Colloids and Surfaces A: Physicochem. Eng. Aspects 451 (2014) 151–160

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Effect of bio-mediated route synthesized silver nanoparticles for modification of polyethersulfone membranes

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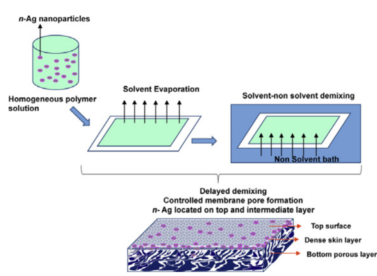
HIGHLIGHTS

- Resulting *n*-Ag nanoparticles exhibited uniform and well defined morphology.
- XPS analysis showed that a significant portion of silver was in silver oxide form.
- Separation of BSA with varying feed concentration and transmembrane pressure.
- Loading of *n*-Ag in neat PES, the enhanced the protein flux.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 November 2013
Received in revised form 3 March 2014
Accepted 7 March 2014
Available online 19 March 2014

Keywords:
Polyethersulfone
Bacillus subtilis
Silver nanoparticles
BSA separation
Membrane fouling

ABSTRACT

This article reports the modification of polyethersulfone (PES) membrane using silver nanoparticles (*n*-Ag), their characterizations and protein separation performances. As a bio-mediated synthesis route, gram-positive *Bacillus subtilis* bacterial supernatants were employed for preparing *n*-Ag. The resulting *n*-Ag exhibited uniform and well defined spherical morphology with size less than 50 nm. The effect of the incorporation of *n*-Ag on PES membrane in terms of cross sectional morphology, surface roughness, crystallinity and hydrophilicity were investigated systematically. XPS analysis showed that a significant portion of silver was in silver oxide form. Depth profiling by argon plasma etching and XPS showed the partition of Ag_2O and Ag between the membrane surface and the bulk. A minor oxidation on the surface of the silver was observed whereas the internal structure of the membrane retained Ag in its metallic state. The potential of the nano composite membrane for the separation of BSA with varying feed concentration and transmembrane pressure were performed. At 1.5 wt% loading of *n*-Ag in neat PES, enhancement in bovine serum albumin (BSA) flux and decrease in the rejection were observed. The results and performance of the PES/*n*-Ag nanocomposite membranes indicate that it would be a deserving candidate for future industrial separations. The experimental results confirm that the incorporation of Ag nanoparticles in PES UF membrane can increase hydrophilicity and reduce the fouling.

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http://dx.doi.org/10.1016/j.colsurfa.2014.03.024
0927-7757/

1. Introduction

Polyethersulfone (PES) is an important material for the preparation of filters, ultrafiltration (UF) and reverse osmosis (RO) membranes. Achievement of an improved water permeability, hydrophilicity and reduced fouling are the main focus of interest in membrane separation processes. To ensure that, properties such as mechanical, thermal, surface and internal structures, chemical and bio-stability of the membranes have to be engineered carefully. The surface chemical activity rendered by nanomaterials is a desired phenomenon and being exploited for a variety of applications especially in water decontamination, catalysis and related environmental remediation applications. The catalytic activity of nanoparticles combined with polymer membranes has a great potential to enhance the treatment efficiency in aqueous pollutant streams based on the concept of "mixed matrix membranes". In such composites, nanoparticles not only render catalytic activity but also alter the properties of polymer membranes such as higher porosity in skin surfaces, higher permeability, reduction of macro voids and increased skin layer thickness, etc. [1]. Modification of membranes incorporated with nanoparticles can trap and deactivate contaminants in the aqueous streams [2]. There are sizeable reports [3–7] demonstrating the blending of nanoparticles to positively tailor the membrane properties in terms of stability and performance (for example, neat water flux and protein rejection and so forth). Two approaches such as *in-situ* and *ex-situ* methods are commonly used to incorporate nanomaterials into the polymer membranes. Considering the simplicity and controlling the chemical reactions, *ex-situ* addition of nanomaterials is relatively easier than *in-situ* formation.

Among various nanomaterials, silver nanoparticles (*n*-Ag) are prominently used in many industries due to its excellent physiochemical properties. Currently most of the applications of *n*-Ag are in biotechnology, textile engineering and catalysis. In recent years many reports showed the importance of *n*-Ag in dictating the required membrane properties for water industries such as porosity, mechanical strength and anti-microbial effects [8–11]. Great many routes for preparing the nanomaterials such as wet chemical [12], vapour phase [13], biosynthesis using the enzymes of microorganisms [14,15] plant leaf and honey mediated method [16,17], etc., have been reported in the literature. Bio-mediated nanoparticle synthesis using bacterial enzymes is well-established, cost effective, eco-friendly, simple and gives reproducibility. However, the state of silver in the nanoparticle has not yet been studied thoroughly, particularly when it is incorporated in the membrane. Such investigation seems important, considering that the state of Ag, either in metal or metal oxide form, likely affects the anti-biofouling capacity of Ag and also its hydrophilicity. Aggregation phenomenon in nanoparticle synthesis is a major concern in all routes of synthesis and so much focus is given to tackle this problem. It is to be noted that the biological routes also have no exception but, to some extent, it helps to stabilize or protect the structure through its organic functionality by surrounding the inorganic nucleation. At the same time, some important drawbacks in biological methods such as total time for synthesis, formation rate, and achievement of mono-disperse materials [18] have to be kept in mind. Considering the inherent limitation of other methods, the advantages of bio-mediated synthesis against conventional chemical synthesis is rather simple. Economical and biological benefits are the main impetus for this approach. Biological routes demonstrate clean, non-toxic and cost effective terms and moreover, the nature itself follows this route to synthesize materials for its food, growth and protection mechanisms [19]. Considering the advantages in the biogenic routes of *n*-Ag preparation and ease of *ex-situ* methodologies, PES/*n*-Ag composite membrane was chosen for this research.

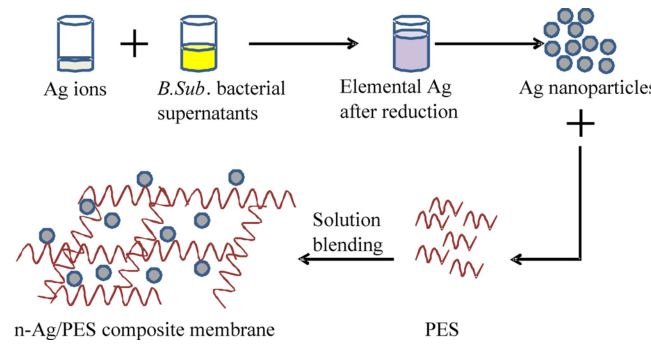

Fig. 1. Schematic representation on the preparation of PES/*n*-Ag composite membranes.

Filtration of BSA is very important in bio-molecular separation and requires membrane materials having high permeability and selectivity. Many works have been reported on the separation of BSA using organic and inorganic membranes based on the membrane characteristics such as hydrophilicity, porosity and structure which are keys for high permeability and rejection [20,21]. The advantage in fabricating the inorganic–organic mixed matrix membranes is their suitability for protein separation than with pure polymeric membranes. Scores of researchers focused their research on the development of membrane by mixing or blending of inorganic nanomaterials such as TiO_2, Al_2O_3 and SiO_2 with various polymers [3,22,23].

In this report, a detailed investigation starting from the *n*-Ag synthesis by bacterium mediation, characterization of *n*-Ag so synthesized, subsequent incorporation with PES by *ex situ* basis, thorough physical and chemical characterizations, and eventually the performance of the nanocomposite membrane for BSA separation were performed. Membrane fouling can be controlled by membrane characteristics, feed nature and operating pressure [21]. Therefore, surface membrane modification is needed to form asymmetric structure with active (top) membrane layer for effective fouling interactions and the membrane separation [24]. The reduction of membrane fouling with BSA is attempted by PES and modified PES membrane surface. The *n*-Ag/PES nanocomposite formation is schematically depicted in Fig. 1, which is self-explanatory. A variety of physical and chemical characterization techniques such as particle size analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM), 3D surface profiling, FTIR, XPS, and water contact angle measurements were used for the material analysis.

2. Materials and methods

2.1. Materials

Silver nitrate and Luria broth were purchased from Thomas baker chemicals, Mumbai, India. PES (Grade: Gafone 3300) was purchased from Gharda Chemicals Ltd., Mumbai. Analytical grade of *N*,*N*-dimethylformamide (DMF) and sodium lauryl sulfate (SLS) were procured from Qualigens Fine Chemicals Ltd, Mumbai. *Bacillus subtilis* bacterial strains was provided by Ponalab Biogrowth Private Limited, Karnataka, India.

2.2. Preparation of silver nanoparticles by culture supernatant of *B. subtilis*

The *n*-Ag was prepared by bacteria mediated biosynthesis method. Luria broth was prepared, sterilized and inoculated with a fresh batch of *B. subtilis* bacterial strains. The culture flask was