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Adsorptive removal of fluoride by activated alumina doped cellulose acetate phthalate (CAP) mixed matrix membrane

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ABSTRACT

Flat sheet mixed matrix membranes were prepared using cellulose acetate phthalate (CAP) and activated granular alumina using phase inversion technique. The membranes were characterized using porosity, permeability, molecular weight cut off (MWCO) and contact angle. Compositional analysis of the membrane was carried out by X-ray diffraction and the morphology and surface roughness were investigated by scanning electron microscope and atomic force microscope, respectively. The permeability of the membrane was reduced from 3.0×10^{-11} to 1.4×10^{-11} m/Pa s as alumina concentration increased from 0 to 35 wt% for constant CAP concentration at 20 wt%. Decrease in porosity from 75% to 45% supported the above fact. Membrane hydrophilicity was improved and most importantly, fluoride rejection from contaminated water increased to 91% using 35 wt% of alumina. Maximum adsorption capacity for fluoride was 2.3 mg/g for the mixed matrix membrane at room temperature. Continuous cross flow experiments revealed that the virgin membrane (24 kDa), having a surface area of 0.01 m^2, could produce water well within the safety limit for a time of 11 h. Regeneration study was conducted for five cycles. Effect of other co-existing anions on fluoride removal efficiency of the membrane was also studied.

1. Introduction

With the progress of human civilization, there is rapid growth in industrial and agricultural sectors. Waste materials emerging from various industries and inorganic components from fertilizers cause the contamination of groundwater by heavy metals like lead, cadmium, chromium and other harmful chemicals like arsenic and fluoride. Fluoride is needed for human health, but it becomes toxic once its concentration exceeds the optimum value (about 1.5 mg/l) [1]. This causes diseases like fluorosis (skeletal and dental) and brown motting of teeth (Colorado brown stain). Therefore, removal of fluoride from groundwater has been an active area of research.

Fluoride contamination of groundwater is observed in various countries like Brazil, Chile, Argentina, northeastern parts of Africa, Pakistan, China and India. In India, several states like Andhra Pradesh, Rajasthan, Karnataka, Madhya Pradesh, Uttar Pradesh and West Bengal are badly affected. Adsorption is one of the popular methods for fluoride removal. In this regard, adsorbents like zirconium–iron oxide complex, bauxite, charcoal and activated alumina [2–5] were found to be effective. Precipitation by chemicals like calcium oxide/hydroxide and alum [6,7] was also used for effective removal of fluoride. However, all these processes have their inherent limitations. Limited by equilibrium, adsorption is a slow process. In precipitation method, residual precipitating agents in the processed stream may be harmful. In this regard, pressure driven membrane based processes can offer an attractive alternative. These processes are physical in nature, do not require any external chemicals, can operate under ambient temperature and easier to scale up. There are reports to use reverse osmosis [8,9] and nanofiltration [10–15] to remove fluoride from aqueous solution. However, the operating pressure required for reverse osmosis and nanofiltration are quite significant, and hence, are expensive. Moreover, other essential co-existing monovalent ions, which are useful for human health, like chloride and iodide are also removed by reverse osmosis and nanofiltration to some extent. Thus, if fluoride can selectively be separated by a more open pore ultrafiltration membrane, its removal from drinking water will be achieved at a higher throughput and at much lower operating pressure, thereby, reducing the cost of operation significantly. Use of mixed-matrix membrane is quite promising in this context. In mixed-matrix membrane, an inorganic material is doped in the polymeric matrix and one can exploit selective separation property of adsorption and filtration capability of membrane by removing suspended materials, microorganism, etc., in one-step.

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Nomenclature

A	membrane area, m^2
C_p	concentration of solute in permeate, mg/l
C_f	concentration of solute in feed, mg/l
C_0	fluoride concentration in the feed, mg/l
C_e	equilibrium concentration of fluoride in solution, mg/l
D_i	dielectric constant, dimensionless
i	number of data points, dimensionless
J_{w0}	distilled water flux, m/s
K	adsorption equilibrium constant (Langmuir isotherm), l/mg
k_f	adsorption capacity (Freundlich isotherm), mg/g
k_i	intraparticle diffusion rate constant, g mg^{-1} $h^{-0.5}$
k_1	first order rate constant, h^{-1}
k_2	second order rate constant, g mg^{-1} h^{-1}
l	membrane thickness, m
n	total number of data points, dimensionless
n'	adsorption intensity (Freundlich isotherm), l/g
Q	amount of permeate collected, l
q_e	amount of fluoride adsorbed, mg/g
$q_{e,meas}$	experimentally measured value of q_e, mg/g
$q_{e,calc}$	fitted value of q_e from isotherm, mg/g
q_t	amount of fluoride adsorbed at any time, mg/g
R	rejection, %
R_s	average pore radius of membrane, cm
t	time of agitation for batch adsorption study, h
V	volume of solution taken, ml
V_m	amount of fluoride ion adsorbed for complete monolayer (Langmuir isotherm), mg/g
V_p	streaming potential coefficient, V/Pa
w_o	weight of the dry membrane samples, kg
w_l	weight of the wet membrane samples, kg
W	weight of the membrane samples taken for batch adsorption study, g

Greek symbols

ε	membrane porosity, dimensionless
ρ_w	density of water, kg/m^3
Δt	time interval over which permeate samples are taken, h
ΔV	voltage difference across the membrane, V
ΔP	transmembrane pressure drop, Pa
ξ	zeta potential of membranes, mV
μ	viscosity of the feed solution, Pa s
λ	conductivity of the feed solution, μS
ε_o	permittivity in vacuum, m^3 kg^{-1} s^4 A^2

Cellulose acetate (CA) and its derivatives being biocompatible, non-toxic, low cost and hydrophilic have widespread application as a polymer base material to cast a membrane [16]. Presence of several acidic and carbonyl groups on its structure improves membrane performance and makes it a popular polymer base material with wide applications. Use of additives like alumina, titanium, zirconium and silica in a polymer matrix has been reported in the literature [17–20]. Doping of these inorganics, improved the selectivity of such membranes significantly [21]. However, CA being chemically resistant, is unsuitable for cleaning [22]. Wara et al., added granular alumina (average size: 0.34 μm) to CA matrix and studied the morphology of the cast membrane [17]. Addition of alumina nanoparticles as fillers helped in improvement of properties like membrane hydrophilicity, porosity and protein retention [23]. On addition of TiO_2 nanoparticles in polysulfone matrix, pure water flux got enhanced due to increased hydrophilicity and porosity [24]. Zirconia (average size: 19 μm) doped with CA improved the pure water flux of the membrane along with its fouling characteristics [19]. Arthanareeswaran et al., reported increase in porosity and hydrophilicity of silica (average size: 14 μm)-CA mixed matrix membrane up to 40 wt% of silica [20]. Bottino et al., reported addition of silica in *polyvinylidene fluoride* matrix and showed that permeate flux increased with silica content along with lower retention of protein [25].

Doping of activated alumina (average size: 109 μm) in cellulose acetate phthalate (CAP) is reported first time in this analysis. In this work, a detailed characterization of this mixed matrix membrane has been undertaken. The surface charge density on the membrane surface was also obtained by determining the zeta potential of the membrane. Fluoride removal capacity along with the membrane's productivity has been analyzed. Fluoride adsorption on the surface was determined by adsorption isotherm. The effect of feed pH and other coexisting anions on the removal efficiency of fluoride was examined. The membrane was operated for five cycles and its efficiency for removal of microorganism was explored as well.

2. Experimental procedure

2.1. Materials

Cellulose acetate phthalate (CAP, acetyl content 20%; pthalyl content 34%) was procured from G.M. Chemicals, Mumbai, India. N,N-Dimethyl formamide (DMF), polyethylene glycol (PEG) (Molecular weight: 35 kDa, 20 kDa, 10 kDa, 6 kDa, 4 kDa, 400 Da) and activated alumina powder were purchased from M/s, Merck (India) Ltd., Mumbai, India. Dextran (molecular weight 70 kDa) was obtained from Sigma Aldrich Chemicals, USA. Sodium fluoride (extra pure) was supplied by Sisco Research Laboratory Pvt Ltd., Mumbai, India.

2.2. Preparation of casting solution

Casting solution was prepared by dissolution of CAP in DMF. Initially DMF was heated to a mild temperature (45 °C) and CAP was added slowly. It was noted that constant stirring was given to the CAP–DMF solution with intermediate heating at times just to ensure proper dissolution of CAP for 4 h. Next, alumina was added at a particular concentration and the mixture was sonicated. Various membranes were cast using 20 wt% CAP and different alumina concentration.

2.2.1. Sonication

A Piezo-U-Sonic (P.U.S.) ultrasonic cleaner (power: 120 W) was used to sonicate the casting solution (after proper dissolution by stirring). Variation of membrane characterization parameters (molecular weight cut off, permeability, porosity) were observed with sonication time. An optimum sonication time was achieved when these characterization parameters became invariant.

2.3. Membrane casting

The cast solution was poured onto a non-woven polyester fabric (product number: TNW006013, supplied by M/s, Hollytex Inc., New York, USA) attached to a glass plate and was drawn manually