Fabrication of zirconia composite membrane by in-situ hydrothermal technique and its application in separation of methyl orange

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A B S T R A C T

The main objective of the work was preparation of zirconia membrane on a low cost ceramic support through an in-situ hydrothermal crystallization technique for the separation of methyl orange dye. To formulate the zirconia film on the ceramic support, hydrothermal reaction mixture was prepared using zirconium oxychloride as a zirconia source and ammonia as a precursor. The synthesized zirconia powder was characterized by X-ray diffractometer (XRD), N_2 adsorption/desorption isotherms, Thermogravimetric analysis (TGA), Fourier transform infrared analysis (FTIR), Energy-dispersive X-ray (EDX) analysis and particle size distribution (PSD) to identify the phases and crystallinity, specific surface area, pore volume and pore size distribution, thermal behavior, chemical composition and size of the particles. The porosity, morphological structure and pure water permeability of the prepared zirconia membrane, as well as ceramic support were investigated using the Archimedes' method, Field emission scanning electron microscopy (FESEM) and permeability. The specific surface area, pore volume, pore size distribution of the zirconia powder was found to be 126.58 m^2/g, 3.54 nm and 0.3–10 μm, respectively. The porosity, average pore size and pure water permeability of the zirconia membrane was estimated to be 42%, 0.66 μm and 1.44×10^{-6} m^3/m^2 s kPa, respectively. Lastly, the potential of the membrane was investigated with separation of methyl orange by means of flux and rejection as a function of operating pressure and feed concentration. The rejection was found to decrease with increasing the operating pressure and increases with increasing feed concentrations. Moreover, it showed a high ability to reject methyl orange from aqueous solution with a rejection of 61% and a high permeation flux of 2.28×10^{-5} m^3/m^2 s at operating pressure of 68 kPa.

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1. Introduction

The annual global productions of dyes are calculated to be more than ten thousand tons. In that, around 15% quantity is lost during the industrial processes, such as dyeing, textiles printing and dye manufacturing (Forgacs et al., 2004). These industrial processes utilize several synthetic chemical dyes for a variety of purposes. Textile dyeing is among the most environmentally unfriendly industrial processes owing to the large quantities of water demanded and the strongly colored wastewater produced, polluted with dyes and other chemical auxiliaries. The highly colored effluents dye streams could pose serious detrimental effects to the environment and thus to human health (Zaghbani et al., 2007; Jana et al., 2010). Specifically, Azo dyes can be toxic upon degradation and this class of dye is widely used in many industries by virtue of present unique properties and technical

characteristics. Among several varieties of dyes, methyl orange (MO) is considered as a model compound for ordinary water soluble azo dyes, which is extensively utilized in chemical, textile and paper industries. Furthermore it is dangerous to the environment (Shiue et al., 2012). The majority of the azo dyes and their breakdown products are toxic and carcinogenic to animals and humans (Weisburger, 2002). Hence, this effluent is necessary to be treated before discharging from the industries. The conventional methods employed for separation of dyes from colored wastewater are flocculation/coagulation (Zahrim and Hilal, 2013), adsorption (Qiao et al., 2009), chemical oxidation (Turgay et al., 2011) and photocatalytic processes (Velusamy et al., 2014), reaction with ozone (Sharma et al., 2013) and biological treatment (Nilesh and Chaudhari, 2006). In flocculation, coagulation and adsorption treatment methods, effluents are converted from the liquid state to a solid state and this way creates secondary

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pollution. Chemical techniques such as photocatalytic and reaction with ozone method need bulk quantity of costly chemicals as well as generating huge amount of waste slurry. The by-products from chemical degradation are also colored and even toxic. Furthermore, biological degradation is inexpensive technique, harmless to the environment and also not generates massive quantities of sludge; however it is selective and time taking. Hence it is unsuitable for many dyes (Tan et al., 2006).

Membrane separation process could be ecofriendly and an auspicious alternative for the separation of dyes. The pressure-driven membrane processes, especially reverse osmosis, nanofiltration, ultrafiltration and microfiltration are being increasingly utilized in the removal of dyes (Al-Bastaki, 2004; Kim et al., 2005; Al-Aseeri et al., 2007; Mo et al., 2008). Within these techniques, ceramic membranes are better than polymeric membranes due to excellent thermal, chemical and mechanical properties (Jedidi et al., 2009). However, nanofiltration and reverse osmosis techniques are described by higher energy utilization. Therefore lower pressure membrane techniques such as microfiltration and ultrafiltration could be inexpensively more favorable for dye separation. Besides, ceramic membranes are made up of a composite formation with an active top layer, which typically decide its separation characteristics. Mostly the active top layers are made by inorganic oxides fabricated via the sol–gel method, dip-coating, hydrothermal crystallization with a controlled particle size. Initially, the research on inorganic membranes was focused to the fabrication of alumina membranes, which is of higher cost and used most widely (Yang et al., 1998). Nevertheless, in recent times, various other porous membrane materials, such as zirconia, titania and silica were used. Amongst these, zirconia is especially attractive material for making the ceramic membranes. The excellent characteristics of zirconia membrane are elevated chemical stability and cleaning actions can be done in the range of 0–14 pH, superior permeability and higher flux in separation owing to its specific surface characteristics, and excellent thermal resistance (Bhave, 1991).

In order to improve the flux of the membrane, the hydrophilic adaptation in microfiltration is an excellent choice, which provides an enhanced hydrophilic character to the membrane surface (Kocherginsky et al., 2003). Nano-scale ZrO_2, TiO_2/Al_2O_3, Al_2O_3 and SiO_2 have been used to enhance the hydrophilic character and it creates the charge on the surface of the membrane (Chang et al., 2014). Several investigations on zirconia membrane have indicated its superior performance in the separation due to its special surface character (Zhou et al., 2010). These hydrophilic and charged membranes facilitate to attain a higher flux with good separation efficiency even though utilizing a realistically larger range of pore size membranes. However, the difficulty of modification of ceramic membranes leads in the way of adding nano-particles uniformly into the porous ceramic membrane without blocking the membrane pores. Several preparation methods have been developed, such as in situ hydrothermal synthesis, vapor phase transport method, secondary growth method for the deposition of nanomaterials on the ceramic matrix (Xu et al., 2004). Amongst these, hydrothermal technique has become basic route for the modification of membrane surface by the deposition of nanomaterial (Kalantari et al., 2015).

In this present study, an inexpensive zirconia composite membrane on a porous ceramic support has been synthesized. The top layer of zirconia is prepared through in-situ hydrothermal crystallization technique by controlling growth of zirconia particle on the porous ceramic support. The separation potential of the membrane is investigated with separation of methyl orange various operating pressure and feed concentration.

2. Materials and methods

2.1. Chemicals

Clays (ball clay, feldspar, kaolin, pyrophyllite and quartz) used for synthesis of ceramic support were of mineral grade and obtained in the vicinity (Kanpur, India). Zirconium Oxychloride ($ZrOCl_2 \cdot H_2O$), Calcium Carbonate and Polyvinyl Alcohol (PVA) were supplied by Loba Chemie (Mumbai). Ammonium hydroxide solution (NH_4OH, 25 wt%) and methyl orange ($C_{14}H_{14}N_3NaO_3S$) were procured form from Merck (I) Ltd. (Mumbai).

2.2. Preparation of zirconia–ceramic composite membrane

The procedure followed for the preparation of ceramic support and its composition were explained in our earlier publication (Monash and Pugazhenthi, 2011a). The zirconia–ceramic composite membrane was prepared through in-situ hydrothermal synthesis by controlling growth of zirconia particle on the porous ceramic support. The reaction mixture for hydrothermal reaction was prepared by dissolving 5 g of zirconium oxychloride in 100 mL of water. Then the pH was adjusted to 10.0 with addition of aqueous ammonia (25%) under stirring condition at room temperature. After that the reaction mixture was stirred vigorously for 5 min, and then transferred to Teflon coated stainless steel autoclave reactor (capacity 200 mL) for in-situ hydrothermal crystallization and a prepared porous ceramic support having 43 mm diameter and 4.5 mm thickness was placed inside the reactor. The reaction mixture was subjected to hydrothermal crystallization at 90 °C for 60 h. After that, the membrane was recovered and washed several times with Millipore water and dried at 90 °C for 24 h followed by calcined at 400 °C for 6 h in air atmosphere.

2.3. Methods for characterization

2.3.1. Characterization of zirconia powder

As-synthesized zirconia powder was collected from the bottom of the autoclave reactor. Then, the zirconia powder was washed, dried and calcined at the same condition adopted for the composite membrane. Precise powder diffraction data of zirconia was measured on a machine (Bruker AXS D8 advanced) with Cu Kα ($\lambda = 1.5406$ Å) radiation. The patterns were obtained in the 2θ range of 5–75° with a scan speed of 0.05° s^{-1}. N_2 adsorption/desorption isotherm was computed at -196 °C in a surface area analyzer (make: Beckman-Coulter; model: SA™ 3100). Thermogravimetric (TGA) analysis of the zirconia powder (before calcination) was carried out in a instrument of Mettler Toledo with model No.TGA/SDTA 851$^®$ in flowing nitrogen atmosphere at a heating rate of 10 °C min^{-1} from 25 to 900 °C. FTIR spectra were recorded using a Shimadzu IRAffinity-1 model Spectrometer in the wavenumber range of 4000–500 cm^{-1}. The particle size distribution (PSD) of the zirconia powder was measured using a machine Malvern Mastersizer 2000 (APA 5005$^®$ model, hydro MU) in wet dispersion mode.

2.3.2. Characterization of zirconia ceramic composite membrane

The morphology of the prepared ceramic support and zirconia composite membrane was investigated with an instrument FESEM (JEOL JSM-5600LV). Energy-dispersive X-ray (EDX) was carried out using SEM (LEO 1430 VP$^®$ Oberkochen, Germany). In order to determine the porosity, the membrane was dried at 120 °C for 3 h and measured the dry weight of the membrane (M_D). Then the membrane was placed in Millipore water for 24 h. After which, the wet weight (M_W) of the membrane was determined after removing all visible water from the surface of the membrane with tissue paper. Then the membrane was immersed in water, the pore filled