Chemical Engineering Journal 334 (2018) 41–53

Contents lists available at ScienceDirect

Chemical Engineering Journal

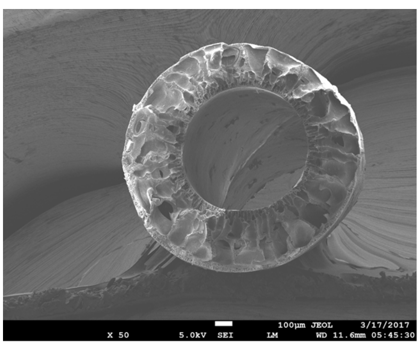
journal homepage: www.elsevier.com/locate/cej

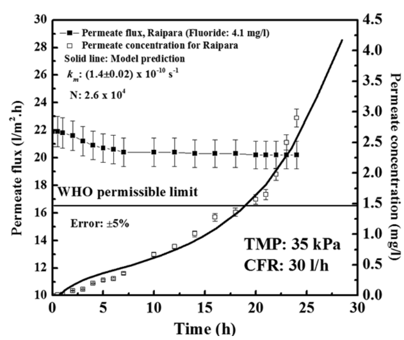
Aluminium fumarate metal organic framework incorporated polyacrylonitrile hollow fiber membranes: Spinning, characterization and application in fluoride removal from groundwater

Sankha Karmakar, Saikat Bhattacharjee, Sirshendu De*

Department of Chemical Engineering, Indian Institute of Technology Kharagpur, Kharagpur 721302, India

GRAPHICAL ABSTRACT





ARTICLE INFO

Keywords:
Aluminium fumarate
Mixed matrix membrane
Metal organic framework
Fluoride removal
Adsorption
Hollow fiber

ABSTRACT

Novel mixed matrix hollow fiber membranes (MMM) were prepared by phase inversion technique using polyacrylonitrile (PAN) as base polymer and aluminium fumarate (AlFu) metal organic framework (MOF) as additive. The membranes were characterized in terms of surface morphology, surface charge, permeability, molecular weight cut off, porosity, pore size and contact angle. Permeability of the membrane increased from 3.5×10^{-10} to 4.5×10^{-10} m/Pa.s with increment of MOF concentration from 0 to 10 wt%. The contact angle of the corresponding membranes decreased from 80° to 51° indicating an increase in hydrophilicity. The MH10 (10 wt% concentration) membrane sustained up to 20, 19 and 17.5 h of operation with fluoride concentration of 4, 8 and 12 mg/l, respectively, at 35 kPa transmembrane pressure and 30 l/h cross flow rate with a membrane area of 0.026 m^2. Regeneration study and performance of the MMM in real life ground water samples were also investigated. Filter performance was successfully predicted by a modified model available in literature.

1. Introduction

About 2.5% of the total water of the earth can be utilized as fresh water [1]. Out of this, only 0.3% fresh water is available on the surface and the rest is groundwater. Thus, the majority of living beings depend on the groundwater. However, groundwater in many places are contaminated by various natural and anthropogenic causes [2]. These contaminants include heavy metals, arsenic, nitrate and other harmful ions [3,4]. One of the major ground water pollutants is fluoride [2].

Many developed countries, like, Australia, China, USA, New Zealand, Japan and Canada are adversely affected by fluoride contamination in groundwater [2,5–7]. India and many other developing

* Corresponding author.
E-mail address: sde@che.iitkgp.ernet.in (S. De).

http://dx.doi.org/10.1016/j.cej.2017.10.021
Received 26 June 2017; Received in revised form 3 October 2017; Accepted 4 October 2017
Available online 06 October 2017

countries are also suffering from this [2,5,8]. According to World Health Organization (WHO), the maximum allowable limit for fluoride in drinking water is 1.5 mg/l [9–11]. Severe skeletal deformation, fluorosis, kidney and liver malfunctioning can occur exceeding this limit [12]. In India, the most affected states are Rajasthan, Gujarat and Andhra Pradesh [5,8,13]. Some parts of West Bengal are also affected severely [14]. Typical fluoride concentration in the affected regions is in the range 4–12 mg/l [15].

Over the past few decades, many researchers have developed processes for fluoride decontamination from water including precipitation [16], electro-coagulation [17], reverse osmosis [18], membrane based processes using mixed matrix membrane [5]. But the most conventional, scalable, cost effective and technically accepted process is adsorption [5,8,19–24]. Among many non conventional adsorbents, hydrous zirconium oxide [25], hardened alumina cement granules [26] and Mg-doped nano ferrihydrite [27] are mostly notable. In the past decade, metal organic frameworks (MOF) have found vast application in gas separation [28], catalysis [29], sensors [30] and many more [31,32]. In the previous work of the authors, it had been established for the first time that Aluminium Fumarate (AlFu) MOF has higher adsorption capacity (600 mg/g) than all other conventional and non conventional adsorbents due to high surface area (1156 m^2/g) and positive zeta potential at pH 7 (6.2 mV) [8]. This MOF has octahedrally coordinated structure with the chemical formula, $Al(OH)(O_2C\text{-}CH{=}CH\text{-}CO_2)$. Being a powdery material, the application of this MOF is limited in treating ground water owing to high pressure drop when used as bed material. Therefore, to exploit high fluoride adsorption capacity, it needs to be immobilized within a matrix. With this notion, a mixed matrix membrane was prepared using polyacrylonitrile (PAN) co polymer as the base polymer and AlFu MOF as the additive. The building block for PAN and AlFu MOF is presented in Fig. 1.

Polyacrylonitrile is one of the most widely used polymers for preparing membranes [33]. Due to its high chemical stability, good solvent resistance, excellent mechanical properties and high thermal stability, it is one of the choices for membrane preparation. Also, polyacrylonitrile membranes can be credited with high flux [33,34] and hence is useful for commercial applications [34]. There are various designs of membrane modules that had been developed over the past decades. One of the most widely used designs is hollow fiber cartridges. Due to their high surface to volume ratio, low operating pressure, easy handling and operation and ease of scalability, hollow fiber designs have found huge application in the field of water purification.

In the present work, a novel mixed matrix hollow fiber membrane was prepared using polyacrylonitrile copolymer as the base polymer and aluminium fumarate MOF as additive using a low cost novel spinning method proposed by Thakur and De [35]. The membrane morphology, surface characteristics, surface charge, wettability were studied. The effect of operating conditions, life cycle of the membrane, regeneration and leaching study were also undertaken in context of fluoride removal. Performance of the membrane in presence of co-ions and for real life groundwater samples was investigated. A suitable model was modified to predict the breakthrough performance of the membrane [36].

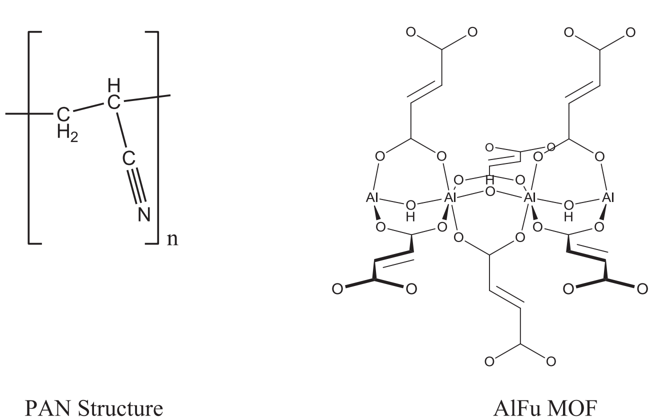


Fig. 1. Building block for (a) polyacrylonitrile (PAN) structure and (b) Aluminium Fumarate metal organic framework (adapted from Karmakar et. al. [9]).

2. Theory

The present modeling scheme encompasses a cylindrical porous conduit (hollow fiber membrane) that acts as the separation media. Hollow fibers MMM have MOF embedded in their matrix, acting as the adsorptive media for fluoride. Following assumptions are made for the modeling purpose:

(i) All fibers in the module are identical and perform equally; (ii) adsorption fronts move radially and uniformly.

The solute mass balance within membrane matrix is given as follows,

$$\phi\frac{\partial c}{\partial t} + J_w\frac{\partial c}{\partial r} + (1-\phi)\rho_m\frac{\partial q}{\partial t} = 0 \tag{1}$$

where, ϕ is the void fraction of the membrane, J_w is the water flux through the membrane pores in the radial direction, ρ_m is the bulk density of MOF-polymer mixture and q is the fluoride adsorption capacity of the MOF. Rate of adsorption is defined as follows,

$$\frac{\partial q}{\partial t} = k_m(q_{eq}-q) \tag{2}$$

Relevant boundary conditions of Eq. (1) are,

$$c(0,t) = c_0; q(R,0) = 0; c(R,0) = 0$$

where, c_0 is the feed concentration, R is the internal radius of the fiber. It is evident from the experiments that the adsorption isotherms follow Langmuir model. Hence, the following coupling relation can be used to solve Eqs. (1) and (2), simultaneously.

$$q_{eq} = \frac{kq_\infty c}{1 + kc} \tag{3}$$

The non dimensional parameters used in this context to make Eqs. (1) and (2) dimensionless are,

$$c^* = \frac{c}{c_0}; r^* = \frac{r}{R}; q^* = \frac{q}{q_\infty}; \tau = \frac{t\rho_m k_m q_\infty}{c_0}.$$

Final form of the dimensionless equations are given below,

$$\phi\frac{\partial c^*}{\partial \tau} + N\frac{\partial c^*}{\partial r^*} + (1-\phi)\left(\frac{\alpha_{ad}c^*}{1 + \alpha_{ad}c^*} - q^*\right) = 0 \tag{4}$$

$$\frac{\partial q^*}{\partial \tau} = \left(\frac{c_0}{\rho_m q_\infty}\right)\left(\frac{\alpha_{ad}c^*}{1 + \alpha_{ad}c^*} - q^*\right) \tag{5}$$

where, $\alpha_{ad} = kc_0$ and the non dimensional number N is defined as $N = \frac{J_w c_0}{\rho_m k_m R q_\infty}$. Parameter N physically indicates the ratio of amount of solute transported towards membrane by convection to that adsorbed by membrane matrix.

2.1. Numerical solution scheme

Eqs. (4) and (5) are solved simultaneously using PDEPE function of MATLAB R2015b. The third term of Eq. (4) is regarded as the linearized source term in the system. Parameter k_m is evaluated by an error minimization algorithm during each iteration and the following error term is minimized.