



## Research Paper

## Single Step Preparation of Zirconia Ultrafiltration Membrane over Clay-Alumina Based Multichannel Ceramic Support for Wastewater Treatment

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## Article info

Received 2017-03-06

Revised 2017-05-13

Accepted 2017-05-31

Available online 2017-05-31

## Keywords

Zirconia nanopowder  
Ultrafiltration membrane  
Slip casting  
Clay-alumina  
Wastewater

## Highlights

- Clay-alumina based ceramic multichannel support was used for membrane preparation.
- UF membrane was prepared in single step coating of zirconia nanopowder.
- Stability of suspension of nanopowder was studied using CE64 with pH variation.
- Defect free zirconia UF membrane was prepared over 19-channel support tube.
- Developed membrane could reduce organic matters and MPN from various effluents.

## Abstract

Zirconia ultrafiltration membranes have been widely developed and used for the past several years. However, the conventional sol-gel methods of zirconia membrane preparation involve many steps. In the present study, an attempt was made to develop the defect free zirconia ultrafiltration (UF) membrane in single step coating of zirconia nanopowder suspension by the slip casting method over multichannel ceramic support. The porous support was made from a novel composition of clay and  $\alpha$ -alumina having a 19-channel circular configuration. The zirconia UF membrane was developed at the inner surface of the support up to 0.2 m length. The membrane had a mean pore diameter of 40 nm. Clean water permeability of  $48 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  was obtained for the membrane under cross-flow filtration mode. The membrane was utilized for the treatment of industrial and domestic wastewater. Membrane treated water was characterized to evaluate the reduction of organic and inorganic contaminants. About 82% and 92% removal of COD were obtained for tannery wastewater and kitchen sink wastewater, respectively and turbidity was reduced below 1 NTU for both the effluents. Complete removal of pathogenic organisms was achieved. Membrane treated wastewater may be reused for agricultural purposes.

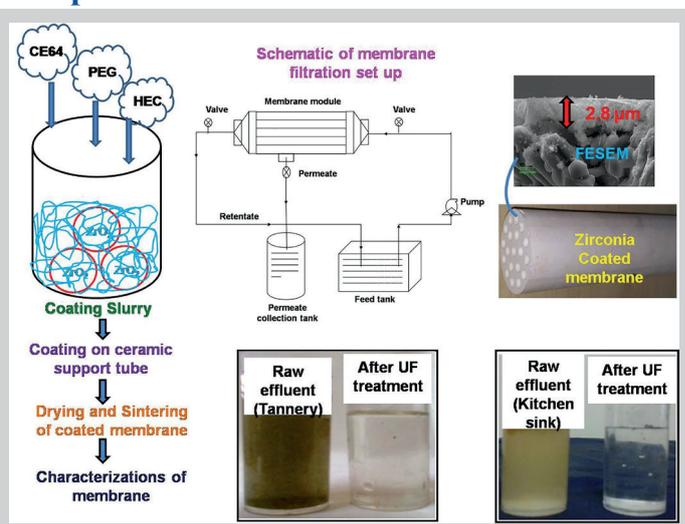
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## 1. Introduction

Recently, ceramic ultrafiltration (UF) membranes are being widely developed for various environmental related applications [1]. UF membranes have a wide range of applications like recovery of paint, latex and PVA (Poly vinyl alcohol), separation of oil-water emulsion, removal of harmful pathogens, organic loading, etc. [2-4]. The UF membrane also has a large impact on the

food industry [5]. The efficiency of ceramic UF and microfiltration (MF) was studied in the dual stage for treatment of high organic loaded domestic wastewater and subsequently reuse in agriculture [6]. The UF membrane of 10,000 Da nominal molecular weight cut off in combination with the anaerobic reactor has been reported for the treatment of

## Graphical abstract



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brewery wastewater with 96% COD removal [7]. The zirconia UF membrane used for soya bean oil/hexane separation was observed. About 17% rejection was achieved using the 0.02mm supported zirconia disc membrane [8].

Membranes prepared with zirconia are chemically more stable than those prepared from titania and  $\gamma$ -alumina [9]. Moreover, zirconia UF membranes have more alkali resilience compared to titania and silica membranes [10]. The sol-gel route of coating for the preparation of ceramic UF membranes has been applied for several years. The sol-gel method results in the formation of smooth and defect free membranes. This method has been employed by Wei et al. [9] for the preparation of zirconia UF membrane. Zirconium butoxide was used for preparation of the crack-free UF membrane by the sol-gel route [8]. However, the sol-gel route of membrane preparation has certain disadvantages. The raw materials used for sol-gel coating involve the use of different metal alkoxides making the process costly [10]. Several steps like hydrolysis, polymerization, gelation, condensation, drying and densification are involved in the sol-gel process; thereby continuous monitoring is required in the process. This renders the sol-gel process cumbersome and difficult to handle. Controlling pH is essential in the sol-gel process to avoid precipitation as well as gelation [10]. On the other hand, powder coating for preparation of UF membranes can overcome these difficulties in the sol-gel method. Powder coatings do not involve the use of metal alkoxides making it relatively cost effective. The uniform UF membrane layer with 2-5 $\mu$ m thickness and tailor made pore size can be achieved in a single step by the powder coating technique. Moreover, coating thickness can be altered by adjusting the coating time [11]. Powder coating of zirconia was carried out by Saffaj et al. [12] for preparation of the MF membrane interlayer for various applications.

In the present work, zirconia UF membrane was prepared by single step coating using zirconia powder suspension by the slip casting method over cost effective clay-alumina based MF tubular support of a 19-channel configuration. The developed asymmetric membrane has been tested for removal of harmful microorganisms and organic loading from industrial and domestic wastewaters for reuse purposes.

## 2. Materials and Methods

### 2.1. Characterization of zirconia powder and dispersion

Zirconia powder of the tetragonal phase (>99% purity) was purchased from M/s CEZUS, France. Multi-point Brunauer, Emmett and Teller ( $M_{BET}$ ) surface area of 47m<sup>2</sup>/g was determined by the N<sub>2</sub> adsorption (Autosorb AS-1-MP, Quantachrome, USA) method. The mean particle size was calculated from the multi point BET surface area.

A commercial polyelectrolyte Dolapix CE64, hereafter denoted as CE64, of mol. wt. 320 g/mol was used as a dispersant. It is a carbonic acid based polyelectrolyte, free from alkali, pH range of 6.8–7.1, density of 1.2 g/cc at 20°C and does not foam.

Aqueous colloidal suspensions were prepared by add-mixing zirconia powder (1.5 wt% solid loading) in 1.5 wt% dispersant solution in distilled water. Analytical grade hydrochloric acid (HCl) and Sodium hydroxide (NaOH) (Merck, Germany) were used for adjustment of the suspension pH. pH was measured with a pH meter (pH tutor, Eutech, India).

Suspension stability of zirconia powder was optimized as a function of dispersant concentrations against zeta potential value. Zeta potential value was measured using the Laser Doppler electrophoresis technique and calculated based on the Smulchowski model (Zetasizer Nano-Z, Malvern, U.K). Suspension containing 1.5 wt% zirconia nano-powder was conditioned overnight at  $1 \times 10^{-2}$  (M) Potassium nitrate (KNO<sub>3</sub>) solution in a magnetic stirrer, to maintain the ionic strength as an indifferent electrolyte. The sample of 50 ml was taken for each test and pH adjustment was done either by HCl or NaOH.

### 2.2. Preparation of unsupported membranes

A quantity of slurry, i.e. stable suspension of zirconia nano-powder (2wt%) in aqueous medium with organic additives such as CE64 as dispersant (1.5wt%), polyethylene glycol (4wt%) as plasticizer and HEC (hydroxy-ethyl cellulose) (62.5wt%) as binder (Figure 1) were prepared by magnetic stirring followed by ultrasonication and poured into a glass Petri dish up to an approximate thickness of 2 mm. The slurry was then dried at 45 °C in a hot air oven for 24 h. The dried green unsupported membrane (green membrane is the membrane which is not sintered) was obtained as shown in Figure 2. It was then calcined at 700 °C for 2 h soaking time in the air to burn off the polymer template in order to obtain the unsupported membrane and was characterized by  $M_{BET}$  pore size distribution.

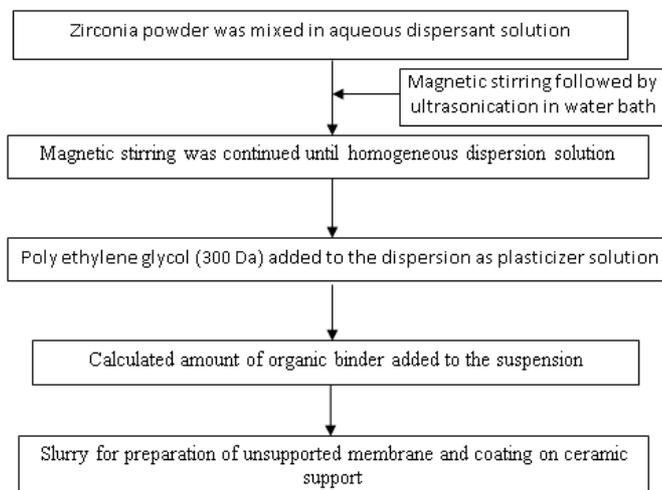


Fig. 1. Flow diagram of zirconia powder slurry preparation.

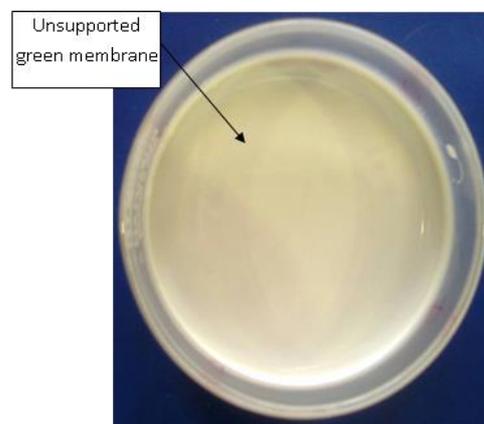


Fig. 2. Unsupported zirconia membrane in a Petri dish.

### 2.3. Preparation and characterizations of ceramic support tubes

The novel clay-alumina based ceramic porous MF support tubes were developed indigenously using the extrusion technique. The support tubes were of 19-channel configuration with 200 mm length. Each channel had a channel diameter (CD) of 4.2 mm [13]. The support tubes were characterized in terms of a Field Emission Scanning Electron Microscope (FESEM) (LEO S430i, UK), mercury intrusion pore size distribution (Quantachrome, PM60, USA) and clean water permeability.

### 2.4. Preparation of supported membrane

Slurry for UF coating of zirconia powder was casted inside the surface of the multi-channel ceramic support using the dip coating technique and slip casting method. After coating, the coated membrane and unsupported membrane were dried at 45°C in a hot air oven overnight to obtain the green supported membrane. Membrane thickness was varied by changing the coating time from 180 - 600 sec. The supported green membrane was calcined in the air at 700°C for 2 h at a heating and cooling rate of 1°C/min and 2°C/min, respectively. The UF membrane was characterized using FESEM, porometry analysis and water flux. The elaborated membrane was subjected to cross-flow filtration of surface water, grey water and industrial wastewater. Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD) and *E. coli* content in the feed and membrane permeate were analyzed for evaluation of membrane performance.

### 2.5. Wastewater collection and characterization

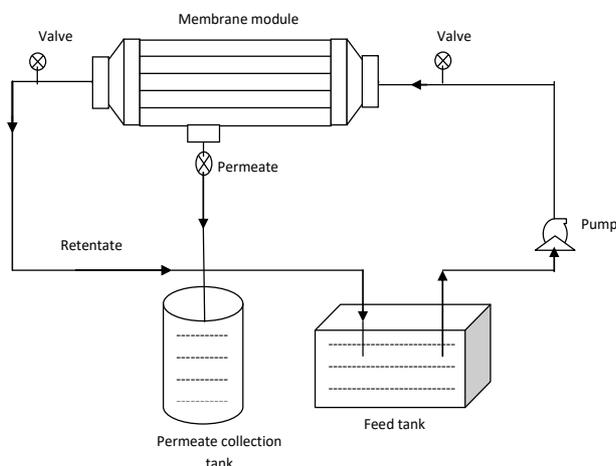
Wastewaters were collected from the tannery and kitchen sink, hereafter denoted as Effluent-A and Effluent-B, respectively. Effluent-A was the water from the secondary clarifier of the common effluent treatment plant (CETP) of the tannery industry. This effluent still contains some organic and inorganic loading, which gets discharged into the environment without further treatment and may cause toxicity to biota [14]. Effluent-B was collected from

the kitchen-sink of the CSIR-Central Glass and Ceramic Research Institute office canteen during lunch time. This effluent was rich in organic loading and represented in terms of COD, BOD, oil and grease, etc. [7]. Immediately after collection, effluents were characterized in terms of pH, turbidity, BOD, COD, conductivity, Total Suspended Solid (TSS) and Total Dissolved Solid (TDS). These parameters were analyzed using instruments by M/s HACH, USA. COD was performed in the COD digester by Spectralab, India. All the analysis was performed as per the standard method described in APHA (American Public Health Association) for water and wastewater analysis [15]. Bacteriological analysis was performed and represented in terms of the most probable number (MPN) per 100 ml [16] (Table 1) for measurement of *E. coli* as an indicator of pathogenic bacteria in water sources.

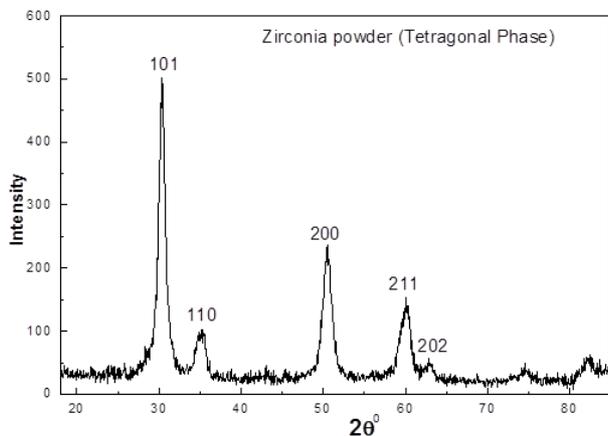
**Table 1**  
Characterization of effluents before and after membrane treatment; A: Tannery effluent, and B: Grey water from kitchen sinks.

Parameters	Effluent-A	Permeate of effluent-A	Effluent-B	Permeate of effluent-B
pH	6.4	7.2	6.8	6.4
COD (mg/L)	1000	180	2700	220
BOD (mg/L)	560	50	480	27
Oil and grease (mg/L)	145	13.2	856	24
Turbidity (NTU)	1.24	0.24	108	0.241
TDS (mg/L)	3124	2752	3478	2799
Conductivity ( $\mu\text{S}/\text{cm}$ )	7.21	7.08	7.33	7.04
TSS (mg/L)	76	BDL	165	BDL
MPN (per 100 ml)	2,80,000	ND	3,40,000	ND

N.B: Data represents average value, BDL: Below detection limit, ND: Not detected.



**Fig. 3.** Schematic representation of membrane filtration set up.



**Fig. 4.** XRD pattern of zirconia powder.

## 2.6. Cross flow UF study of clean water and wastewater

Filtration tests were performed in the cross flow membrane filtration (CMF) mode at various transmembrane pressures (TMP) on the laboratory scale unit using a recycling configuration (Figure 3). The set up was equipped with a centrifugal pump, feed tank (10L capacity) and single element membrane module for 19-channel membranes. The module was made of stainless steel materials (SS316L). Zirconia membranes (length 200 mm and CD of 4.2 mm) having an effective filtration area of 0.05 m<sup>2</sup> were used for the filtration study. Prior to the experimental run, membranes were conditioned by immersing in distilled water overnight to obtain a stabilized flux right from the beginning of the experiment. Permeate flow was monitored by regulating the control valve at the retentate flow path. Feed temperature was maintained at 25°C using a cooling water jacket. For clean water permeability tests, 8L of distilled water was used and turbidity was measured at frequent intervals. About 8L of feed (each for Effluent A and B) was taken in the feed tank and the experiment was run for 120 min at 1bar TMP. The permeate was collected after 10min, 15min or 30min time intervals and was characterized for reduction in organic and inorganic loading.

## 3. Results and discussions

### 3.1. Powder and slurry characterization

The X-ray diffraction (XRD) pattern of the zirconia powder shows that it exists in the pure tetragonal phase (Figure 4). The tetragonal phase is metastable in nature and is desirable for membrane application over porous ceramic support. Similar explanations were provided by Erdem and Ciftcioglu [17] where they concluded that the phase transformation property of zirconia is beneficial for tailor-made membrane pore size. The XRD peak values of 30.32°, 35.25°, 50.5°, 60.0° and 63.0° correspond to the miller indices of (101), (110), (200), (211) and (202), respectively [JCPDS File No: 42-1164]. The crystallite size of about 109.98 Å was obtained using the highest intensity peak, i.e. miller indices (101) of the XRD plot (Scherrer equation including Ruchinger correction). The theoretical particle size was obtained using M<sub>BET</sub> data by the following equation [18].

$$D = \left( \frac{6}{SA \times \rho} \right) \times 1000 \quad (1)$$

where,  $D$  is the mean particle size (nm),  $SA$  is the surface area (m<sup>2</sup>/g) from M<sub>BET</sub> analysis data, and  $\rho$  is the theoretical density of zirconia powder (5.68 g/cm<sup>3</sup>). The theoretical particle size determined was about 22.42 nm. The theoretical particle size and crystallite size values show that the zirconia particle is polycrystalline in nature.

Zeta potential measurements of the suspended ZrO<sub>2</sub> powder were carried out with and without the addition of dispersant (CE64). CE64, the water soluble dispersant with low molecular weight (320 daltons), can modify the surface properties of the nano-particles in the aqueous dispersion medium. The variation of dispersant concentrations (0.1-2.5 wt%) at a fixed solid loading (1.5 wt%) was studied for suspension stability of ZrO<sub>2</sub> by measuring the zeta potential. The zeta potential value of 1.5 wt% dispersant concentrations with a solid loading of 1.5 wt% shows suspension stability (Figure 5). This concentration was found suitable for slurry preparation and this concentration, i.e. 1.5wt% of dispersant and 1.5wt% solid loading of zirconia powder was selected for the present study. Rao *et al.* [19] had also studied the effect of CE64 concentration (0.04 - 0.8 wt%) on the dispersion of monoclinic zirconia powder (solid loading only 0.03wt%) and found that on increasing CE64 concentration, the surface becomes more negatively charged which was supported by zeta potential data. It is evident from Figure 5 that concentration of CE 64 of  $\geq 1.5$  wt% had the most stable zeta potential value (-52 mV) for dispersing zirconia nano-powder. With increasing solid loading, flocculation or aggregation of Zirconia nano-powder occurs that leads to unstable suspension. Solid loading was fixed at 1.5wt% because the stable zeta potential value of suspension was achieved and homogeneity of suspension was maintained. If solid loading was less than 1wt%, then it would not be sufficient to form a continuous coating layer for membrane preparation. The Zero Point Charge (ZPC) of the powder suspension was determined from the plot of pH vs. zeta potential as shown in Figure 6. ZPC at a pH of 5.2 was determined from the plot for the zirconia powder suspension in distilled water (without dispersant) and was found very close to the reported values of 5.3 to 5.4 for zirconia suspension in distilled water [20-21]. With the addition of dispersant CE 64 (1.5 wt%), the ZPC value shifted down to 4.0 indicating zero zeta potential charge. Below a pH of 4, the dispersion of zirconia takes place in the presence of CE 64 as dispersant, because at this pH, the suspension starts ionizing. Ionization occurs because

of some weak interaction between undissociated CE64 and zirconia surface through hydrogen bonding; thereby some reduction in the magnitude of zeta-potential is observed. Above a pH of 4, the zeta-potential value of the suspension becomes negative and attains a constant value of -55 mV. In ZrO<sub>2</sub>-CE64 colloidal suspensions, the van der Waals attractive force can be countered by a greater repulsive force separating the particles from one another which can be achieved either by the addition of negative charge to the particles termed electrostatic stabilization or by the addition of a polymeric molecule. When adsorbed onto the powder surface, CE64 molecules prevent the particles from interacting with each other and thereby prevent the formation of flocs known as steric stabilization. A combination of these two effects is known as electrostatic stabilization, which may be the probable stabilization mechanism for polyelectrolyte adsorption onto the particles [22-23]. With increasing pH, the zeta potential value increases which may be due to the complete dissociation of the dispersant. The zeta potential values attain a constant value within the pH of 8-10 (Figure 6). This phenomenon occurs because with an increase in pH, the prevalence of zirconium hydroxy complexes on the surface of the suspension interacts chemically with the carboxylic group present in the dispersant, thereby increasing the overall surface charge resulting in more stable suspension. The high negative value of suspension indicates that CE64 adsorbs strongly on the zirconia surface and that changes the ZPC value. Thus, CE64 as dispersant is capable of altering the surface charge of zirconia powder in the suspension resulting in stable zeta potential value. This stability of suspension is desirable for coating formulation.

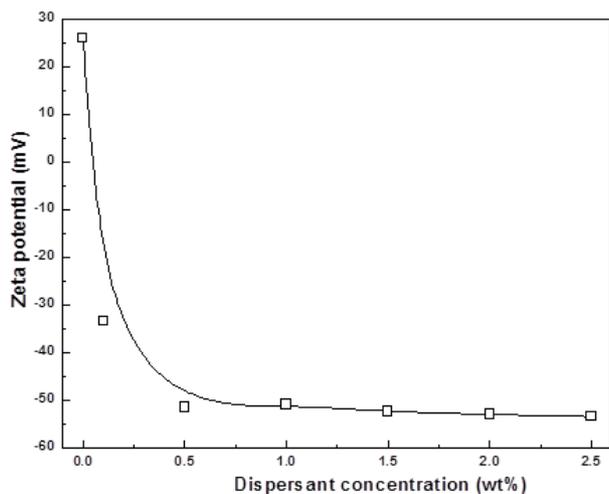


Fig. 5. Plot of dispersant concentration vs. zeta potential of suspension of zirconia powder.

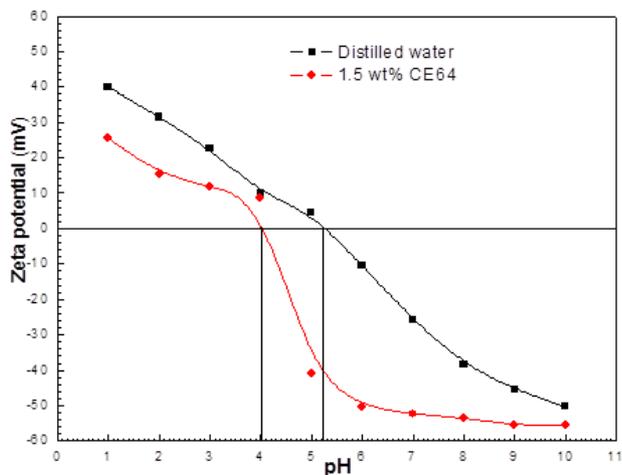


Fig. 6. Plot of zeta potential vs. pH of suspension of zirconia powder.

### 3.2. Characterization of unsupported fired membranes

The unsupported membrane was prepared to determine the nominal pore diameter using the gas adsorption – desorption method to get an idea of pore size while applied on a porous support. The unsupported membrane obtained after firing at 700 °C was characterized by M<sub>BET</sub> pore size distribution. The average pore diameter of 40 nm was obtained from the BJH desorption pore volume analysis (Figure 7).

### 3.3. Support tubes and coated membrane characterization

A clay-alumina based 19-channel ceramic support tube 200 mm in length is shown in Figure 8a and its cross sectional view is shown in Figure 8b. The support tube and channel are spherical in shape with each channel being equidistance from each other and no channel merging. The support tube was characterized by mercury intrusion porosimetry and the average pore size obtained is about 0.8 μm (Figure 9). As shown in Figure 10a, FESEM micrographs of the support tube clearly indicate elongated grains and an average pore size of 0.8-1.0 μm. Thus, the clay-alumina based 19-channel ceramic support tube was the MF membrane as it is evident from these characterizations. Figure 10b shows the cross sectional view of the zirconia coated membrane. The average coating thickness of 2.8 μm and pore diameter of 30-40 nm (Figure 10c) were obtained over the multichannel support from FESEM micrographs.

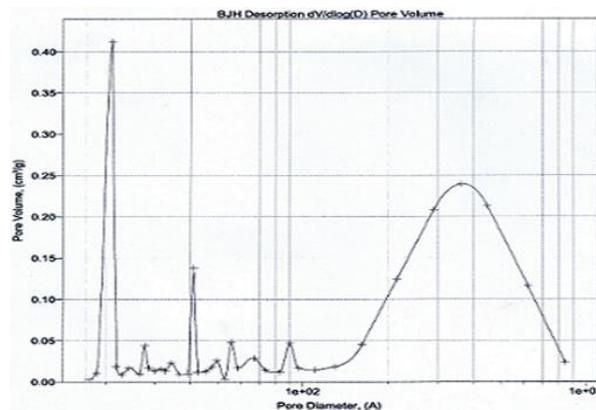


Fig. 7. BJH pore volume vs. pore diameter plot of unsupported fired zirconia membrane.



Fig.8. Support tube images (a) horizontal and (b) cross sectional view.

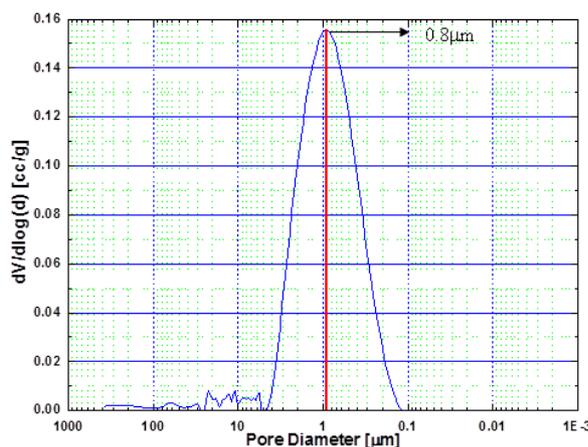


Fig. 9. Mercury intrusion pore size distribution of 19-channel support tube.

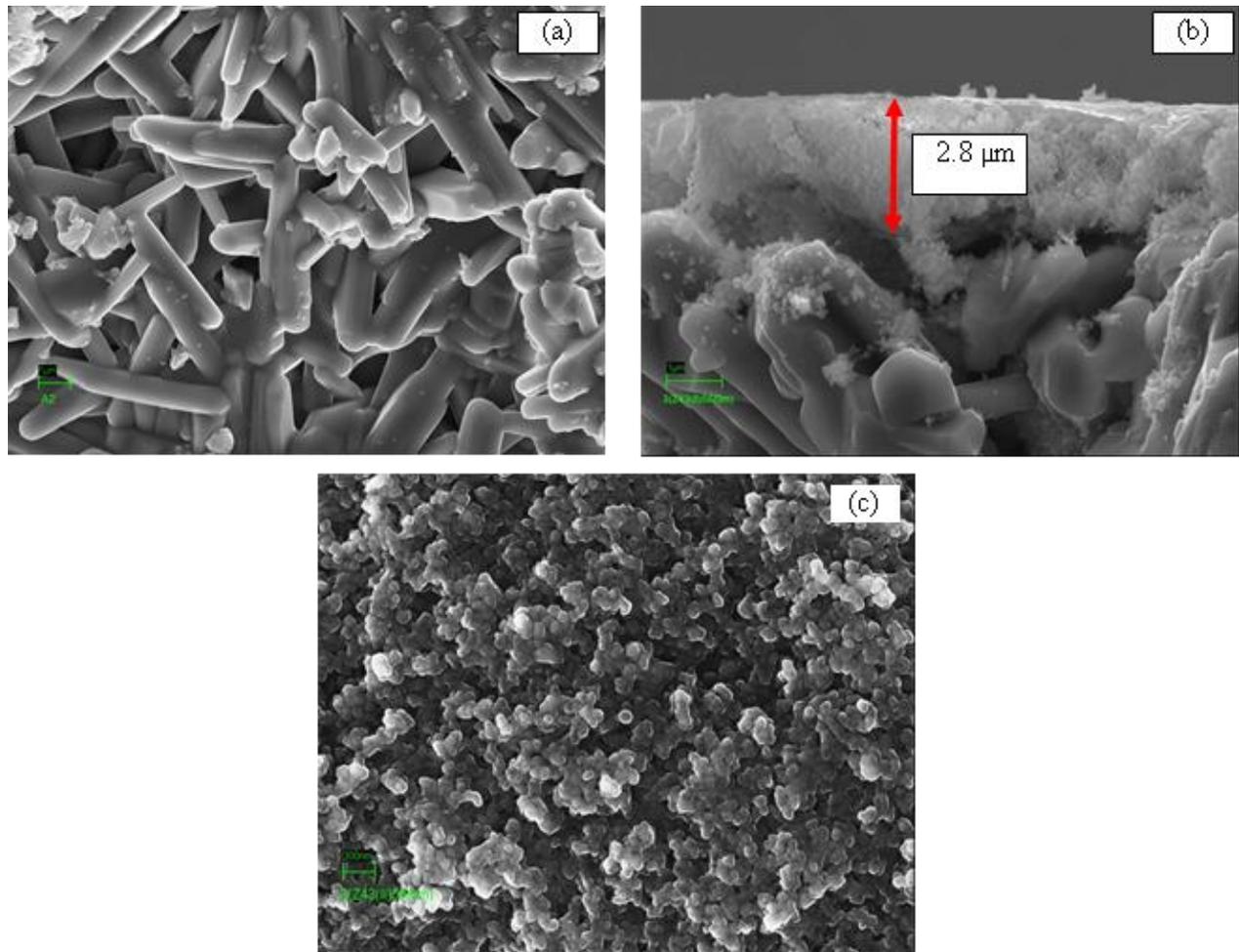


Fig. 10. FESEM micrograph (a) surface view of support tube, (b) cross-section and (c) surface view of zirconia UF over support tube.

#### 3.4. Determination of membrane permeability

Chao *et al.* [24] had reported the MF zirconia/ $\alpha$ -alumina membrane preparation where they had used symmetric and asymmetric alumina support. The pure water flux was 400 and 1500  $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$  and the avg. membrane pore diameter was 0.2  $\mu\text{m}$  determined by the gas bubble pressure method for both cases. Similarly, Minghui *et al.* [25] had studied the preparation of supported zirconia ultrafiltration where asymmetric alumina support (Avg. pore diameter of 0.5  $\mu\text{m}$  and pure water flux of 5000  $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ ) had been used and homogeneous zirconia membrane thickness was 3-4  $\mu\text{m}$  and membrane permeability was 1000  $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ .

Here, the zirconia ultrafiltration membrane was first characterized by the clean water (18.2 M $\Omega$ ) permeability in cross flow filtration mode. It was observed that the clean water flux of the membrane and support tube were 38  $\text{Lm}^{-2}\text{h}^{-1}$  and 429  $\text{Lm}^{-2}\text{h}^{-1}$  respectively at 1 bar TMP. Experiments also showed that water flux through the prepared zirconia UF membrane increased linearly with increasing TMP. The membrane permeability of clean water was calculated from the slope of the linear fit of  $\text{Lm}^{-2}\text{h}^{-1}$  vs. TMP. It was 197  $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$  and 48  $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$  in the case of support tube and zirconia UF membrane, respectively (Figure 11). The permeability obtained is within the UF membrane range. Hence, from this macroscopic property, it may be said that the zirconia UF membrane was successfully prepared by the single step dip coating technique and slip casting method over novel clay-alumina ceramic support.

#### 3.5. Effluent treatment using membrane

The variation of the permeate flux of both the effluents as a function of time is shown in Figure 12. All experiments were carried out at 1 bar TMP using the zirconia membrane. The permeate flux of wastewaters is low in comparison to those obtained with clean water. The permeate flux of effluent-A and B obtained with zirconia membrane are 28  $\text{Lm}^{-2}\text{h}^{-1}$  and 23  $\text{Lm}^{-2}\text{h}^{-1}$ , respectively at 1 bar TMP. Lower flux data for effluent-B may be due to higher turbidity (108 NTU) compared to effluent-A (1.24 NTU). From Figure

12, it is evident that the duration for steady membrane flux takes approximately 30 min and 50 min, respectively. This may be due to the presence of high loading organic and inorganic contaminants present in wastewaters, whose presence changes the dynamic properties like the viscosity and turbidity of water. The presence of contaminant particles in wastewater causes partial blockage of membrane pores, thereby causing a flux decline. However, the blockage was temporary and reversible in nature and the membrane could be regenerated by backwashing with clean water only. A steady state flux was obtained after initial flux decline for both the effluents.

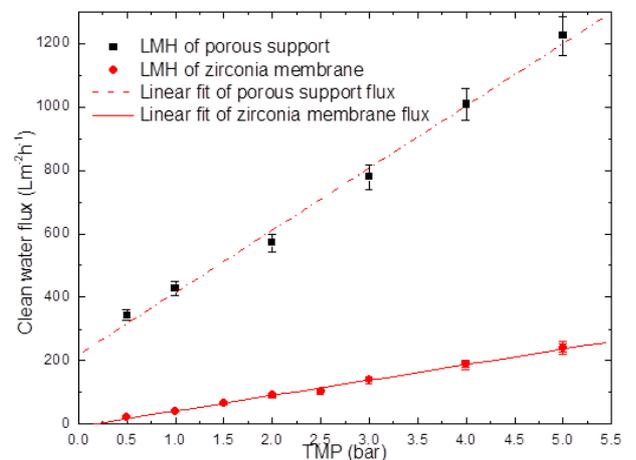


Fig. 11. Variation of clean water flux with transmembrane pressure for both support tubes and 19-channel zirconia UF membrane.

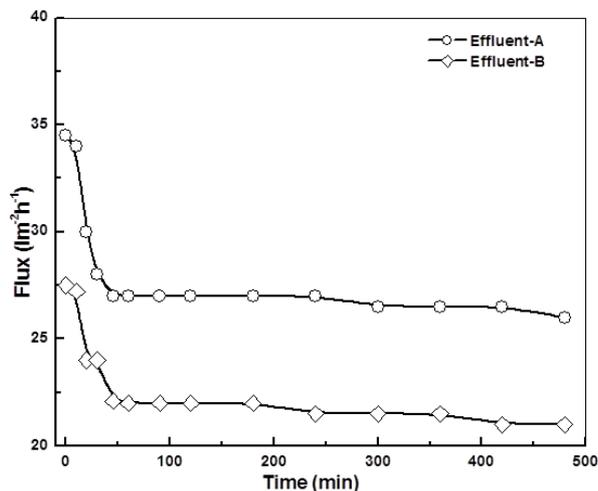


Fig. 12. Effect of time on permeate flux for different effluents using zirconia UF membrane.

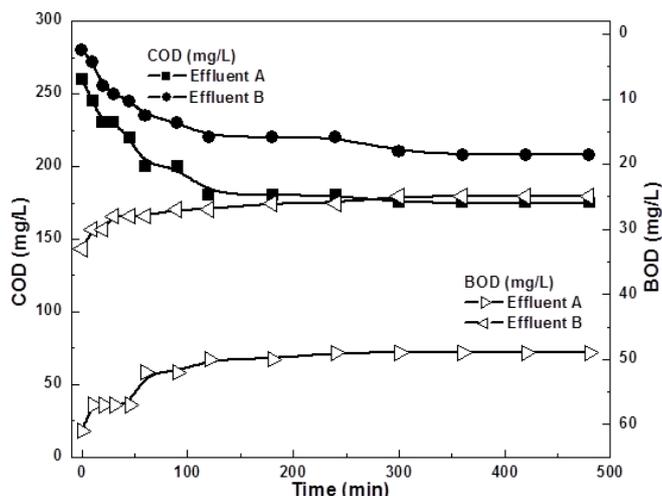


Fig. 13. Variation of COD and BOD in UF permeates with time for different effluents.

### 3.6. Characterization of effluents

The characteristics of Effluent-A and Effluent-B are shown in Table 1. It was observed that after UF study, turbidity was reduced below 1 NTU for both the effluents. COD reduction in case of Effluent -A was 82% whereas for Effluent -B it was 92% (Figure 13). Complete removal of pathogenic organisms for both the effluents was obtained as evident from MPN results, which were below detection limit.

## 4. Conclusions

Although zirconia membranes were widely used, the conventional sol-gel method involved multi step processes that were cumbersome and difficult to handle. The study depicts that single step coating using zirconia powder suspension by the slip casting method can be followed for preparation of the zirconia based UF membrane. The developed UF membrane had a pore diameter ranging from 30 nm to 40 nm with 2.8 $\mu$ m of average thickness. The crack free membrane was developed as evident from FESEM micrograph. The membrane was used for the treatment of two types of wastewater. Membrane filtrates from effluents provided an improved quality permeate with effective removal of turbidity (<1 NTU), considerable reduction of COD, BOD, oil and grease content and complete removal of TSS and MPN. The prepared UF membrane may be used for recycling and reuse of different effluents like tannery effluent and domestic wastewater for various purposes like irrigation in agricultural fields.

## Acknowledgements

The authors wish to express their thanks to CSIR for sponsoring MATES (CSC 0104) under 12<sup>th</sup> FYP network project.

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