Chemical Engineering Journal 228 (2013) 449–454

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

The influence of pore generating agent on the efficiency of copper and iron ions removal from liquid phase by polyethersulfone membranes

Katarzyna Jasiewicz, Robert Pietrzak *

Laboratory of Applied Chemistry, Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b, 61-614 Poznań, Poland

HIGHLIGHTS

- Addition of various amounts of PVP affects the physical and chemical properties of the membranes.
- For copper solutions an increase in the content of PVP leads to an increase in FRR.
- For iron solutions an increase in the content of PVP leads to an decrease in FRR.
- Concentration of 15 mg/L is a limiting value ensuring high efficiency of removal of both Cu and Fe ions.
- The values of cake resistance of the membranes increases with increasing content of PVP.

ARTICLE INFO

Article history:
Received 8 January 2013
Received in revised form 16 April 2013
Accepted 4 May 2013
Available online 15 May 2013

Keywords:
Polyethersulfone (PES) membrane
Different porosity
Phase inversion
Surface chemistry
Copper and iron ions removal

ABSTRACT

Preparation of polymeric membranes based on polyethersulfone (PES) modified by adding different amounts of pore generating agent (PVP) is presented and potential application of the membranes obtained for removal of copper and iron ions from the liquid phase is examined. It has been shown that addition of various amounts of PVP affects the physical (porosity, equilibrium water content and permeability) and chemical (content of the surface oxygen group, pH) properties of the membranes. Filtration of iron and copper solution leads to significant changes in the total content of surface oxides, however the acidic groups remain dominant. The membranes were proved to be more effective in removal of iron ions than copper ones. The most efficient in iron ions removal was the membrane of the lowest content of PVP. For the majority of membranes the cake resistance brings the greatest contribution to the total resistance.

1. Introduction

Recently membrane technology has attracted much interest because of increasing range of membranes application in many branches of industry. The use of membranes in the activities related to the environment protection have proved to be particularly beneficial for ecological and economic reasons. The membrane processes make the favoured alternative to the classical methods of separation because they do not release harmful side products, are easy to operate, use little energy and do not employ chemical means [1–3]. Moreover, on membrane separation the separated components do not undergo any thermal, chemical or biological transformations. The choice of membrane is closely related to the process in which it is going to be used, e.g. the process of reduction of water hardness or removal of certain gases or chemical substances [4]. Polymer membranes are most often used in the processes of reversed osmosis, ultrafiltration, microfiltration and gas separation. Organic membranes are usually made of synthetic polymers such as polysulfone, polyethersulfone, cellulose acetate or polyamide [4,5]. Recently polyethersulfone has been most often chosen because of its specific properties. It shows thermal stability and thermal resistance, chemical resistance to acids, petrol, oils and oxidising substances such as fluorine and hydrogen peroxide in addition to mechanical strength, tolerance of a wide range of temperatures and pH, physiological neutrality, low sensitivity to UV [2,6–11].

For ultrafiltration and microfiltration most of the asymmetric polymer membranes are obtained by the method of phase inversion [6,12]. The parameters determining the structure of membranes obtained by this method are the composition of the polymer solution and the kinetics of precipitation, i.e. the rate of solvent evaporation [13]. The range of application of membrane technology depends on design and development on new membrane materials of higher selectivity, greater chemical and thermal resistance [14].

Membrane processes are increasingly often used for removal of impurities from the liquid phase [15–18]. Pollution of water with

---

* Corresponding author. Tel.: +48 618291581; fax: +48 618291555.
E-mail address: pietrob@amu.edu.pl (R. Pietrzak).

1385-8947/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2013.05.005

excessive amounts of heavy metals (e.g. copper, cadmium, iron) is hazardous to human health. Increased presence of iron ions in drinking water endows it with s specific smell and brown–red colour, increased amount of copper intake by humans leads to headaches, depression and problems with learning. To prevent a high level of heavy metal ions pollution in water, increasingly restrictive rules have been imposed on the concentration of heavy metals in industrial wastewater.

This paper reports results of a study on the synthesis of polymer membranes of different porosity and their performance in the processes of copper and iron removal from the liquid phase. The membranes studied were made of polyethersulfone and were obtained by the phase inversion method with addition of different amounts of pore generating agent (PVP).

2. Experimental

2.1. Materials

Polyethersulfone (Ultrason E 6020 PES) was purchased from BASF and used as a membrane material. 1-Methyl 2-pyrrolidone (NMP) was purchased from POCh and used without further purification. Polyvinylpyrrolidone (PVP, 10000 g/mol) as a pore former was supplied by Sigma–Aldrich.

The sources of copper and iron ions were copper(II) sulphate ($CuSO_4{\cdot}5H_2O$) and ammonium iron(III) sulphate ($NH_4Fe(SO_4)_2{\cdot}12H_2O$), from POCh.

2.1.1. Preparation of PES membranes

Membrane forming solutions were prepared by mixing the ingredients in a flask of 14 wt.% PES, 1, 2, 3 or 4 wt.% of PVP and NMP to supplement to 100 wt.%., the latter was used as a solvent.

The casting solution obtained was left to rest for about 12 h to allow complete release of bubbles. After that, it was cast onto a glass plate using a stainless-steel knife to get a casting film of 300 μm thickness, exposed to the atmosphere for 40 s, and then immersed into a coagulation bath of pure water. The as-prepared cast solution films were immersed and kept for 24 h in a deionised water bath conditioned at 25 °C to complete the exchange between the solvent and non-solvent. Directly prior to use, each electrode was washed with a small amount of deionised water.

2.2. Membrane structure characterisation

2.2.1. Porosity and equilibrium water content

The membrane porosity was determined by the mass loss of wet membrane after drying. The membrane sample was mopped with water on the surface and weighed under wet status. Then, the membrane sample was dried until a constant mass. The membrane porosity ε was evaluated from Eq. (1):

$$\varepsilon = \frac{W_w - W_d}{\rho \cdot v} \cdot 100\% \tag{1}$$

where W_w is the mass of a wet membrane sample, W_d is the mass of dry state membrane sample; ρ pure water density and v is the volume of a membrane in wet state.

The equilibrium water content (EWC) was determined by Eq. (2):

$$EWC = \frac{W_w - W_d}{W_w} \cdot 100\% \tag{2}$$

2.2.2. Contact angle

The contact angle between water and membrane was directly measured using a contact angle measuring instrument G10, KRUSS, Germany. For evaluation of the membrane hydrophilicity de-ionized water was used as a probe liquid in all measurements. To minimize the experimental error, the contact angle was measured at five random locations for each sample and then the average was reported.

2.2.3. Surface oxygen groups

The surface properties were characterised using potentiometric titration experiments using 809 Titrando equipment manufactured by Metrohm. The instrument was set at the mode when the equilibrium pH was collected. Materials studied in the amount of about 0.100 g in 50 mL 0.01 M $NaNO_3$ were placed in a container thermostated at 25 °C and equilibrated overnight with the electrolyte solution. To eliminate the influence of atmospheric CO_2, the suspension was continuously saturated with N_2. The carbon suspension was stirred throughout the measurements. Volumetric standards NaOH (0.1 M) or HCl (0.1 M) were used as titrants [19].

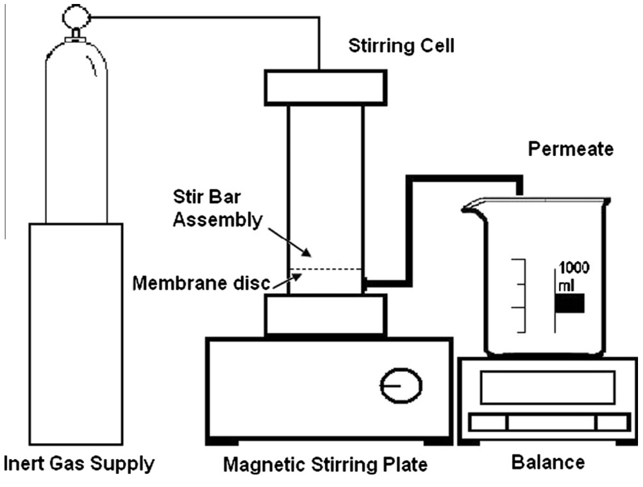
2.3. Membrane performance characterization

Water permeability of the membranes prepared was measured in a stainless steel cell, holding the effective membrane area of 19.6 cm^2. The membranes were initially subjected to deionised water of 3 bar for about 1.5 h before testing. Then, the pure water flux was measured at 3 bar, 23 ± 1 °C and 0.22 m/s cross-flow velocity. The pure water flux was calculated from the following equation:

$$J_w = \frac{V}{A \cdot \Delta t} \tag{3}$$

where J_w (L/(m^2 h)) is the pure water flux, V (L) is the volume of permeated water, A (m^2) is the effective membrane area and Δt (h) is the permeation time.

The experiments were conducted using compressed nitrogen gas and iron or copper solutions of different initial concentrations (5, 10, 15 or 20 mg/L) and all measurements were made at 3 bar, in triplicate. Measurements were made with the use of a membrane modulus made by Sterlitech Corporation (USA), (Scheme 1) in which the membrane studied was placed and then it was filled with a solution of an appropriate concentration. The process of filtration was conducted for 30 min. The final concentration of iron or copper in the solution was analysed using a double beam UV–Vis spectrophotometer (Varian Cary 100 Bio) at 487 nm wavelength for iron solutions and at 620 nm wavelength for copper solutions. The iron or copper rejections (%R) were calculated from Eq. (4):



Scheme 1. The schematic diagram of the ultrafiltration equipment.