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# Fly ash based ceramic microfiltration membranes for oil-water emulsion treatment: Parametric optimization using response surface methodology

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ABSTRACT

This article addresses the fabrication of ceramic microfiltration membranes (M1-M3) with uni-axial dry compaction method and fly ash, quartz and calcium carbonate as inorganic precursors. Raw material and membrane characterizations were conducted using particle size (PSD), thermo gravimetric (TGA), X-ray diffraction (XRD), scanning electron microscope (SEM), mechanical stability, chemical stability, porosity, pore size and pure water permeability analyses. Dead-end flow microfiltration (MF) experiments were conducted to evaluate the membrane performances with 50–200 mg/L synthetic oil-water emulsions. The MF experiments enabled to evaluate (M1-M3) membrane performance in terms of flux and rejection for variant combinations of feed concentrations and applied pressures. Among all membranes, M2 membrane demonstrated superior rejection (80.82–99.99%) and membrane flux (0.337–4.42 $\times 10^{-4}$ $m^3/m^2$ s). Response surface methodology (RSM) via central composite design (CCD) was employed to optimize and understand the interaction of possible influencing process variables on the treatment efficiency in terms of flux and rejection. The optimum parametric conditions are found to be at an applied pressure of 345 kPa and feed concentration of 176.07 mg/L at which M2 membrane exhibits a maximum oil rejection of 97% with permeate flux of 2.6 $\times 10^{-4}$ $m^3/m^2$ s.



## 1. Introduction

Various industries, including metallurgical, petroleum, and food processing produce highly concentrated (500–1000 mg/L) oil-water emulsions [1], which are harmful threat to aquatic and human life. The destructive impact of oil-water emulsions on ecosystems and environment necessitates the separation of oil from oily wastewater from ecological safety perspective [2]. Thereby, maximum discharge values have been set to restrict oil/grease concentration in industrial effluents by pollution control board and several government agencies. Therefore, several researchers have been exploring new technologies and to upgrade existing technologies to produce treated oily wastewater with oil concentration below the standard discharge limit i.e. 5–10 mg/L [3]. In the last two decades, several methods such as electrocoagulation process [4], coagulation [5], dissolved air floatation [6], gravity separation [7], de-emulsifications process [8], skimming [9] and flocculation [10] have been suggested and studied for the separation of oil from oily wastewater. Among these, many methods are not efficient to achieve the norms/standards set by the pollution control agencies. Further, they also produce a secondary waste stream/product in large quantities [11]. In the past few years, owing to their promising features such as higher chemical, mechanical and thermal stability, longer shelf life, excellent defouling characteristics, good combinations of separation efficiency and membrane flux and susceptibility and ease for process clean up, there is a renewed interest in ceramic membranes for industrial applications [12]. Thereby, ceramic membrane technology has been proven for the treatment of industrial effluents, including pharmaceutical, beverages, refinery, dairy, food and electronic industry [13].

Recently, membrane based separation processes proved to be effective for the separation of oil from wastewater, even though there are few discrepancies for the same [14,15]. For example, reverse osmosis [15,16] is restricted with the requirement of high-applied pressure in the oily wastewater treatment and higher fouling problem with which low permeability is resultant. On the other hand, ultrafiltration [17–19] and nanofiltration [20,21] also produce low permeate flux. On the other hand, microfiltration is a favorable technology for the treatment and separation of oil-water emulsions from wastewater streams owing to its higher water per-

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**Nomenclature**

| | |
|---|---|
| $P$ | the average pressure acting on the membrane (Pa) |
| $\nu\nu$ | the molecular mean velocity of the gas (m/s) |
| $\eta$ | the viscosity of gas (Pa s) |
| $q$ | the tortuosity |
| $lp$ | the length of the pore (m) |
| $K$ | the effective permeability factor |
| $\Delta P$ | the applied pressure (Pa) |
| $Q$ | the volumetric flow rate ($m^3/s$) |
| $P_2$ | the membrane pressure at permeate side (Pa) |
| $S$ | the permeable area of the membrane ($m^2$) |
| $r_g$ | the average pore size of the membrane (μm) |
| $Y$ | the predicted response |
| $b_0$ | Offset term |
| $b_i$ | the linear effect |
| $b_{ii}$ | the squared effect |
| $b_{ij}$ | the interaction effect |
| $X_i$ and $X_j$ | Indicate the coded independent variables |
| $V$ | the volume of permeate ($m^3$) |
| $A$ | the membrane area ($m^2$) |
| $t$ | Filtration time (s) |
| $R$ | Rejection of oil (%) |
| $C_f$ | the concentration of oil in feed (mg/L) |
| $C_p$ | the concentration of oil in the permeate (mg/L) |
| $d_i$ | the diameter of the $i$th pore (μm) |
| $n_i$ | the number of pores on the membrane |
| $D_{avg}$ | the average value of membrane pore diameter (μm) |
| $J$ | the liquid flux through the membrane ($m^3/m^2$ s) |
| $\Delta P$ | the applied pressure across the membrane (Pa) |
| $L_h$ | the permeability of the membrane ($m^3/m^2$ s kPa) |

meability and low pressure requirements [1–3,22]. The separation of oily wastewater using a membrane by microfiltration occurs due to the oil droplet interaction with the surface of the membrane. It also affected by the size of the oil droplet. The microfiltration membrane with wider average pore size and narrow pore size distribution facilitates high permeability with better rejection [22].

The removal of oil droplets from oil-water emulsions depends on the feed oil concentration, membrane properties and operating parameters. The feed properties and the efficiency of a membrane in a microfiltration process are influenced by various parameters such as initial feed concentration, applied pressure and cross flow rate [22]. An optimization technique is used to appropriately choose process variables for the identification of optimal parameters at which effective performance of the process can be envisaged to carry out oil water emulsion treatment. Recently, few researchers [23–26] used response surface methodology (RSM) to analyze the variation of performance involved during wastewater treatment. This is due to the reason that RSM facilitates effective search in the design space, which is not possible in conventional experimentation that involves discretized variation in a parameter of interest for constant values of all other parameters. Thus, RSM with its ability to provide maximum or minimum reference points further extends the limitations of experimental investigations in the design space [25]. Thereby, the methodology allows the identification of influential or significant terms that contribute towards process efficiency with small number of simulation experiments. Till date, RSM based parametric analysis and optimization has been studied for various processes including nanofiltration [23,24], microfiltration [25,26], biosorption [27], adsorption [28,29], electrocoagulation [30–34], electrochemical [35–39], coagulation-flocculation [40–45], ion exchange [46,47] and wet peroxide oxidation [48]. However, the RSM based oily wastewater treatment using ceramic membrane based microfiltration process has not been reported till date and is the primary objective of this work.

**Table 1**
Materials used to make ceramic membranes.

| Raw materials | Membrane, M1 (Wt.%) | Membrane, M2 (Wt.%) | Membrane, M3 (Wt.%) |
|---|---|---|---|
| Fly ash | 80 | 80 | 70 |
| Quartz | 20 | 10 | 20 |
| Calcium Carbonate | – | 10 | 10 |

The RSM methodology involves a three step hierarchy in which the first step allows analysis from the perspective of both individual and combined process parametric effect. The second step allows the evaluation of process efficiency in terms of influencing parameters. The final and third step facilitates process parametric optimization by using a RSM based regressed model to target maximum rejection and permeate flux as a response. For the studies, applied pressure and feed concentration of oily wastewater are selected as independent variables with oil rejection, permeate flux as response variables. Central composite design method enables the determination of response matrix and experimental design. ANOVA analysis is used to the competence of developed second order regression model based on the comparative assessment of model and experimental process responses. The next section summarizes the experimental sub-section of the article.

## 2. Experimental

### 2.1. Membrane fabrication

The inorganic precursors used for ceramic membrane (M1-M3) fabrication are presented in Table 1. The procedure for membrane fabrication is reported elsewhere [12,49]. Firstly, the required materials and 4 mL of PVA solution (2 wt.%) were thoroughly mixed in a ball mill for 1200 s at 40 rpm. Subsequently, the mixture was screened using 40 mesh screen. The obtained powder after screening (22 g) was taken in a homemade circular shaped mould (made up of stainless steel) and then pressed using a hydraulic press at a load of 150 kg/cm$^2$. Thereby, after drying the membranes sequentially at 100 °C and 200 °C, they were subjected to sintering at 1100 °C. Eventually, silicon carbide paper (C-220) was used to polish the membranes. Subsequently, the membranes were subjected to cleaning in aqueous ultrasonic bath for the removal of loose particles adhering to the membrane surface.

### 2.2. Characterization

In order to examine the thermal transformation during sintering, thermo-gravimetric analysis (TGA) was conducted for the mixture of inorganic precursors using TGA instrument (Make NetzscR, Model: STA449F3A00). TGA was conducted using argon as a carrier gas and 10 °C/min heating rate from ambient temperature to the sintering temperature. Nano-particle size analyzer (NPSA) (Make: Beckmann Coulter, Model: Delsa nano C) was used to determine the particle size distribution of powder mixtures.

The XRD patterns of the powder mixtures were carried out in XRD instrument (Make: Bruker, Model: D8 ADVANCE) at 2θ values in the range of 1–80°. The instrument was operated at 0.05°/s scanning rate, 40 kV, 40 mA and Cu Kα(λ = 0.154506 nm) radiation. Scanning electron microscopy (SEM) was conducted to examine the surface morphology using SEM instrument (Make: LEO, Model: 1430VP®, Oxford). ImageJ analysis software based SEM image analysis was further carried out to determine the average membrane pore size. Average membrane porosity was evaluated with water