Ceramics International ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Preparation and characterization of a nigerian mesoporous clay-based membrane for uranium removal from underground water

Muazu Abubakar [a,c], Mohd Nasir Tamin [a], Muneer Aziz Saleh [b], Uday M.B.[a,d], Norhayati Ahmad [a,*]

[a] Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, Skudai, 81310 Johor Bahru, Malaysia
[b] Nuclear Engineering Program, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, Skudai, 81310 Johor Bahru, Malaysia
[c] Department of Mechanical Engineering, Bayero University, Kano, Nigeria
[d] UTM Centre for Low Carbon Transport in Cooperation with Imperial College London, Institute for Vehicle Systems and Engineering, Universiti Teknologi Malaysia, Skudai, 81310 Johor, Malaysia

ARTICLE INFO

Article history:
Received 4 November 2015
Received in revised form
1 February 2016
Accepted 4 February 2016

Keywords:
A. Pressing
B. Porosity
D. Clay
D. Mullite
E. Membrane

ABSTRACT

This study reports the removal of uranium in underground wastewater using a Nigerian clay-based membrane. The clay and sintered clay were characterized using XRD, XRF, TGA/DTA, FESEM and PSD. The raw clay was mixed with cassava starch (10, 15, 20 and 25 wt%) and sintered at a temperature of 1300 °C. A multi-point BET analysis of the produced clay-based membranes was conducted to determine the surface area, pore volume and average pore size. Sintering characteristics were determined by apparent porosity, bulk density and flexural strength. The radioactivity of the feed and the permeated water was counted using a gamma spectrometer with an HPGe detector. From the XRD, TGA and FESEM, 1300 °C was found to be optimum for the mullite formation from the clay. The average pore sizes of the produced membranes from the BET results were observed to be in the range from 51 to 70 Å and with a steady state flux range of the tested membranes in the range 1.92×10^{-5}–2.09×10^{-4} $m^3\ m^{-2}\ s^{-1}$. The permeation flux produced is of high quality with a rejection in the range of 1.78–2.56 Bq/l of the uranium activity by the tested membranes. This low-cost membrane will have an application for the treatment of uranium-containing wastewater from fracking, oil exploration and phosphate mining industries.

1. Introduction

Recently, the contamination of the environment has been caused by anthropogenic activities, such as fracking, oil exploration and water from phosphate ore mining site, which produce wastewater containing radionuclides. Among the radionuclides, uranium is a radionuclide for which the chemical toxicity is comparable to the radiation toxicity. The uranium toxicity in drinking water can lead to kidney failure [1]. Because of the high risk of uranium to the environment and the stringent regulation of uranium in industrial wastewater, it is important to treat such wastewater to reduce the content of enriched uranium to an allowable level before discharging to the environment or reusing in the industries. The recirculation of the treated wastewater would be more advantageous than discharging non-treated wastewater to the environment. Underground water can contain uranium levels as high as 620 μg/L (11.57 Bq/L) [2]. United Nations Scientific Committee on the Effects of Atomic Radiation reported that the uranium concentration in oil and gas industry wastewater can be in the range of 8–42 Bq/L [3].

The treatment of the wastewater containing radionuclides involves the use of a complex process of pretreatment followed by a reverse osmosis filtration; this increases the cost of treating the wastewater. This method is characterized as a high energy consumption leading to a high operating cost and a use of particle-free feed water. In addition, the industrial treatment of uranium involves an ion exchange and a chemical precipitation, which are often not-cost effective [4]. Membrane filtration for the removal of uranium from contaminated water by ultrafiltration method is an effective method of the uranium removal from contaminated water [5].

Inorganic membranes have been proven to be more efficient for the membrane application than their polymeric counterparts. Inorganic membranes possess excellent mechanical properties, good thermal and chemical resistances and adsorption properties [6,7]. Clay-based ceramic membranes were proven to be efficient in the

* Corresponding author. Tel.: +6075534676.
E-mail addresses: nhayati@mail.fkm.utm.my, muazumani2004@yahoo.com (N. Ahmad).

http://dx.doi.org/10.1016/j.ceramint.2016.02.031
0272-8842/

treatment of the industrial effluent at par with their engineering ceramic counterparts. Many researchers have used clay-based membranes for the filtration applications in the treatment of wastewater containing heavy metals and anions with a relatively low energy consumption. Jana et al. [8] reported that a 100% removal of chromium ion in an aqueous solution was obtained using a clay-based microfiltration membrane. Several years later, Ghosh et al. [9] extended the study by using the clay-based microfiltration membrane for the removal of fluoride in contaminated drinking water, and the results indicated a significant rejection of fluoride ions. The clay-based microfiltration membrane was used to remove chromium (VI) ions from wastewater and achieved a percentage rejection of 94% [10]. For microfiltration and ultrafiltration applications, the clay-based membranes for the dye and salt removal from water have been reported to attain a rejection rate in the range of 87–95% [11].

In addition, clays from many countries were reported to be a source of clay-based membranes for wastewater treatments. Tunisian clays have been used as a membrane material for the treatment of various effluents. Khemakhem et al. [12] conducted a study on the Tunisian clay as a membrane material for the removal of dextran polymer solutions of different molecular weights. In another study, Khemakhem et al. [13] reported the treatment of cuttlefish effluent using the Tunisian clay-based membrane. Hamdi and Srasra [14] extended the study by using the Tunisian clay-based membrane for the removal of phosphate ions from wastewater. In addition, Indian clays have been used in the clarification of mosambi juice [15]. Nigeria has large deposits of clay in the African continent, but such deposits are highly underutilized [16].

A membrane module that provides a large surface area per volume is required for the membrane filtration process. In a dead-end module, the flow of feed water is perpendicular to the membrane surface. The feed water is forced through the membrane by pressure. The feed water that is introduced in the dead end cell passes through as permeated water; in other words, there is no rejected water. In the dead end filtration, the retained particles build up with time on the membrane surface or within the membrane. The particles built on the membrane surface cause an increased resistance to the filtration and thus the permeated flux to decline [17]. As a result, the dead-end filtration requires a stop of the filtration to clean or replace the membrane. Therefore, this type of filtration is also called batch filtration [18]. However, a dead-end membrane is easy to fabricate by pressing. This brings down the production cost of the membrane compared to tubular, spiral wounds and hollow fiber modules.

Several studies have reported the production of the clay-based membrane dead-end module by pressing for the treatment of different effluents of a diameter in the range of 50–53 mm, and a thickness in the range of 4–5 mm [8,19]. However, there is no literature discussion of the clay-based membrane for removal of uranium from water. Therefore, in this paper, we report the use and characterization of an inexpensive clay from Nigeria for the production of a mesoporous ceramic membrane for uranium removal from water. The characterization of the raw material was done to ascertain the appropriate sintering temperature for the ceramic membrane production. Pore properties such as pore size, pore specific area and average pore volume were taken to evaluate the type of membranes suitable for a specific filtration application using BET. The produced porous membranes were tested to reduce the activity of uranium in wastewater.

The objective of this work is to prepare mesoporous membranes from Nigerian clay. The produced membranes were tested for reducing the activity of uranium in wastewater. The steady state flux and the uranium activity were evaluated.

2. Materials and methods

2.1. Raw material characterization

The as-received clay was obtained from local miners in Kankara, Nigeria. The chemical composition of the as-received clay is given in Table 1. The clay was washed to reduce the reddish-brown iron oxide content, dried, ground to reduce the lumps into fine powders and finally screened through 270 Mesh. The particle size distribution was measured and evaluated using a Malvern particle Mastersizer. The cassava starch, which acted as a pore former, was prepared using the method reported elsewhere [20]. The TGA/DTA analysis of the clay mixture with glycerol was carried out with a PerkinElmer thermal analysis from 50 °C up to 1200 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

The chemical composition of the clay sample, after crushing to fine powder, was determined by X-ray fluorescence spectroscopy using a Philips PW 2400 spectrometer. As shown in Table 1, the raw clay contains silica and alumina as major constituents. X-ray diffraction (XRD) analysis was performed on both as-received and sintered clay samples with sintering temperatures of 900–1300 °C using an automated Siemens Diffractometer D5000 equipment with a Cu Kα radiation source. The result was analyzed using X' Pert High Score Plus software to identify the phases before and after sintering. The microstructure of the raw clay and cassava starch was recorded using a field emission scanning electron microscopy FESEM (Gemini Supra™ 35vp).

2.2. Membrane preparation and characterization

The clay and the cassava starch were mixed with different percentages of starch (10, 15, 20 and 25 wt%) using ethanol, milled with the aid of zirconia balls for 4 h, dried in an oven for 24 h and pressed into circular disks at a pressure of 60 MPa using an INSTRON 600DX press. The sintering of the pressed samples was carried out at 1300 °C for 2 h to obtain circular clay-based membranes of average dimensions of 4 mm in thickness and 30 mm in diameter. The apparent porosity and the bulk density of the sintered compacts were determined according to conventional methods [21,22]. The microstructures of the clay-based membranes were recorded using FESEM.

The specific surface area, average pore size, adsorption and desorption isotherm of the samples were determined by BET measurements carried out on a TriStar II 3020 surface area and pore analyzer with N_2 as the adsorbate at −196 °C for 4 h in a vacuum condition according to the Kelvin equation. The BET surface area S_{BET} was determined with the adsorption branch of isotherm in the relative pressure p/p_o range of 0.05–0.3 based on the conventional Brunauer–Emmett–Teller (BET) equation from the adsorption data at −196 °C. The total pore volume was

Table 1
Chemical composition of the as-received Kankara clay.

Compound	SiO_2	Al_2O_3	K_2O	Fe_2O_3	CaO	TiO_2	MgO	MnO	P_2O_5	LOI
%wt	48.86	37.83	1.15	0.27	0.05	0.04	0.04	0.01	0.01	11.81

Please cite this article as: M. Abubakar, et al., Preparation and characterization of a nigerian mesoporous clay-based membrane for uranium removal from underground water, Ceramics International (2016), http://dx.doi.org/10.1016/j.ceramint.2016.02.031