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Clay Hybrid Membranes in Wastewater Treatment

Tanushree Choudhury

Abstract

Most of NF membranes which are developed recently are composite membranes, whose support layer is covered with an active layer. Among different ceramic support materials that are currently used as support layer, α -alumina supports are integral part of the membrane which is made of artificial materials like alumina and thus adds to the high price of the membrane. This draws our attention in making low cost support material of natural clay which aims to be an excellent membrane support as it possesses high mechanical strength, high permeability, narrow pore size distribution and low manufacturing cost. Titania as active layer for ceramic membrane is preferred over Al_2O_3 membranes. One of the problems encountered when photocatalysts are immobilized on support is the detachment of the micro particles from the support for high flow rates of liquid effluent. This can be overcome by using Montmorillonite clay as support material as it is a great binder.

Keywords: pillared clay, Titania, photocatalysis, dye removal, wastewater treatment, regeneration

1. Introduction

Wastewater encompasses potential contaminants from toxic wastes to natural organic matter and minerals that augurs for a definite treatment and reuse method so as to make water available for the ever increasing population. Some of the typical methods include adsorption, electrocoagulation, sedimentation, chemical oxidation and biological digestion. Each of these processes has its own advantages and disadvantages. Thus the search is on to find effective nanomaterials/technology for the remediation/purification of contaminated water [1–9]. Though titania is an important solid acid photocatalyst, the use of titania pillared clay membranes for wastewater treatment finds less mention in the literature. As a consequence, catalyst screening and design are imperative for efficient wastewater treatment [10]. The integration between catalysis and membrane is a very relevant area to mention for the development of a sustainable novel water treatment technology [11].

Titania as an active layer for ceramic membrane is preferred to Al_2O_3 membranes because of the following reasons such as (a) no neurological toxicity (b) high chemical stability in organic solvents and caustic soda (c) high material purity (d) small crystallite size (e) high surface area and porosity (f) narrow pore size distribution (g) low cost of crystalline anatase form and (h) extreme photostability and (i) extremely amphoteric character [12–14]. Moreover if the TiO_2 material (active layer) is immobilized onto porous support (clay), the photocatalytic membrane

reactor renders immense advantage due to the multiple functions ranging from decomposition of organic pollutants to self antibiofouling action [15].

2. National and international status of the work

Membrane separation processes have attracted the attention of researchers of late due to its manifold advantages such as cost effectiveness, ease in material recovery, and environmental impact reduction as compared to other separation techniques [16]. The performance of such a system can be further enhanced by the incorporation of nanomaterials and nanotechnology. Composite materials of polymers and ceramics can be used to synthesize membranes with increased permeability, selectivity, and resistance to fouling. Nanofiltration membranes are thus finding applications in wastewater treatment processes too.

Nanofiltration membranes are widely classified into i) organic polymeric membranes and ii) inorganic polymeric membranes. Polymers such as polysulfone, cellulose acetate, polyamide, etc. are commercially used to make polymeric nanofiltration membranes. Conventionally cellulose membranes are used in ultrafiltration and reverse osmosis membrane process. The performance of cellulose acetate membranes can be improved by blending it with appropriate polymers in view of the fact that polymers in view of the fact polymer blends have provided an efficient way to fulfill new requirements for material property. Cellulose acetate/sulfonated Polyethyl ether ketone blend ultrafiltration membranes have been used for separating Cr (III) ions [17].

Phenol is a potential human carcinogen and is of considerable health concern, even at low concentration. A. Bodalo et al. studied the behavior of different nanofiltration membranes of polyamide thin film composite membranes to remove phenol in wastewater in different operating conditions [18]. It has been observed that the concentration of As in drinking water can be considerably reduced by nanofiltration and reverse osmosis techniques. Literature finds mention of these methods in abundance, but they are not cost effective.

Membrane based separation techniques have been widely employed in different countries for treating a wide variety of industrial effluents. The effectiveness of nanofiltration membrane processes in water and wastewater treatment has now become one of the most reliable standard techniques to obtain good drinking water. Harisha et al. investigated the feasibility of arsenic removal from simulated arsenic contaminated water by an indigenously built nanofiltration plant with commercial thin film composite membrane of polyamide [19]. The potential use of nano filtration polyamide membrane for removing Co and Pb ions from wastewater was investigated by Saliha et al. [20]. Polyaniline because of its high degree of solvent resistance is employed to be used as an ultrafiltration membrane by Jinwen Wang et al. [21].

Cr, a typical example of class of pollutant, is generated in aircraft maintenance, electroplating, dye, textile and leather industries. Cr is highly toxic and traditional techniques for Cr removal include adsorption, precipitation, and extraction using aliquat 336 solvents. The membranes used for Cr separation are mostly organic polymer (for example cellulose acetate, polyaniline, etc). The major drawback is that the chemical stability of conventional polymeric membranes is limited with respect to corrosive media like strong acids and organic solvents. Therefore research focuses on ceramic nanofiltration membranes, though only few studies exist on use of ceramic membranes for Cr removal. A novel separation scheme for the removal of As and Cr from water based on adsorption and ultrafiltration processes using porous ceramic membranes has been proposed by A. E. Pagana et al. [22]. In recent years, great advances were made regarding the development of non-silicate ceramic

membranes as these membranes have a high selectivity against small macro molecules, drugs, hormones and antibodies. $\text{ZrO}_2/\text{TiO}_2$ microporous ceramic membranes were developed by U. Aust et al. for gas separation applications [23].

Ceramic nanofiltration membranes can be used to separate solvents from multivalent ions and small organic molecules. Promising membrane materials for separation of highly charged molecules are Nafion, Nafion/silica hybrid membranes, supported γ -alumina membranes and mesostructured silica layers supported on porous α -alumina. Sandwich type ceramic composite membranes with NF characteristics became available having pore size in the range 0.5–2 nm which can be used efficiently for large ion recovery. Chowdhury. S et al. studied the transport and retention properties of potentially suitable membranes for recovery of highly charged large polyoxomethylate (POM) catalyst molecules from aqueous solution [24].

Wastewater in petrochemical industry is currently treated by activated sludge process with pretreatment of oil/water separation. Tightening efficient regulation and increasing need for reuse of treated water have generated interest in the treatment of petrochemical wastewater by membrane bio-reactor process [25]. Ceramic membranes under micro, ultra and nanofiltration conditions have proven to be economically attractive for the removal of oil from oil produced water [26]. Of all ceramic NF membranes in literature, sol-gel derived $\gamma\text{-Al}_2\text{O}_3$ membranes have emerged as perhaps the most intensively studied inorganic membrane system, because of their unique surface charge characteristics. $\gamma\text{-Al}_2\text{O}_3$ membranes may acquire either a positive or negative charge due to their amphoteric behavior of their surface sites ($-\text{OH}$ groups). This allows controlling the sign and charge of the membrane through pH of the solution [27]. Majority of the reported $\gamma\text{-Al}_2\text{O}_3$ membranes were derived from the expensive Al alkoxides that makes them very costly. Hence, research should be focused on the development of an alternative cost effective membrane material.

Clay minerals find potential application as a choice for membrane support material due to its low cost, environmentally benign, good rheological, barrier, adsorption, and binding properties. Though not much work has been done in this regard, development of clay based membrane material would usher in a new technological advancement in the field of Clay Science.

Utilization of clay minerals is now of growing interest. Unmodified and modified UF zeolite clay composite membranes (pore size of the order 10–30 nm) have been used for the separation of Cr by A. Shukla and A. Kumar [28]. Low cost $\gamma\text{-Al}_2\text{O}_3$ composite membrane on clay support has been prepared by Abhijit et.al for the separation of electrolytes from its aqueous solutions [29]. Removal of phenol and o-cresol from water by a combined process of clay adsorption and ultrafiltration was investigated by Liu. S. Hsia et al. [30]. Low cost $\gamma\text{-Al}_2\text{O}_3$ clay composite membrane on a clay support has been prepared using local available cheap clays by Abhijit et al. for the separation of Bovine Serum albumin [31].

However, membrane fouling is still a critical problem of NF plants, which results in flux decline with operating time. TiO_2 has received much attention because of its important role in various applications such as photocatalysts, oxygen sensors, antimicrobial coatings, pigments etc. Among them, the photocatalytic properties to decompose organic compounds can be used in filtration membranes which possibly overcome fouling phenomenon [32]. Zhang. H et al. prepared $\text{TiO}_2/\text{Al}_2\text{O}_3$ composite membranes with photocatalytic ability by sol-gel technique which has the multi-function of separation and photocatalysis simultaneously [33].

Going by the literature, there are many reports about the preparation of TiO_2 composite membranes, especially using Al_2O_3 as support, but work needs to be done using clay as support material. Development of such low cost membranes shall offer to remove heavy metal ions from industrial wastewater and thus provide a sustainable solution.

2.1 Methods of preparation

2.1.1 Preparation of titania pillared clay membranes

Scientific description of the process **Figure 1:**

Preparation of asymmetric membranes: The development of such a configuration includes shaping of an appropriate support material and formation of mesoporous interlayers with a cut off value less than 1000 Da.

Preparation of flat disk support: Montmorillonite (Mt) was fabricated into flat disks of 25 mm diameter and 2 mm thickness, and was sintered at 600°C in a temperature controlled muffle furnace with a heating and cooling rate of 2°C/min with a hold time of 30 minutes. Mechanical hardness of such membranes was analyzed using Micro vickor, Shimadzu, Model No HMVG20S (load range of 10 g to 2 kg) in Mechanical Workshop in VIT Chennai. It was found to be 26.4 Hv.

Preparation of interlayer Titania sol by colloidal sol–gel process: The precursor for the colloidal sol–gel process was Ti (IV) isopropoxide, common titanium based organometallic compound, purchased from Avra chemicals, India, and was

Figure 1. The flat disk TiPILC membranes prepared at pH 2 and pH 3.5 and sintered at 300°C can be used for filtration of organic contaminants, over a wide range of pH (1–11), with a MW less than 1000 Da. The direct beneficiaries include textile industries (to remove coloring agents), food and pharmaceutical industries (small organic molecules), and wastewater recycling.

hydrolysed by adding excess water. The sol was then stirred at room temperature for 3 hrs after which it was peptized by the addition of glacial acetic acid (99%, Sigma Aldrich, USA) to attain pH 2 and pH 3.5 respectively.

Preparation of interlayer binary (Titania and clay) sol: 0.1 g of Mt. (Montmorillonite K10 with CEC of 80–100 meq/g, Himedia) was dispersed in 10 mL deionized water and was kept for stirring for 3 hrs. 0.1 wt% of cetyl trimethyl ammonium bromide (CTAB, Himedia) solution was added to the clay sol as an organic modifier. The resulting clay sol was then added dropwise to titania sol prepared at pH 2 and pH 3.5 respectively and was stirred overnight for complete intercalation of Ti^{4+} ions into the interlayer spaces of Mt. [34].

Preparation of TiPILC membranes: The interlayer sols thus prepared were immobilized on the flat disk supports by a dip coater with a withdrawal rate of 25 mm/sec. 5 wt% of binder carboxymethyl cellulose (CMC, Avra chemicals, India) was added to the sol as pore directing agent. After uniform coating, the membranes were dried at room temperature and then in air oven at 40°C for few hours. They were then sintered in programmable temperature controlled muffle furnace at 300°C, 500°C, 600°C, which was ramped at a heating/cooling rate of 2°C/min and was kept for hold time of 1 hour. The excess drained from supports were poured onto petri dishes, dried in oven and sintered at same temperatures as above for characterization by Fourier Transform-Infra Red Spectroscopy (FT-IR), X-Ray Diffraction (XRD), Brunnauer Emmett Teller specific surface area (BET), Zeta Potential analysis and Scanning Electron Microscope (SEM).

Number of samples prepared: 24 (12 supported membranes and 12 unsupported ones).

Nomenclature (Supported Membranes).

S1, S6, S10 - Membranes with TiO_2 interlayer at pH 2 sintered at 300°C, 500°C, and 600°C.

S2, S5, S11 - Membranes with binary interlayer of TiO_2 and clay at pH 2 sintered at 300°C, 500°C, and 600°C respectively.

S3, S4, S12 - Membranes with TiO_2 interlayer at pH 3.5 sintered at 300°C, 500°C, and 600°C respectively.

S8, S9, S13 - Membranes with binary interlayer of TiO_2 and clay at pH 3.5 sintered at 300°C, 500°C, and 600°C respectively.

Unsupported Membranes.

PS1, PS6, PS10 - Powder membrane materials with TiO_2 interlayer at pH 2 sintered at 300°C, 500°C, and 600°C respectively.

PS2, PS5, PS11 - Powder membrane materials with TiO_2 and clay binary interlayer at pH 2 sintered at 300°C, 500°C, and 600°C respectively.

PS3, PS4, PS12 - Powder membrane materials with TiO_2 interlayer at pH 3.5 sintered at 300°C, 500°C, and 600°C respectively.

PS8, PS9, PS13 - Powder membrane materials with binary interlayer of TiO_2 and clay at pH 3.5 sintered at 300°C, 500°C, and 600°C respectively.

2.1.2 Instrumentation

XRD was done using Bruker AXS D8 advance powder diffractometer equipped with Cu-K α generator ($\lambda = 1.5405600 \text{ \AA}$). The generator tension was 35 kV. IR was done on Thermo Nicolet Avatar 370 in the spectral range of 4000–400 cm^{-1} . Zeta potential was measured using Horiba Scientific Nano Partica Nano Particle Analyzer SZ-100. SEM of cross section of membranes was taken using High Resolution Hitachi S-4800 Scanning Electron Microscope. BET surface area of samples was characterized by Nova 1000 Quantachrome Instrument by N_2 sorption at 77.35 K. The concentration of the permeate samples from filtration experiment

was measured using Thermoscientific UV-Vis Spectrophotometer in the visible range of 200–800 nm. The membrane filtration unit consisted of a cylindrical chamber with a membrane adapter connected to a pressure gauge of 2 Pa and a peristaltic pump Model No RH-P120 VS [34].

Figure 2.
(a) And (b) FT-IR spectra of unsupported membrane materials at pH 2 and pH 3.5 respectively.

Figure 3.
(a) And (b) XRD diffractograms of unsupported membrane materials at pH 2 and pH 3.5 respectively.

Figure 4.
(a) And (b) zeta potential values of unsupported membrane materials prepared at a) pH 2 and b) pH 3.5 respectively.

2.1.3 Characterization

FT-IR (Figure 2)
XRD (Figure 3)
Zeta potential analysis (Figure 4)
Pore size distribution (Figure 5)
SEM (Figures 6 and 7)
Figures 2–7

Figure 5.
(a) And (b) pore size distribution curves of TiO₂ interlayer and binary interlayer of TiO₂ and clay respectively.

Figure 6.
(a) To (d) SEM of membranes S1, S2, S3, and S8 sintered at 300°C respectively. (e) To (h) SEM of membranes S6, S5, S4, and S9 sintered at 500°C respectively. (i) To (l) SEM of membranes S10, S11, S12, and S13 sintered at 600°C respectively.

Figure 7.
SEM of asymmetric membrane showing the interlayer of thickness 5.2 μm on the support.

3. Result and discussion

Temperature affects the pore size distribution pattern as can be clearly seen from **Figure 5(a)** and **(b)**. It can be clearly observed that a narrow pore size distribution is observed at a sintering temperature 300°C for membrane materials with interlayer of TiO_2 and binary interlayer of TiO_2 and clay. Addition of clay to TiO_2 alters its pore size distribution facilitating removal of organic dye molecules. XRD diffractograms show the presence of single phase of anatase TiO_2 at temperature 300°C. As the temperature increases to 500°C and 600°C, the anatase phase is the major crystal type which is very efficient for photocatalytic degradation of organic pollutants. FT-IR spectra show the presence of strong bands at 3399.03 cm^{-1} and 1621.55 cm^{-1} due to bonded $-\text{OH}$ stretching and bending vibrations of water, thus indicating the formation of anatase phase. Characteristic bands at 1049.31 cm^{-1} and 523.68 cm^{-1} which correspond to Si-O-Si stretch and Si-O stretch respectively are lost completely, indicating complete intercalation of Ti^{4+} ions into the interlayer space resulting in formation of a delaminated and homogeneous TiPILC material [34]. **Figure 4** shows the results for the zeta potential of powder suspensions of membrane materials and model TiO_2 obtained from measurements of the electrophoretic mobility in an aqueous medium. Zeta potential values obtained for membrane materials at pH 2 and sintered at a lower temperature show more negative value as the number of hydroxyl groups in the anatase phase is higher than that of rutile obtained at higher sintering temperature.

3.1 Determination of membrane cut off through filtration with methylene blue (MB) dye

30 ppm of 30 mL MB (Sigma Aldrich, USA) dye solution was prepared. Filtration test was carried by using a peristaltic pump and a cylindrical membrane adapter fitted with a pressure gauge. An average flux rate of 70–110 $\text{L}/\text{m}^2/\text{h}$ was obtained at a constant pressure of 1.2–1.7 Pa. Permeates from the separation experiments were collected and their concentrations were measured by Uv-vis spectrophotometer using the equation:

$$\% \text{ Removal} = (C_0 - C_r / C_0) \times 100 \quad (1)$$

As can be seen from **Figures 8–10** which correspond to percentage removal of MB dyes by membranes sintered at 300°C, 500°C, and 600°C respectively in 3 cycles of filtration, around ~100% removal is achieved. This retention can be explained by high polarity of compounds which causes interactions with the charged membrane.

Figure 8.
% removal of MB dye by membranes sintered at 300°C.

Figure 9.
% removal of MB dye by membranes sintered at 500°C.

Figure 10.
% removal of MB dye by membranes sintered at 600°C.

Thus the feed solution pH can be considered one of the most important parameters influencing hydrophobicity, the adsorption, and the chemical separation of dissociable organic compounds as well as the membrane surface charge during the experiment.

3.2 Static corrosion test

The corrosion test was performed by dipping the membranes in 50 mL of four different pH solutions i. e pH 1, pH 3, pH 11, and pH 13 for 24 hours followed by drying in oven at 100°C for 4 hours. These membranes were then studied for MB dye rejection test. Corrosion measurements as that of **Figures 11** and **12** indicate that membranes prepared at pH 2 are most stable in mild aqueous media (pH 3–11) as compared to those prepared at pH 3.5.

Thus in aqueous media with a lower/higher pH, the membrane configuration composed of anatase at pH 2 with a MW cut off <1000 Da on Mt. support is preferred.

Figure 11.
% removal of MB dye by membranes prepared at pH 2 after corrosion.

Figure 12.
% removal of MB dye by membranes prepared at pH 3.5 after corrosion.

4. Conclusion and outlook

Titania pillared clay membranes are amphoteric membranes, whose surface charge depends on the pH of the solution. It is a hybrid membrane reactor which integrates the functions of both separations with photocatalysis. These hybrid membranes are characterized by their asymmetric configuration, i. e a top layer of titania in nanometer range immobilized on a porous ceramic support. The separation depends on the thickness of the top layer deposited on the base membrane. The pore size, and the microstructure of the membranes can be governed by choosing the right solvent, suitable pH, temperature of the reaction and peptization during the sol-gel process that governs the key to fine separation. Sintering temperature is a function of the porosity developed in the membranes. TiPILC membranes sintered at 300°C yielded only anatase phase with a narrow pore size distribution for effective separation of organic contaminants. It has been observed during the treatment of such membranes with synthetic dyes such as Methylene Blue (MB), a thin cake is adsorbed on the surface which decreases the flux rate with time thus resulting in the loss of efficiency of the membrane. Titania immobilized on clay support not only increases the hydrophilicity and the flux rate, but also helps in self-cleaning mechanism of the membrane for prolonged use.

Development of field membrane out of that developed in the laboratory is desired for complete utilization. The developed membranes can also be used for removal of heavy metal ions from wastewater followed by their recovery from the membranes would yield the maximum benefit. The product developed can best treat textile effluent from dye industry with concentration in the range of 50 ppm.

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