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Research paper

Optimal fabrication of carbonate free kaolin based low cost ceramic membranes using mixture model response surface methodology

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ABSTRACT

This article aims to address the relevance of D-optimal mixture model based RSM design methodology for the optimal fabrication of carbonate free low cost ceramic membranes. The RSM design methodology was validated by targeting alterations in the composition of kaolin, feldspar and saw dust precursors during low cost ceramic membrane fabrication. Experimental findings of key dependent membrane product variables namely average pore size and porosity were regarded as biases to identify optimal kaolin, feldspar and saw dust precursor compositions. Further, a comparative study was conducted to evaluate upon the sensitivity of optimal compositions while considering flexural strength as an additional response variable. The optimal precursor compositions were 48.19 mass % kaolin, 28.62 mass % feldspar and 8.19 mass % saw dust for which optimal responses of average pore size and porosity were 1.00 ± 0.05 μm and 28.47 ± 0.29%. However, while considering flexural strength as additional response variable, the optimal compositions varied marginally (48 mass % kaolin, 27.81 mass % feldspar and 8.26 mass % saw dust) for which the optimal responses of pore size, porosity and flexural strength were evaluated as 0.93 ± 0.02 μm, 29.98 ± 1.10% and 8.75 ± 0.57 MPa. Hence, the most relevant RSM model refers to the model designed without considering flexural strength as an additional variable and with reduced model complexity.

1. Introduction

Recent and ongoing advances in ceramic membrane technology have widened the economic competitiveness of ceramic membranes in comparison to the conventional and widely deployed polymeric membranes. Ceramic membranes possess superior characteristics such as mechanical strength, high chemical and thermal stability, high flux and better shelf life (Cheryan, 1998; Mulder, 2012). Alterations to the precursor formulation during ceramic membrane fabrication is a very important approach to facilitate cost reduction of ceramic membranes which are otherwise fabricated with expensive precursors such as α-alumina (Hristov et al., 2012), γ-alumina (Anderson et al., 1988), silica (Xomeritakis et al., 2009), zirconia (Hristov et al., 2012) and titania (Anderson et al., 1988; Hristov et al., 2012). Among various alternate choices of low cost inorganic membrane precursors, kaolin or clay (Nandi et al., 2008, 2009, 2010; Vasanth et al., 2011; Ali et al., 2017), fly-ash (Fang et al., 2011; Wei et al., 2016), starch (Lorente-Ayza et al., 2015) are familiar as base materials and calcium carbonate, sodium carbonate (Nandi et al., 2008, 2009, 2010; Vasanth et al., 2011; Emani et al., 2014) or saw dust (Bose and Das, 2013, 2014) are familiar as pore forming agents. Till date, numerous investigations carried out with kaolin based low cost membranes indicated promising applications for oily-water emulsion treatment (Vasanth et al., 2011; Emani et al., 2014), water purification (Vasanth et al., 2011; Kaniganti et al., 2015) and mosambi/orange juice microfiltration (Nandi et al., 2009, 2012).

The conventional approach for low cost ceramic membrane fabrication is based on trial and error approach to identify the optimal precursor formulations. Kaolin, quartz, feldspar, calcium carbonate, sodium carbonate, sodium metasilicate and boric acid are the most commonly used membrane fabrication materials and optimum formulation of these constituents were generally identified using conventional trial and error method by carrying out minimal variation in the mixture composition. (Nandi et al., 2008, 2009, 2010; Vasanth et al., 2011). PVA (polyvinyl alcohol) and fly ash also were considered as additional constituents in few studies along with the above mentioned components (Emani et al., 2013; Kaniganti et al., 2015; Wei et al., 2016). In most cases, due to easy availability and efficient pore formation, calcium carbonate was used as the pore forming agent. However, these membranes had an inherent disadvantage in terms of carbonate leaching during microfiltration test runs which resulted in undesirable pH rise in the permeate sample. To circumvent this problem, saw dust could be effectively used as a pore former instead of

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Table 1
XRF data (mass %) of Kaolin and Feldspar samples.

Material	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5
Kaolin	48.81	32.85	0.81	0.00	0.19	0.25	0.14	1.36	0.43	0.06
Feldspar	59.72	18.08	0.00	0.02	0.03	10.44	2.27	9.50	0.01	0.00

calcium/sodium carbonates (Bose and Das, 2013). The saw dust based membranes exhibited promising characteristics of mechanical strength, pore size and porosity.

Response Surface Methodology (RSM) is a viable optimization tool to facilitate integrated simulation and experimental investigations for the optimization of a process involving parametric as well as compositional optimization. Till date, very few research groups have integrated RSM design methodology and membrane fabrication. Historical data design (HDD) and central composite design (CCD) based RSM was employed for the optimization of process and fabrication parameters and optimization of some of the precursor components (Arzani et al., 2016; Hubadillah et al., 2016; Suresh et al., 2016). A detailed investigation with respect to optimization of binder (boric acid and sodium metasilicate) composition and fabrication pressure was conducted by Bose and Das (2014), for the fabrication of ceramic membranes using kaolin, feldspar and sawdust.

A careful insight into CCD indicates its inability in circumstances that require optimization of all components in a mixture. For such cases, mixture models are used. The most common area for mixture model RSM methodology deployment (d-optimal mixture model being the most common), is the medicinal sector in which the optimization of each component of a drug formulation is desired. (Mura et al., 2005; El-Malah et al., 2006; Furlanetto et al., 2011). However, use of mixture design in membrane science for optimizing the overall membrane precursor composition is yet to be explored.

In summary, in the chosen field of RSM design methodology based optimal fabrication of low cost ceramic membranes, only few research groups contributed towards design based optimization (Bose and Das, 2014; Arzani et al., 2016; Hubadillah et al., 2016). While these design methodologies are effective to identify optimal parameters in relevant case studies, they do have limitations in comparison with the mixture model design (MMD) methodology such as manual setting of design runs and data sets in HDD and lack of flexibility to vary compositions within a maximum total precursor composition in CCD. In other words, MMD offers greater flexibility to systematically identify optimal precursor formulations in comparison with CCD.

The limitations of CCD in comparison with MMD are evident in the work conducted by Bose and Das (2014) which referred to the optimization of binder composition only (sodium metasilicate and boric acid) for fixed composition choices of pore former (saw dust) and other inorganic precursors (kaolin and feldspar). However, pore former composition is very important to optimize since it strongly affects membrane porosity, pore size distribution and average pore size. The binder composition optimization primarily affects mechanical strength of the membrane which is a secondary issue in the context of pore size and porosity, as these are regarded to be primary factors of interest in ceramic membrane technology research. Thus, there is a need to improve and develop mature RSM based methodology for the optimization of all membrane properties namely pore size, porosity and mechanical strength by targeting optimization of pore former and inorganic precursor compositions. For such combinatorial optimization problems, mixture design approach is to be adopted which is superior and relevant in comparison with the conventionally adopted CCD design approach.

This work demonstrates upon the efficacy of MMD based RSM design methodology for low cost ceramic membrane fabrication. Since targeting MMD for large precursor size is tedious and time consuming, the article targeted utilization of data available in the literature and emphasizing upon refinement in the precursor formulation. To do so, the binder composition (metasilicate and boric acid) of Bose and Das (2014) was chosen to be relevant and optimization of all other inorganic precursors (kaolin, feldspar and saw dust) was targeted using D-optimal mixture model. RSM design methodology targeted upon the optimality of said precursor interactions on three response variables namely average pore size, average porosity and flexural strength. Further, the sensitivity of optimal precursor formulations with either pore size and porosity bias or bias involving a combination of all three response variables (including flexural strength) was also considered.

2. Material and methods

2.1. Raw materials

Kaolin powder (pure) and sodium metasilicate nanohydrate (95% pure (min)) procured from Central Drug House (P) Ltd., New Delhi; feldspar obtained from National Chemicals, Gujarat; boric acid (99.5% pure) purchased from Merck India and saw dust prepared from wood flakes obtained from local furniture shops were used as inorganic precursors for low cost ceramic membrane fabrication. The quantitative analysis of both kaolin and feldspar was carried out with X-ray Fluoroscence (XRF) analysis (Table 1). Along with trace quantities of other metal oxides, kaolin composition was found to be 48.81 mass % SiO_2 and 32.85 mass % Al_2O_3, which is similar to that reported with X-ray Diffraction (XRD) by Nandi et al. (2008) (46.5 mass % SiO_2, 39.5 mass % Al_2O_3 and 14 mass % H_2O). The kaolin composition indicates ideal kaolinite in the chosen raw material. The XRF analysis of feldspar conveys it to be a mixture of K-Feldspar (microcline and orthoclase) and Ca-Feldspar (plagioclase). Among these precursor materials, kaolin affirms high refractory properties to the membrane and reduces its plasticity. Under room temperature conditions, despite inducing plasticity, kaolin loses such plasticity characteristics at higher sintering temperature. In these conditions, kaolinite in kaolin undergoes transformation to metakaolinite, which reduces plasticity of the material and enhances refractory properties of the membrane (Chena et al., 2006). By forming a glassy matrix in the membrane matrix, feldspar enhances bonding between raw materials and contributes to membrane strength, toughness and durability. Saw dust acts as a pore former and facilitates porous structure formation during high temperature sintering process. Sodium metasilicate and boric acid act as binders to improve mechanical strength and dispersion properties of the precursors.

2.2. Membrane fabrication process

Wood flakes were collected from local wood shops. The flakes were grinded in a mixer grinder and were sieved through 44 B.S·S (British Standard Specification based sieve number, equivalent to 355 μm) mesh sieves. The obtained saw dust was then mixed with adequate quantities of kaolin, feldspar, boric acid and sodium metasilicate using ball mill equipped with 19 mm diameter steel balls. The ball mill was operated at 40 rpm speed for 1 h. The mixture was then taken out from the ball mill and was pressed using hydraulic press onto the membrane mould, at 100 kgf/cm^2 pressure for 2 mins. The green membrane thus obtained was disk shaped material that was subjected to drying at room temperature at 24 h followed with drying at 100 °C for 12 h and 250 °C for 24 h. The sample was then finally sintered at 850 °C for 6 h (Bose and Das, 2013). The mass loss of the membrane material beyond 850 °C is