer of soil.It was found that clay from Rourkela region of Odishacontains a higher percentage of sand and hence difficult to handle for membrane fabricationand it needs more processing. The method of paste casting was followed for the synthesis of final membrane. The details are given below:

The soil collected was made free from all the impurities, and then drying in sunlight for 7 days followed by 24 hrs drying in oven at 100^oC for complete moisture removal. Dry soil was fed into a ball mill for 3 hours to reduce particle size of soil so that paste made for membrane preparation yield good viscous properties. The resultant fine powder was sieved with BSS 36 mesh screen. The composition of membrane was similar to as suggested by Jana et al. in which clay (70%), sodium carbonate (3%), sodium metasillicate (1.5%), and boric acid (1.5%) materials were mixed with distilled water (24%) and the paste was casted on an aluminium foil in the shape of a circular mould to form a membrane support. Three membranes were casted for experimental. After partial drying of membranes in room temperature for 24 hrs, the disc was removed carefully and heated at 373 K for 12 hrs prior to sintering at different temperatures 773 K, 1073K and 1173K for 4 hours. On cooling, membranes were finally polished with silicon carbide abrasive paper (C-180), to give a good aesthetic look. Ample care was taken while sintering and cooling down so as to avoid crack formation on membrane support surface. Each additive has got their own properties influencing the membrane properties. The components sodium metasilicate increases mechanical strength by creating silicate bonds, sodium carbonate improves dispersion properties, thereby creating homogeneity and boric acid also increases mechanical strength of support by creating metaborates during sintering.

Table1: Composition of each membrane

Materials	**Wet Basis**	**Dry Basis**
Clay (%)	58.26	85.81
Sodium Carbonate (%)	5.01	7.38
Sodium Meta Silicate (%)	2.40	3.54
Boric Acid (%)	2.20	3.252
Water (%)	32.10	0

3.3 Characterization

Characterization of the samples was performed using SEM, Powder XRD, TGA, BET surface area analyzer, mercury porosimetry and optical microscopy. The membrane morphologies were observed via scanning electron microscopy (SEM, JEOL JSM-6480 LV) .The synthesized samples were subjected to X-ray diffraction by a diffractometer (XRD, Philips Analytical, PW-3040) equipped with the graphite monochromatizedCuKα radiation(λ=1.5406Å) in 2θ angles ranging from 5^{o} to 70^{o}with a step size of 3 degrees and scanning rate 1^{o} per minute. BET surface area analysis was performed by BET surface area analyzer (Autosorb-1, Quantachrome). The relative pressure in BET surface area calculation was between 0.05-0.35. Finally, thermal stability of samples was carried out in detail in a TGA apparatus, Shimadzu (DTG 60 H). Data regarding pore size distribution and total porosity of the membrane sample was obtained using Mercury Intrusion Porosimeter (QuantachromePoremaster 32).

Results of characterization yield that membranessinitered at 900^{o}C is best suited for oil water treatment as is has the smallest pore size.

3.4 Permeation and Filtration Studies of membrane (sintered at 900^{o}C)

Any kind of membrane fabrication and related studies gains importance only if there is an experiment elaborating its permeation characteristics and separation efficiency for a particular feed condition is performed. This section explainsutilization of claymembrane synthesized for hydraulic permeability and liquid based separation studies respectively.

Filtration set up:-

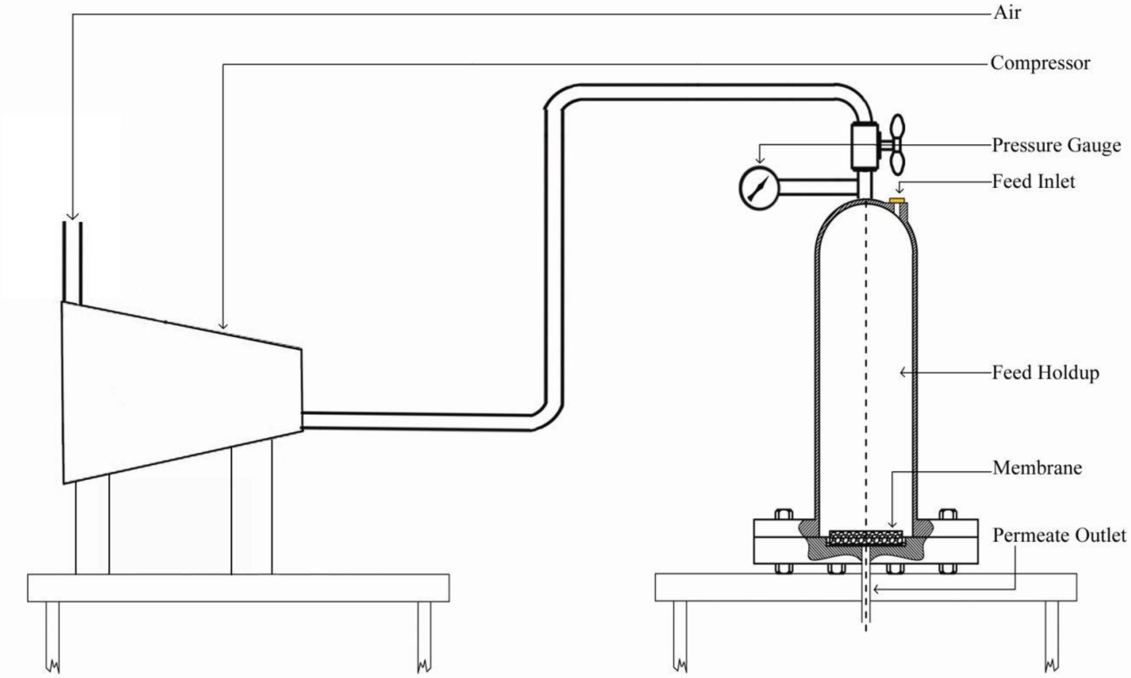


Figure 3.1 Schematic diagram of experimental set up for permeation and separation studies.

The hydraulic permeability and filtration experiments for clay membranes were done by the experimental set up as shown in Figure 3.1.

As shown in Figure 3.1, experimental set up is divided into two main parts *namely*membrane module and compressor section, each described below:-

Membrane Module: The membrane module made of stainless steel consists of two sections; feed hold up section and grooved membrane holding plate, with extended flanges bolted tightly together. Feed hold up section is a hollow cylindrical portion capable of holding 300 ml of feed per batch. Top of cylinder consists of inlet port for introduction of feed and valve connecting the line to compressor for passage of compressed air. A pressure gauge is also fitted in order to measure the pressure at the time of filtration.

Membrane holding plate is a circular disk, designed to hold membrane tightly during the process. It consists of concentric circular grooves (shown below), with a provision to incorporate an 'O' ring, which help to arrest the possible leakage upon pressurizing the system. The flanges holding both parts are tightened with 'nut and bolt' arrangement in order to leak proof the system.

Compressor Section: Compressor as shown in Figure 3.1 provides compressed air to the membrane module, hence pressurizing the feed to the desired level. The pressure gauge monitors the system pressure and the system pressure is adjusted using the valve.

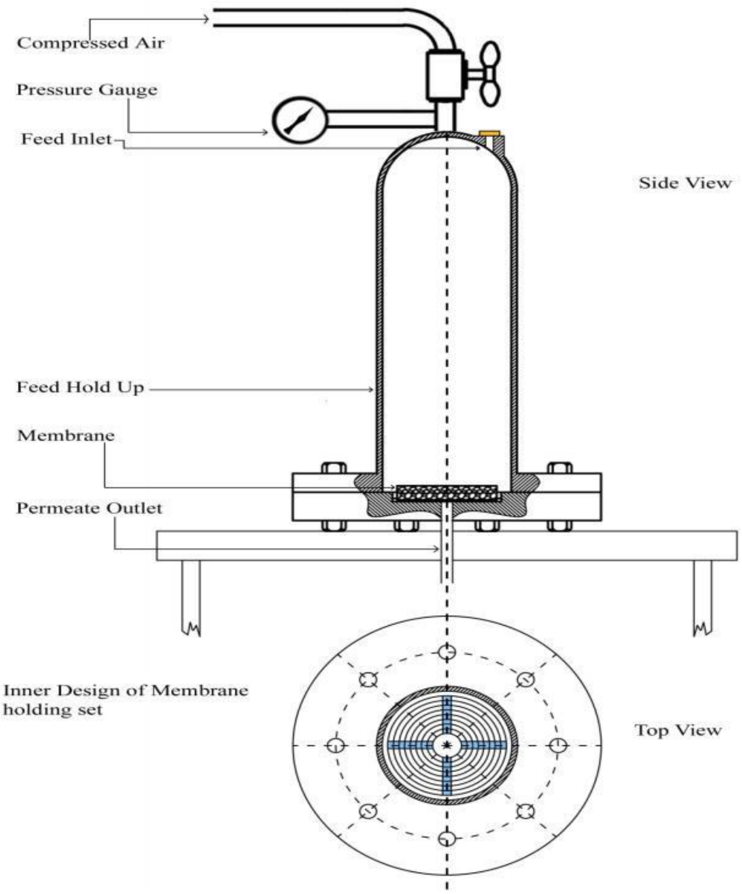


Figure 3.2 Side view and top view of membrane module experimental set up for permeation and separation studies

Hydraulic Permeability or Conductivity signifies the ease with which water passes through the porous media particularly through rocks or soil. It largely depends on the inherent permeability of material and degree of saturation of media. The hydraulic studies of clay membranes were carried out using the standard membrane module shown in Figure 3.1. Distilled water was used for all the experiments.

Hydraulic permeability (L_h) and average pore radius (rl) of membrane were determined using equation suggested by Almandoza et al. [8]

$$J = (n\pi r^4 \Delta P)/(8\mu l) = L_h \, \Delta P \qquad (3.1)$$

where, J is the liquid flux ($m^3\ m^{-2}\ s^{-1}$), ΔP is the transmembrane pressure (in kPa), μ is the viscosity of water and l is the pore length (assumed as membrane thickness). Considering porosity of sample as $\varepsilon = n\pi r2$, Equation (3.1)changes to

$$r_l = [\frac{8\mu l L h}{\varepsilon}]^{0.5} \qquad (3.2)$$

Porosity was figured out using the principle of Archimedes' [9] given by equation

$$P = \frac{mw - md}{mw - ma} \qquad (3.3)$$

Where, *md*is the dry support mass, *mw* is the mass of the support with pores filled with water (pores are filled with water under vacuum), *ma*is the mass of the water saturated support measured in water (A refers to Archimedes'), and *P* is the porosity.

All the experiments were performed at room temperature and pressure maintained at 300 kPa. Membrane support was fixed tightly using common epoxy resin 'M-Seal' tothe grooved membrane plate. A very high flux was observed at the initial stages but reduced gradually to steady state value with time due to compaction of membrane. Permeate volume with respect to time was noted down to study flux variation and the steady state flux was used to calculate the hydraulic permeability and estimate pore radius.

The rejection was calculated using the Equation 3.4given below.

$$\text{Rejection \%} = \frac{(ci - cf)}{ci} * 100 \qquad (3.4)$$

After permeation studies of membrane sintered at 900^{o}C it is found that its results were not so good for the study of oil water separation study. So another additive kaolin is used and another membrane is casted having 25% (of soil weight)kaolin (sintered at 900^{o}C). Again the permeation study of that membrane was done.

Separation of crude oil from water membrane

Separation of the crude oil from water was investigated using 900^{o}C membrane (membrane A) and membrane with 25% kaolin as additional ingredient (membrane B) synthesized as described earlier. The filtration experimental set up was utilized to perform dead end filtration process with no recycle. This experiment can be considered as liquid-liquid two phase separation process with crude oil as lighter phase and water as heavier phase. The synthetic feed carefully prepared was used for all the experiments and the quality of separation was analyzed using quantitative estimation of crude oil using spectrophotometer at 245 nm.

Experimental procedure for feed preparation & estimation

Feed preparation

Crude oil was obtained from the Indian Oil Corporation Limited refinery located at Rajahmundry, Andhra Pradesh, India. 10 ml crude oil was mixed with 90 ml of water and mixed well with stirrer at high rpm for 3 hours for homogenous mixture preparation. Then the resulting solution was sonicated in bath sonicator for 10 minutes to further destruct the oil layer and then again mixed well enough using stirrer for 1 hour. Upon sonication, oil breaks into fine droplets in aqueous medium forming stable emulsion. Emulsion is characterized by milky white solution and a very fine layer of oil slick on the top.

This solution was used for separation studies and prior to the experiment, a sample of initial mixture was used for spectrophotometer analysis of crude. Enough care was taken so as to discard the oil slick in sampling as we need only the concentration of oil in milky white system.

Analytical procedure for estimation of crude oil

Initially standard calibration curve was obtained using pure crude oil with n-hexane as solvent as crude oil completely dissolves in n-hexane. The standardization of crude oil concentration with respect to optical density is show below.

(i) A crude oil working solution was prepared by adding 200 µl oil in 10 ml hexane system. An adequate amount of working standard was pipette out to obtain variation of concentration of oil in each test tube.
(ii) A set of 6 test tubes were taken and 0, 10, 20, 30, 40 and 50 µl of working standard diluted to 10 ml system with n-hexane were used.
(iii) Solution was mixed well and the absorbance of each solution was read in wave length range of 200-350 nm.

Maximum absorbance was obtained at 245 nm and optical density at this wave length was used to plot standard curve. The concentration of crude oil was determined by standard curve for all the experiments further.

Quantitative estimation of crude oil in permeate

Even though a stable emulsion is obtained, the two phase mixture forming semi-transparent solution is not suitable for spectrophotometer analysis. Hence we use a method for calculations of crude oil concentration based on mass transfer of oil between permeate and n-hexane and stated as follows:

(i) Two milliliters of permeate was collected and mixed with equal volume of n-hexane to form a two phase solution.
(ii) 100 µl of hexane from two phase mixture is taken and diluted to 5 ml system using n-hexane as solvent.
(iii) Optical density of resulting sample was measured using spectrophotometer at 245 nm. (Wave length of maximum absorbance)

Calculation of concentration of solution is done using the standard calibration data and corresponding rejection % has been calculated. Even though calculation of concentration is mainly dependent on the mass transfer of crude oil between the water and hexane, since all the procedures are performed in standard conditions, we can obtain a relative value of concentration of crude in all samples. But rejection percentages can be considered as absolute values and they are calculated with respect to time.

3.5 Filtration experiments

Separation experiment was done using the permeation set up previously described using dead end filtration technique. Feedsolution (100ml) was carefully transferred and whole module was perfectly sealed using Teflon tape to avoid leakage of pressure and liquid. In the experiment air compressor was used to pressurize the feed. Pressure was maintained at 3 kg cm^{-2} throughout the process. To evaluate the quality of separation, quantitative estimation of crude oil in permeate was checked at regular intervals taking spectrophotometer reading and corresponding time was noted down.Sampling was performed at regular time interval in order to determine if there was any variations of quality of permeate obtained with respect to time.Permeate volume was also noted to find the variation of flux with respect to time since possibility of chocking of membrane due to oil film formation couldn’t be ruled out. It should be noted that the experiments were performed in batch process with no recycle.

Support and membrane recoverability

An attempt to recover the membrane wasdone by back washing and permeating first with n-hexane followed by acetone and water. During the initial step, n-hexane was used which dissolves all the crude trapped on surface and pores. Acetone being soluble in n-hexane removes all n-hexane from support surface and acetone is finally removed by washing with water.

Performance of the recovered membrane was checked by performing hydraulic permeability studies once again to determine the flux.

CHAPTER 4

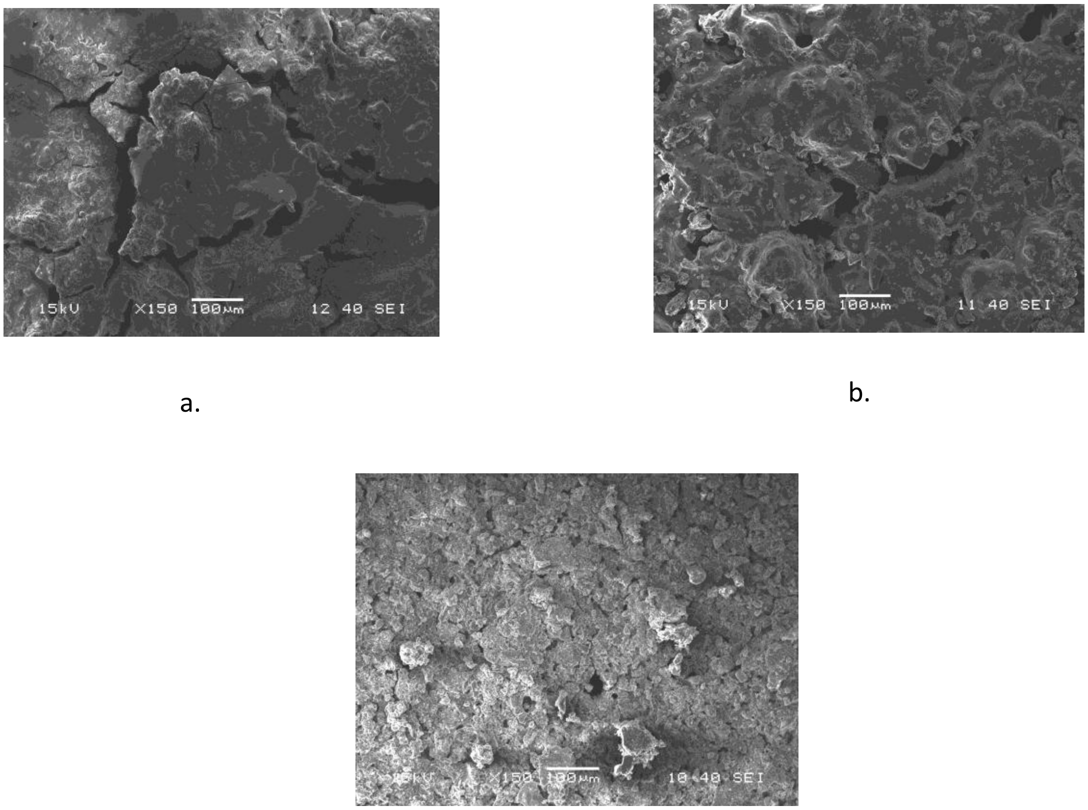
RESULTS AND DISSCUSSIONS

This section explains various findings while performing experiments. All the observations are systematically noted down and carefully compared with the existing literature.

Section A: Synthesis, Characterization and Selection of a suitable membrane

4.1 SEM image analysis

Surface morphology of membrane samples



a.

b.

c.

Figure 4.1 SEM images of [a] Membrane sintered at 500^oC [b] Membrane sintered at 800^oC [c] Membrane sintered at 900^oC

Surface morphology studies are considered to be primary evidence for formation of necessary sample before any chemical or physical analysis. Hence surface morphology studies were performed using high resolution scanning electron microscope.The surface morphology studies of clay membranes are quite essential in a sense that it helps us to find out the surface defects, if any, occured during synthesis (like crack formation etc.).

SEM images show the surface morphology of the membranes (Figure 4.1). The SEM image of membranes (Figure 4.1), gives a good impression about their porous nature. Furthermore, the noticeable roughness of the surface and irregular pores are also visible in the images. It can be also be seen that the pore size of 500°C membrane is the largest having some small cracks while pore size of 900°C is the smallest.

4.2 XRD patterns of membranes and soil

XRD patterns provide characteristic patterns for ceramic structures depending upon the composition and phase changes related with the processing of ceramic substances. Hence XRD patterns are regarded to be an important characterization tool for quantitative and qualitative phase analysis of ceramic membranes. The XRD patterns was obtained for 4 membranes sintered at different temperatures and soil sample.

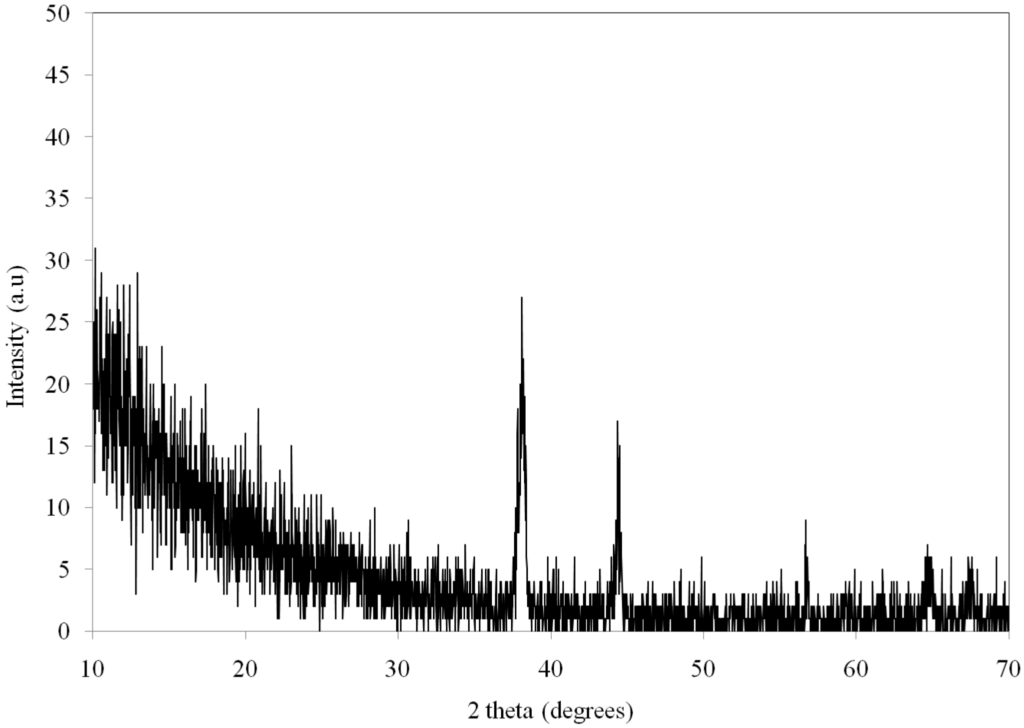


Figure 4.2 XRD pattern of 500°C membrane

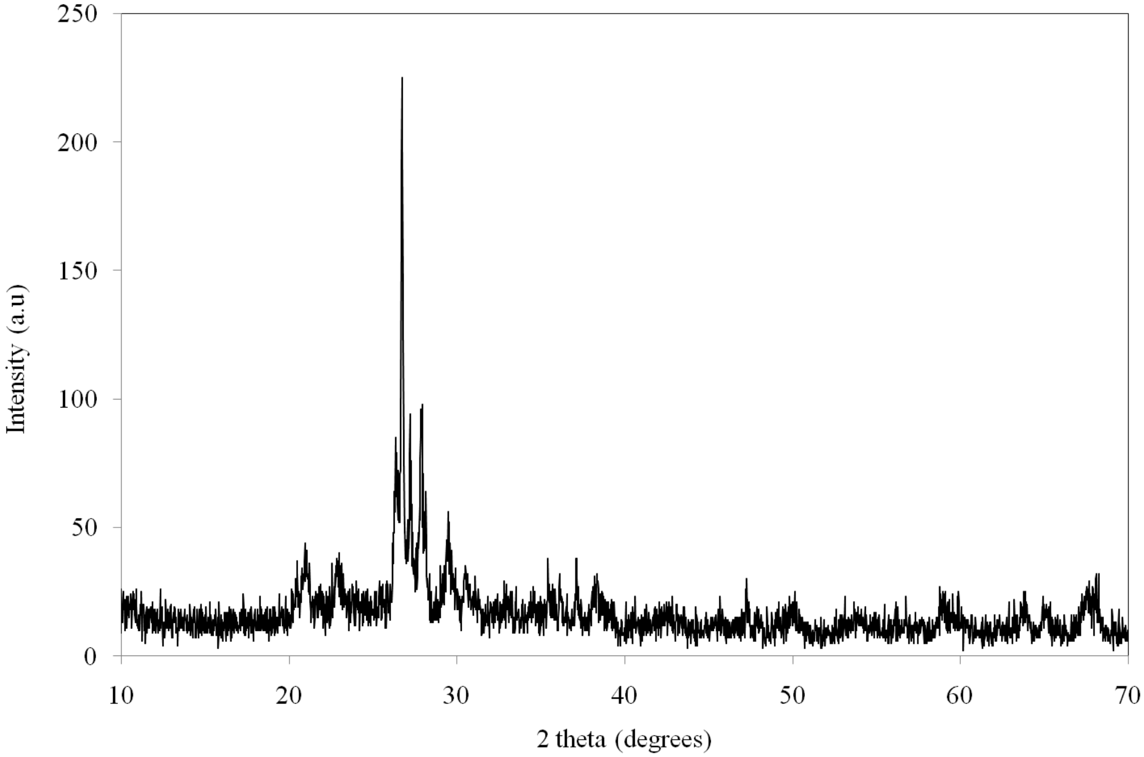


Figure 4.3 XRD pattern of 800°C membrane

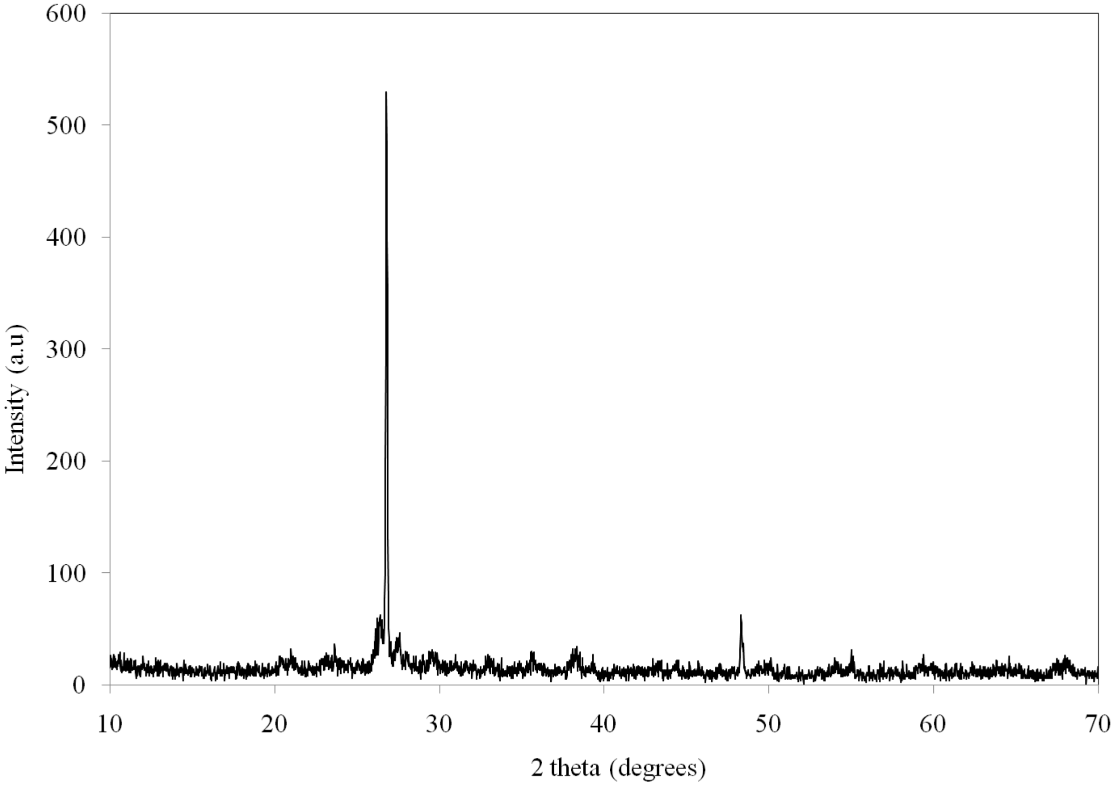


Figure 4.4 XRD pattern of 900°C membrane

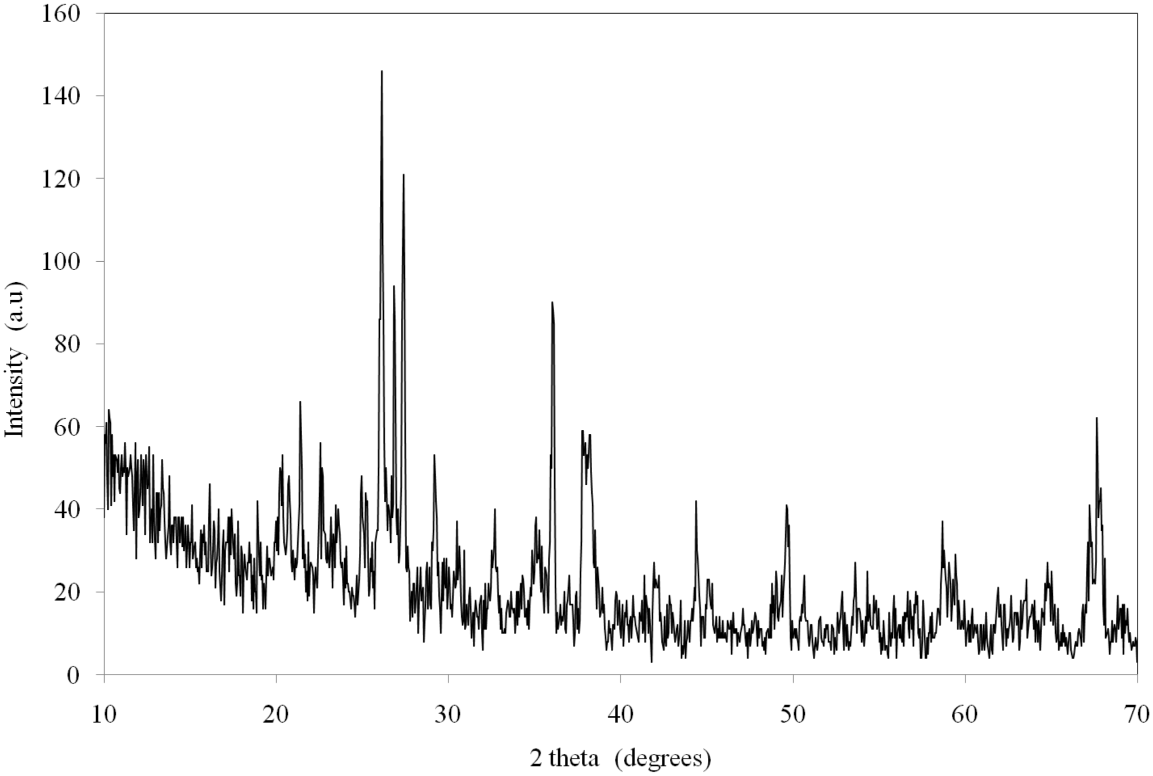


Figure 4.5 XRD pattern of Soil sample

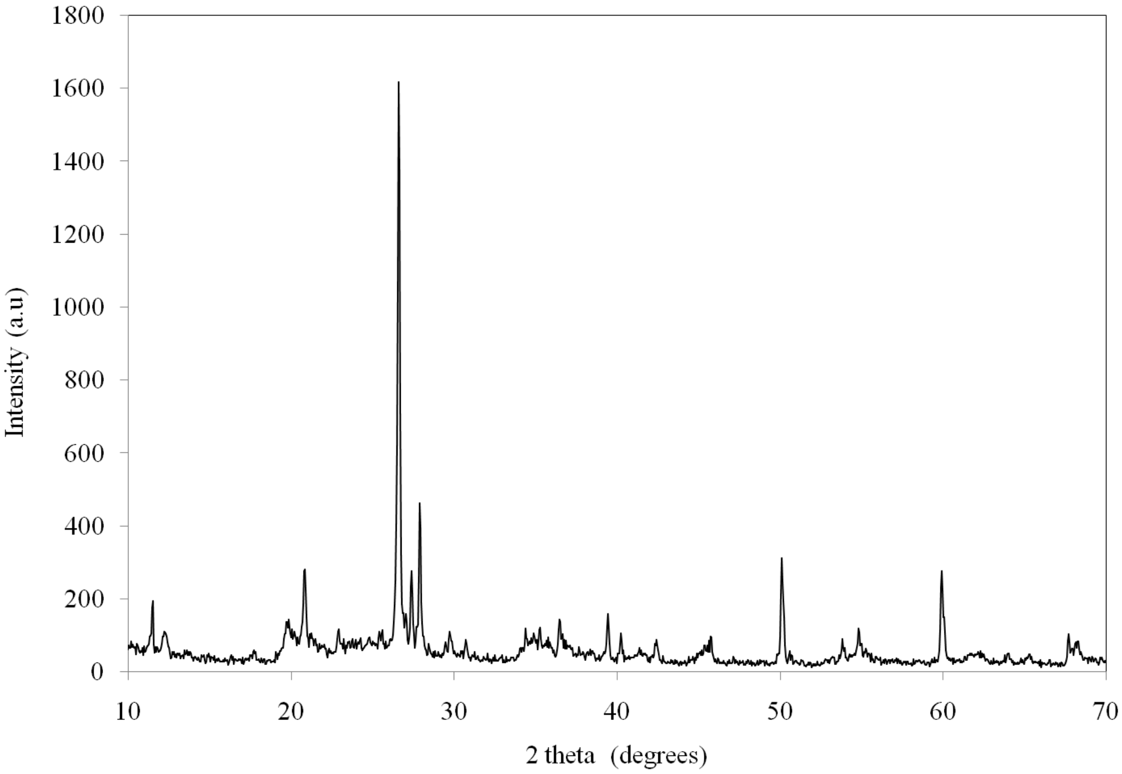


Figure 4.6 XRD pattern of membrane with kaolin

The peaks of membranes indicate quartz as a constituent of clay [10]. Nearly all XRD patterns show the presence of quartz but membrane sintered at 900°C shows only quartz peak indicating all the constituents are converted to quartz. Membrane with 25% kaolinshows no peaks of kaolinite on the sintered claydue to transformation of kaolinite into metakaolinite [11] after sintering. Clearly sintered membranes show less amorphous character than pre-sintered support (soil), indicating the phase transformation.

4.3 Mercury porosimetry analysis of membranes

Membranes were prepared by paste casting method and characterized using Hg porosimetry and support features like average pore size, pore size distribution, permeability and pore tortuosity were determined. Mercury intrusion curve with Pore size diameter *vs*. Cumulative pore volume from the intrusion Hg through the sample and is shown in Figure 4.7.

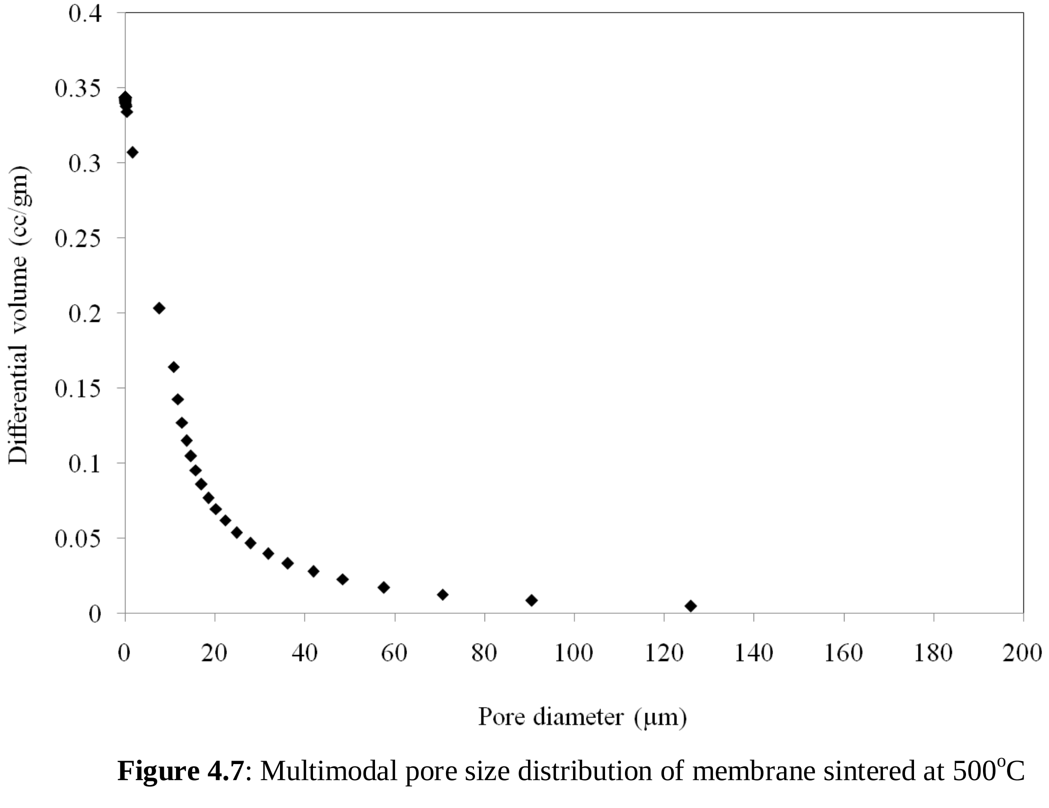


Figure 4.7: Multimodal pore size distribution of membrane sintered at 500°C

The first step upward near 10 µm range may be attributed to macro pores present in the membrane sample. These are the pore mainly present in inter particle region which is resulted from the removal of CO_2 gas from the support upon disintegration of Na_2CO_3. Additionally as the support is not subjected to any compression to high pressure while paste casting, this results in macro pore size range beyond 12 µm in synthesized support. The second and third step in the pattern near 7 µm and further near 1 µm is due to internal pore structure and properties of the mixture constituents. The membrane showed mean pore volume of 0.23cc $g^{-1}$and pore diameter of 17.69µm.

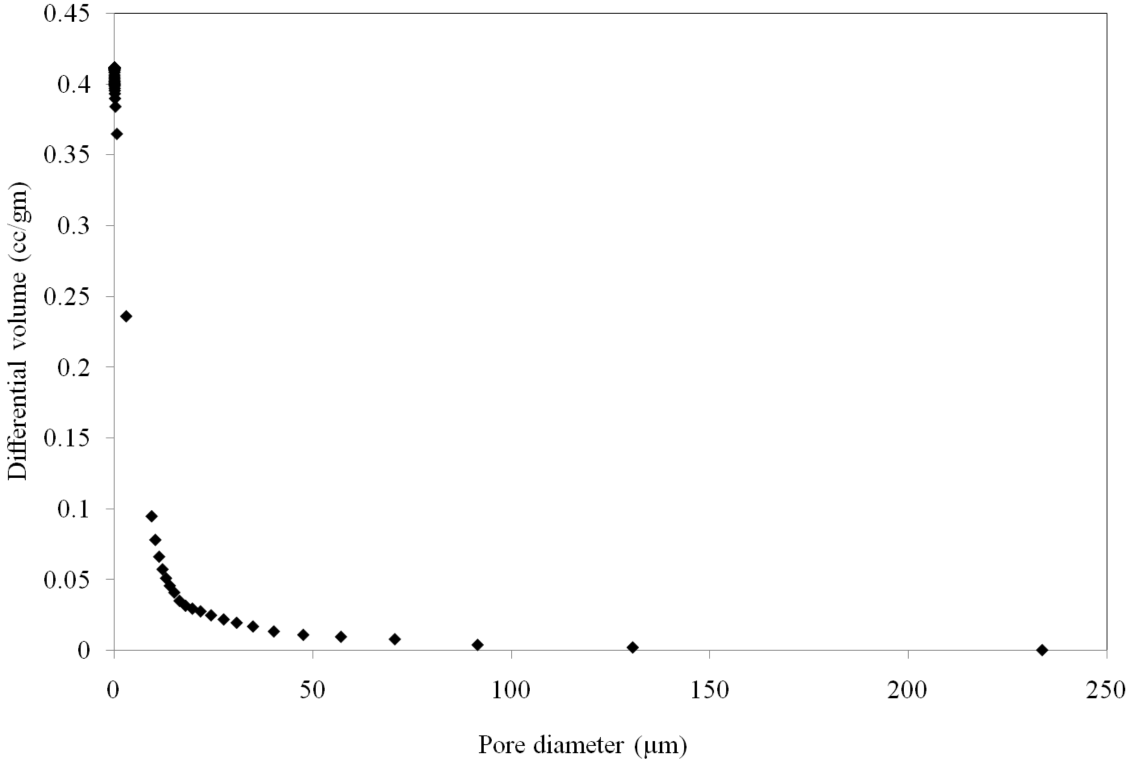


Figure 4.8: Multimodal pore size distribution of membrane sintered at 800°C

The membrane sintered at 800°C has average pore volume of 0.224 cc g^{-1} and pore diameter of 17.66 µm.

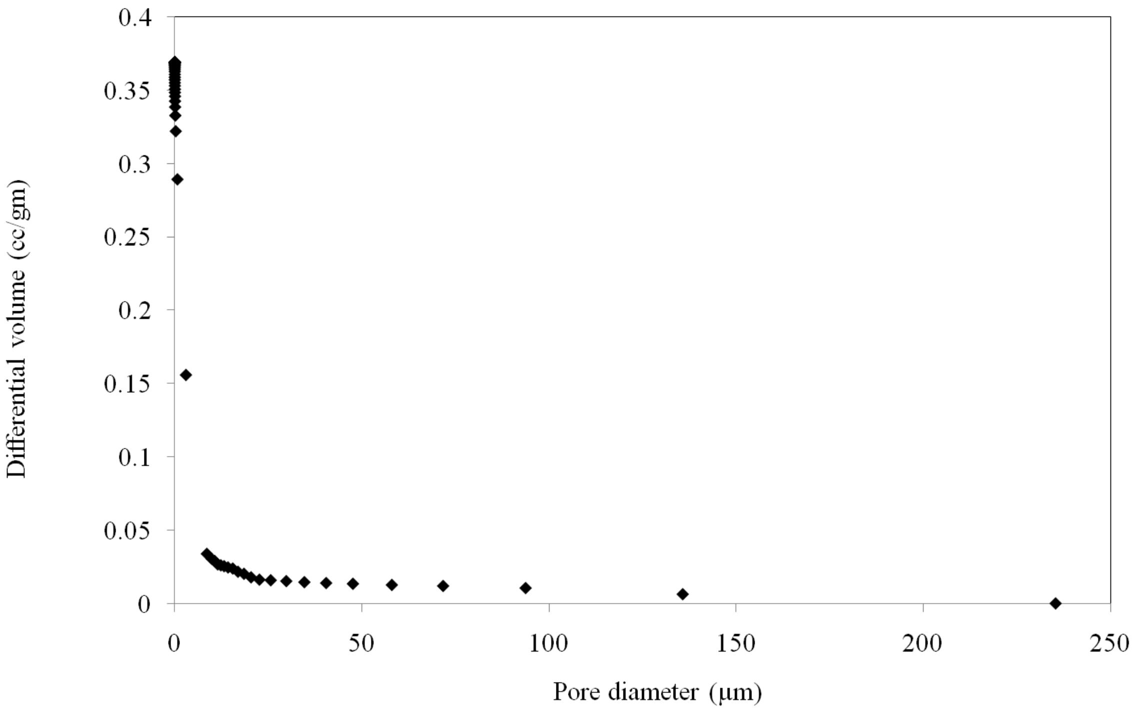


Figure 4.9: Multimodal pore size distribution of membrane sintered at 900°C

This 900°C sintered membrane has average pore volume of 0.22 cc g^{-1} and pore diameter of 17.61µm

Pore tortuosity of the porous media can also be obtained directly which can be used to predict pore shape and permeability. Conventionally while modeling the diffusion characteristics through the porous solids, it is reported that effective diffusivity (D_{eff}) deviates from the theoretical diffusivity (D_b) by a factor given by the following equation[12]

$$D_{eff} = \frac{D_b \theta_c}{\tau} \tag{4.1}$$

Where θ_c is the pore volume fraction and τ is the tortuosity factor.

This effective tortuosity factor accounts for all the deviation from the idealized straight diffusion paths into a single dimensionless parameter, value of which ranges from 1 to 7, with value approximating 2 signifies cylindrical pore shape. The tortuosity value for membranesare calculated to be 2.19, 2.11 and 2.04 for 500°C, 800°C and 900°C membrane respectively,whichis a sound assumption for presence of cylindrical pores suitable for permeation of liquid smoothly.

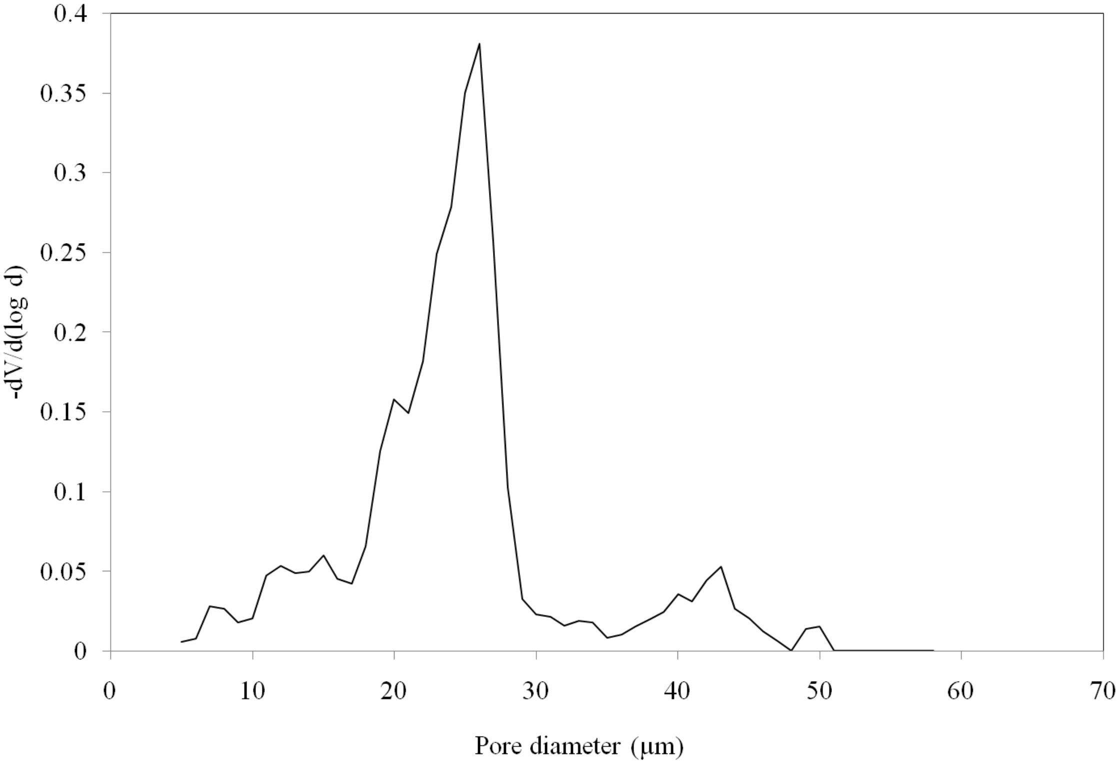


Figure 4.10: Pore size distribution of 500^{o}C membrane

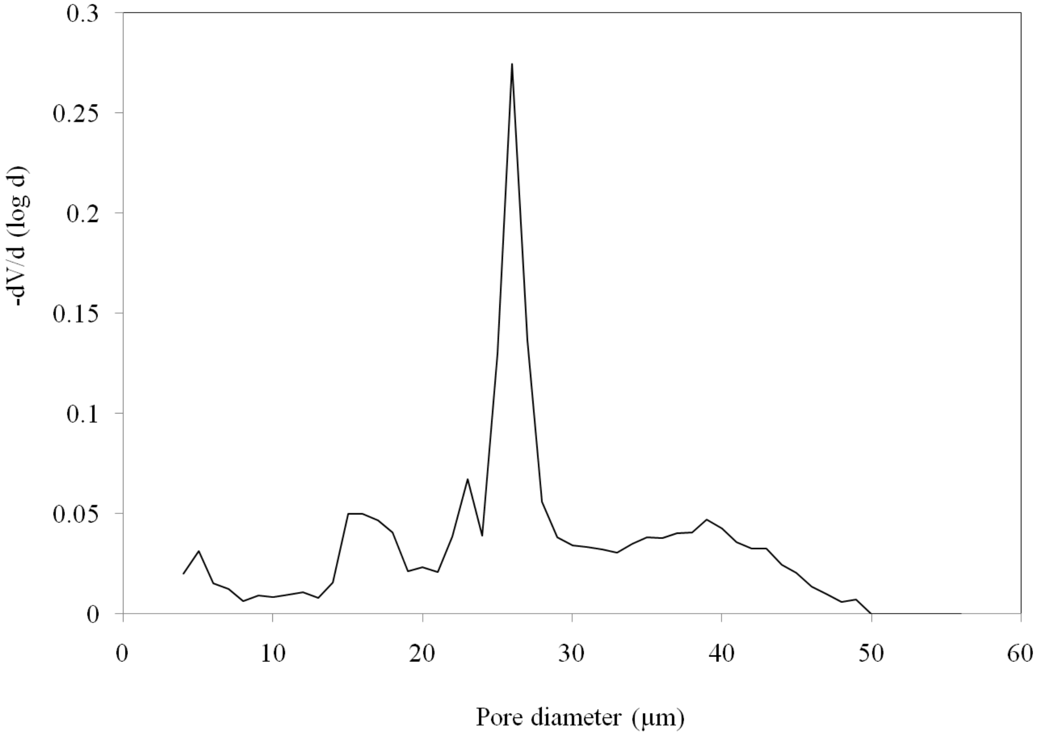


Figure 4.11: Pore size distribution of 800^{o}C membrane

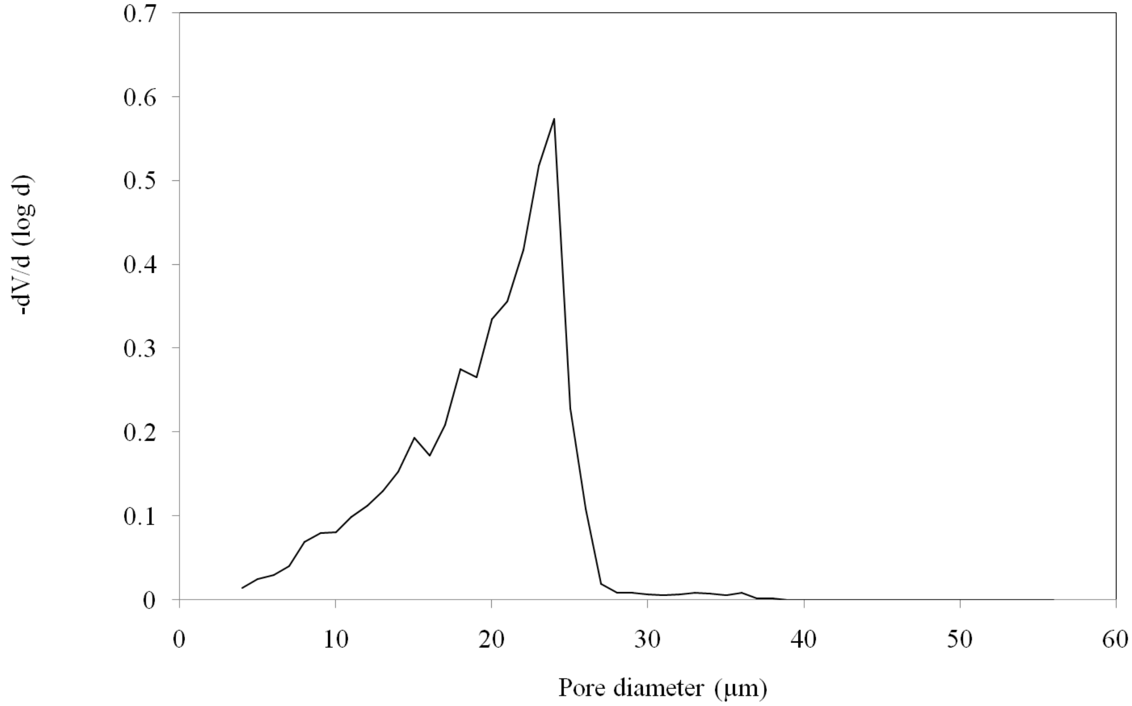


Figure 4.12: Pore size distribution of 900^{o}C membrane

4.4 Thermo gravimetric analysis

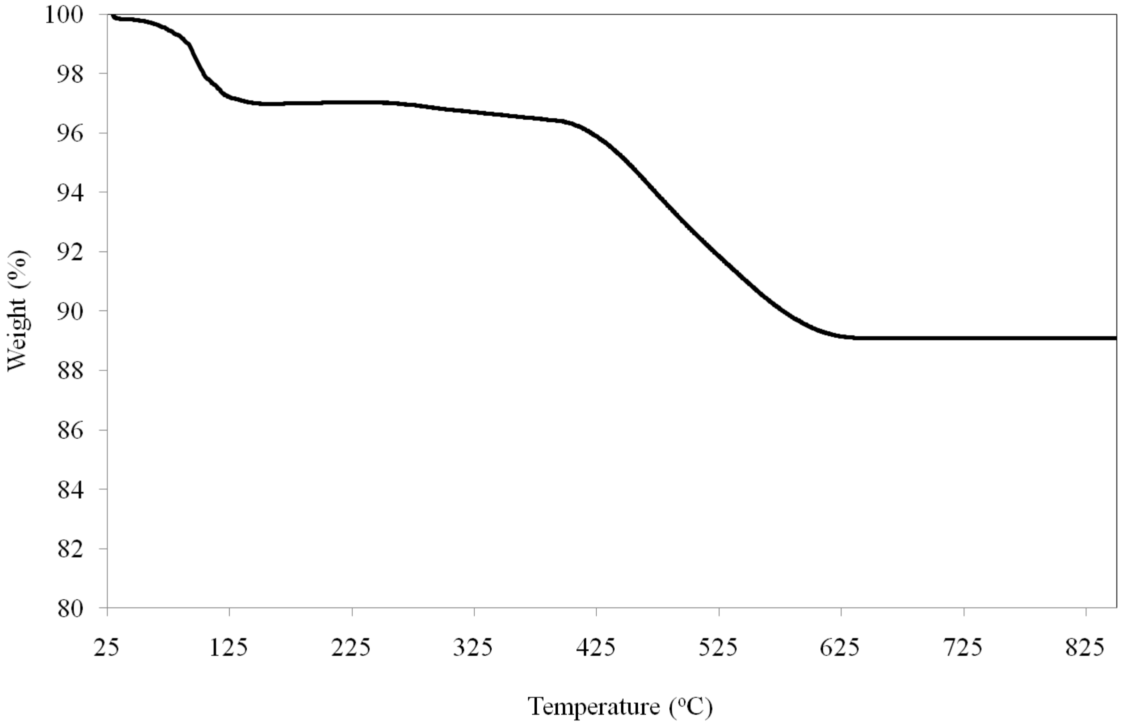


Figure 4.13: TGA of soil sample

This typical TGA profile shows two distinct weight loss steps for all the samples. In the temperature range of 25-125°C the weight loss is purely due to removal of moisture and trapped methanol. The second step from 125°C to 425°C is a horizontal plateau, where the weight remains quite constant. Beyond 625°C, the soil irrespective of their post-synthesis treatments start degrading permanently. This is an indication that for all experimental purposes using this soil, the temperature shouldn't go beyond this value.

4.5 BET surface area analysis

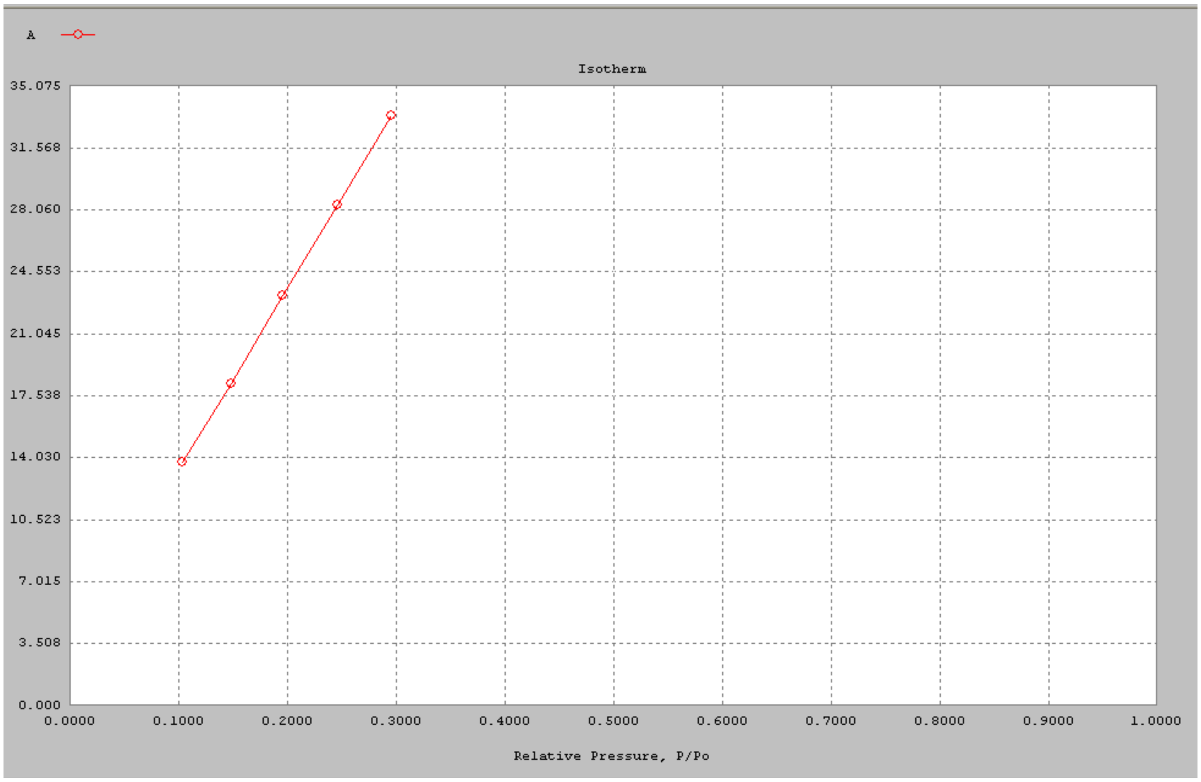


Figure 4.14: BET isotherm of soil sample

BET isotherm studies were performed in the relative pressure range of 0.05 to 0.35. The figure shows the complete adsorption curve. For BET surface area, isotherm is valid within a relative pressure between 0.05-0.35, giving total surface area of 11m^2/g for the soil.

4.6 Permeation experiment

The inorganic membranes are subjected to liquid permeation test using de-ionized water in batch mode operation. The hydraulic permeability, average pore diameter and porosity of the membrane are determined experimentally. Transmembrane pressure drop for water permeation test is maintained at 0-250kpa (microfiltration range). Before using each fresh membrane, membrane compaction has been conducted using de-ionized water at a transmembrane pressure 300kpa. During these experiments, the membrane (without kaolin) flux was observed to be high initially and reduced to a steady state. At beginning flux of $0.00068 m^3 m^{-2} s^{-1}$which reaches to steady state value of $0.0000553 m^3 m^{-2} s^{-1}$ shown in Figure (4.15). These data was taken by measuring the permeate of 250ml volume. The porosity of the membrane is determined by psychometric method using water as wetting liquid.

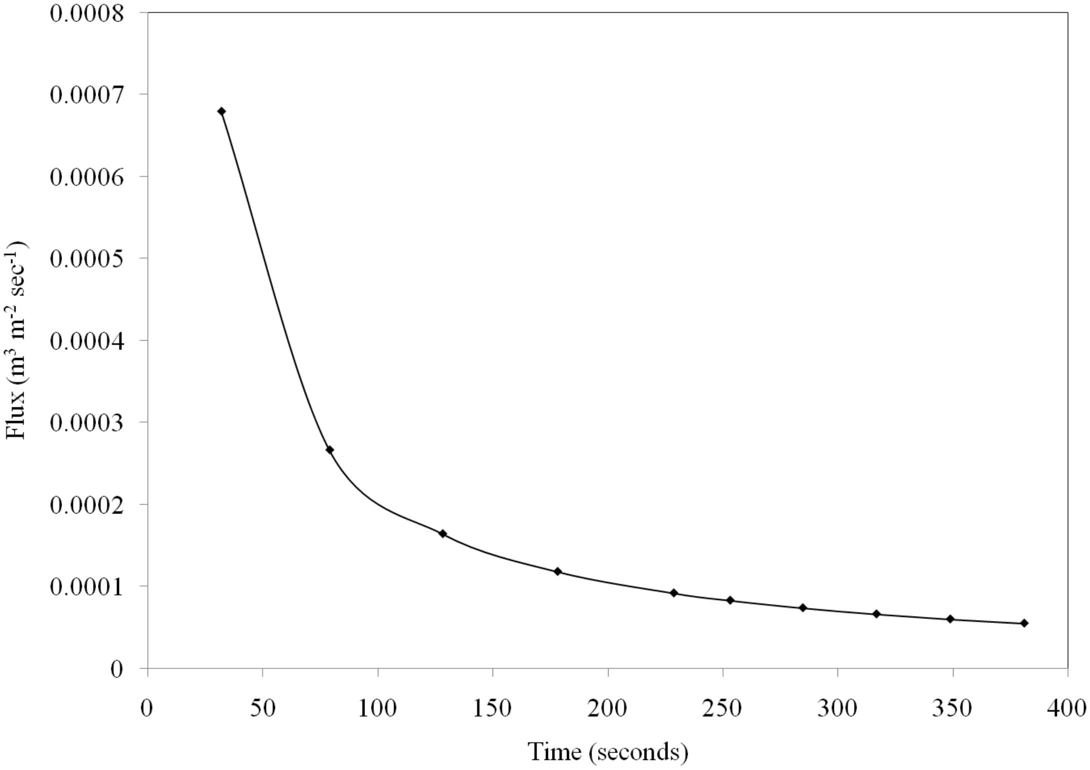


Figure 4.15: Permeability curve for 900°C membrane without kaolin

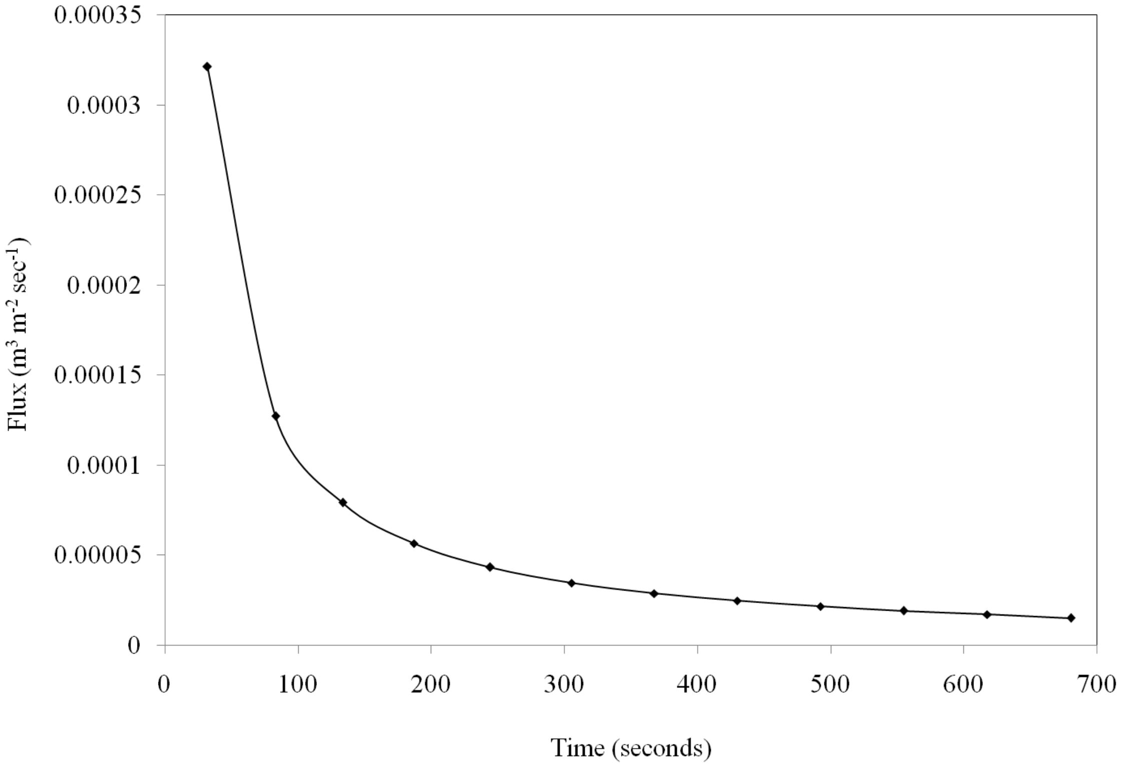


Figure 4.16: Permeability curve for 900°C membrane with kaolin

4.7 Separation experiment

Two Separation experiment where performed.

1) Microfiltration of oil-water using 900°C membrane without kaolin.

2) Again microfiltration of oil-water using 900°C membrane with kaolin.

Crude oil water emulsion system prepared following the procedure described earlier (See Section 3.4). A brief overview of results on rejection of crude oil is summarized in the Table 2..Here; we report a rejection percentage of approximately 48.42 % for crude from oil-water emulsion system using membrane with kaolin. By using membrane without kaolin separation is decreased to 37.59%.As indicated, cumulative rejection % increases as time of process increases. This is mainly attributed to blockage of larger pores by oil emulsion and formation of oil slick. Blockage of pores by the oil slick also causes increase in pressure drop across the membrane. However, higher operating pressure is not recommended for this micro-filtration system. Literature also reports the gradual reduction of flux with an increased oil concentration [10]. This is due to increase in the adsorptive and concentration polarization resistances because of higher feed concentration.

Table.2 Summary of crude oil-water emulsion separation using 900^{o}C membrane with kaolin.

Sl No	**Volume of Permeate (m^3)**	**Time Taken (Sec)**	**Area of Membrane (m^2)**	**Flux ($m^3m^{-2}s^{-1}$)**	**Rejection %**
1	$1x10^{-5}$	122.52	0.002371	$3.66x10^{-05}$	29.25
2	$2x10^{-5}$	345.92	0.002371	$1.449x10^{-05}$	34.63
3	$3x10^{-5}$	490.12	0.002371	$9.37x10^{-06}$	40.81
4	$4x10^{-5}$	792.31	0.002371	$5.1x10^{-06}$	48.42

Table.3 Summary of crude oil-water emulsion separation using 900^{o}C membrane without kaolin.

Sl No	**Volume of Permeate (m^3)**	**Time Taken (Sec)**	**Area of Membrane (m^2)**	**Flux ($m^3m^{-2}s^{-1}$)**	**Rejection %**
1	$1x10^{-5}$	98.07	0.002371	$4.30x10^{-05}$	22.34
2	$2x10^{-5}$	179.06	0.002371	$2.355x10^{-05}$	28.89
3	$3x10^{-5}$	315.12	0.002371	$1.3 x10^{-06}$	32.75
4	$4x10^{-5}$	568.42	0.002371	$7.4x10^{-06}$	37.59

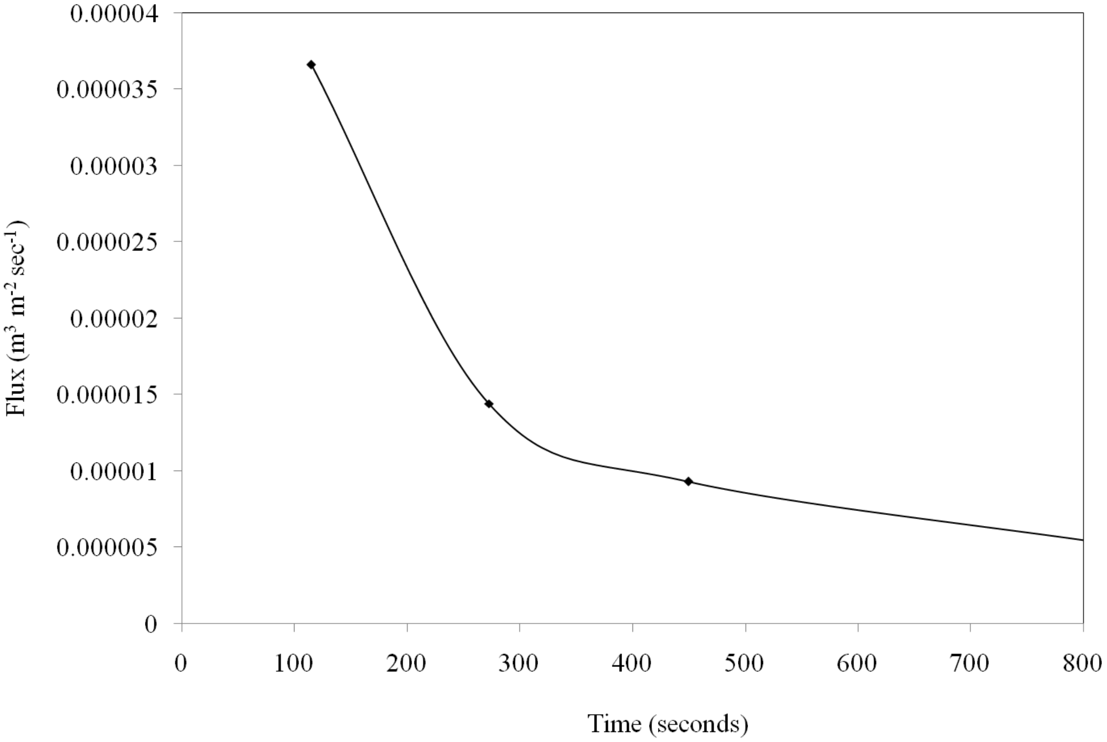


Figure 4.17. Permeate flux of Oil water at 300KPa of membrane with kaolin

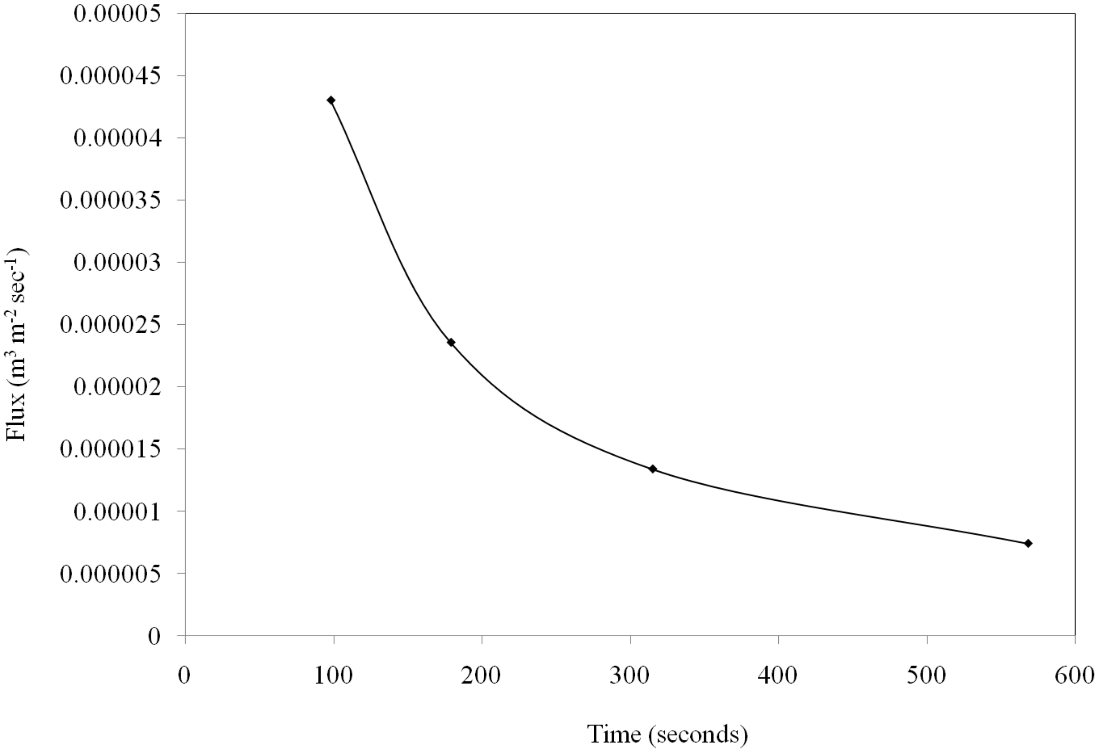


Figure 4.18. Permeate flux of Oil water at 300KPa of membrane with kaolin

4.8 Estimation of material cost of the membrane

The material cost of the fabricated membrane is calculated in terms of Rupees per square meter. 42gms of clay has been taken in addition with the other materials in their respective composition as described earlier. From this total 04 supports are fabricated. Diameter and thickness of each sample has been measured using verniercalliper. Total surface area of each sample was calculated assuming them cylindrical in shape. The purchasing cost of each chemical in rupees per gram was known. From this material cost of the required chemicals can be determined. Dividing this cost with total surface area of sample prepared we can get the material cost for fabrication of ceramic membrane in rupees per square meter.

Table.4 Materials used with their cost for membrane without kaolin

Name of the Material	Cost (rupees/gram or ml)	Amount required (gm or ml)	Total cost (rupees)
Clay	-	29	-
Water	-	8	-
Sodium carbonate (MERCK)	0.432	2.5	1.08
Sodium metasilicate (LobaChemie)	0.644	1.4	0.9016
Boric acid (RANKEM)	0.9	1.1	0.99
Total			2.9716

Table.5 Materials used with their cost for membrane with kaolin

Name of the Material	Cost (rupees/gram or ml)	Amount required (gm or ml)	Total cost (rupees)
Clay	-	28	-
Kaolin	0.46	8	3.68
Water	-	10	-
Sodium carbonate (MERCK)	0.432	2	1.08
Sodium metasilicate (LobaChemie)	0.644	1	0.9016
Boric acid (RANKEM)	0.9	1	0.99
Total			6.6516

CHAPTER 5

CONCLUSIONS AND FUTURE SCOPE

This work highlights the fabrication of ceramic microfiltration membranes using *drill mud* as the raw material. The raw material was pre-processed and paste casting method was used for fabrication. Three different membranes (same composition) were successfully fabricated (keeping a standard stoichiometric composition of raw materials and binders) at three different sintering temperatures e.g. 500, 800 and 900^{o}C. Comprehensive characterization techniques *viz.* scanning electron microscopy (SEM), powder X-ray diffraction (PXRD), BET surface area and Mercury porosimetry were followed to ascertain the nature of the membrane fabrication. This study confirmed that a defect-free ceramic membrane could be fabricated with high content of drill mud and low content of expensive precursors.

The membrane sintered at 900^{o}C (**membrane A**), having an average pore size of 18µm was found best suited for oil-water emulsion studies. A rejection of *ca*. 38% was observed for this membrane. Another variant of ceramic membrane (**membrane B**) was fabricated at 900^{o}C with an addition of 25% kaolin. A better rejection of *ca*. 49% was found for this case which can be attributed to better structural properties of the membrane surface and uniformity in pore size distribution. All the membranes were studied for their regeneration and reusability confirming their ease in operation. A detailed cost analysis was also performed and it was seen that the membranes fabricated were much cheaper than the similar products reported in literature. These results provide significant opportunity to develop ceramic micro-filtration membranes with flexible pore sizes for industrial applications.

The present work holds potential in many applications. Preparation of ceramic composite membranes using novel adsorbents may lead to developing tunable pores within the membrane matrices which can be exploited for tailor-made gas phase as well as liquid phase separation applications.

CHAPTER 6

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