

Polysulfone Membrane Reactors for Derivatization of Carbon Nanotubes

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ABSTRACT

We propose a new method for derivatization of amino carbon nanotubes with enzymes (carbonic anhydrase, invertase, and diastase) and crown ethers amino derivatives using a polysulfone membrane reactor. The principle of method consists in the synthesis of polysulfone-amino carbon nanotubes composite membranes (by phase inversion) with controlled porosity, the access of reagents to reactive centres being favoured by diffusion through membrane pores. Composite membranes were used for proteins retention (Bovine Serum Albumin and Haemoglobin for enzymes derivatized carbon nanotubes – polysulfone composite membranes) and cations retention (lead, copper, sodium and iron for composite membranes with crown ethers derivatized carbon nanotubes – polysulfone composite membranes).

Keywords: polysulfone, membrane, carbon nanotubes, derivatization

1 INTRODUCTION

Composite polymeric membranes with carbon nanotubes have been extensively studied for different applications like water desalination [1], antimicrobial effect [2], carbon dioxide separation [3], proteins separation [4], or haemodialysis [5]. Usually, the use of carbon nanotubes as fillers in composite polymeric membranes is limited to the improvement of mechanical [6] and thermal [7] properties or are used for increasing retention behaviour [8]. Previous reported works initiated a new application for composite polymeric membranes with carbon nanotubes – membrane reactors for functionalization and derivatization of carbon nanotubes [9, 10]. In terms of modern organic chemistry, functionalization reactions refer to the introduction of a functional group (amino, carboxyl, carbonyl, etc.) and derivatization refer to a chemical reaction between a functional group and a larger molecule with complex functions [11]. Due to their aggregation in solutions, carbon nanotubes are heavy to functionalize or to be implied in derivatization reactions with good yields. We present a new method for derivatization of amino carbon nanotubes with enzymes and crown ethers amino

derivatives using a polysulfone membrane reactor. The principle of method consists in the synthesis of polysulfone-amino carbon nanotubes composite membranes (by phase inversion) with controlled porosity, the access of reagents to reactive centres being favoured by diffusion through membrane pores (Figure 1). A part of carbon nanotubes will be trapped and fixed in polymeric structure of membrane and a part will be free in membrane pore (which will allow the access of reagents to reactions centres).

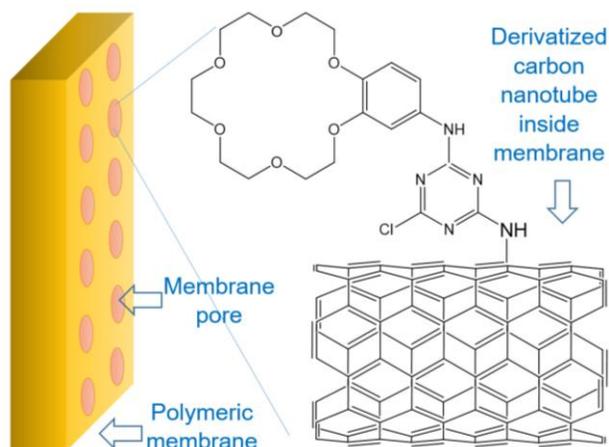


Figure 1: Method principle for carbon nanotubes derivatization with crown ethers inside composite membrane pores.

Composite membranes were used for proteins retention (Bovine Serum Albumin and Haemoglobin for enzymes derivatized carbon nanotubes – polysulfone composite membranes) and cations retention (lead, copper, sodium and iron for composite membranes with crown ethers derivatized carbon nanotubes – polysulfone composite membranes).

2 MATERIALS AND METHODS

In order to obtain polysulfone-carbon nanotubes composite membranes, a polymer (Polysulfone, Mw 34000, purchased from Sigma Aldrich) solution was prepared in N-methyl-pyrrolidone (purchased from Sigma Aldrich,

analytic purity) at 12% wt. concentration. Amino carbon nanotubes (purchased from Nanocyl short DWCNT 90+% purity and surface modified NH_2) were dispersed under sonication for 60 min at 5% concentration related to polymer. The membranes were prepared by phase inversion method by immersing a polymer solution film (deposited onto a glass substrate at a standard thickness of 300 μm) in a bath with iso-propanol (purchased from Sigma Aldrich, analytical purity). Membranes were washed and kept in deionized water.

In order to functionalize amino carbon nanotubes with cyanuric chloride (purchased from Fluka), 50 cm^2 of membranes were heated at 40°C in a solution of cyanuric chloride in ethanol (5%) for 4 hours. 0.5 g of potassium hydroxide were added for neutralizing hydrochloric acid released from reaction. After reaction, the membranes are washed with iso-propanol and deionized water.

The carbon nanotubes were functionalized inside membranes with three different enzymes and amino crown ethers derivatives. Carbonic anhydrase (purchased from Sigma Aldrich), invertase (purchased from Fluka), and diastase (purchased from Riedel de Haen) were immobilized on carbon nanotubes in membrane pores by keeping the membranes for 72 hours in a solution of enzyme in deionized water (10^{-4}M) at 5°C. Long-time reaction and low temperature were necessarily for preventing the deactivation of enzymes and also because after first reaction step of functionalization with cyanuric chloride, the aromatic ring need improved conditions for second substitution step.

Crown ethers (4' amino-benzo-18-crown-6 ether, purchased from Sigma Aldrich) were immobilized using a membrane with same surface (50 cm^2) into a solution of crown ethers in water and dioxin (1:1 vol.) at 60°C for 4 hours. After reaction, membranes were also wash with iso-propanol and deionized water.

For fluxes and retention tests, membrane discs with 4.5 cm diameter were used in a Sartorius laboratory installation working a 0.1 atm vacuum. Retention studies for membranes with enzymes immobilized on carbon nanotubes were performed using 500 mL of Bovine Serum Albumin (purchased from Merck) and Haemoglobin (purchased from Merck) solutions in deionized water at 10^{-6}M concentration. Cations retentions for membranes with crown ethers immobilized on carbon nanotubes were studied using sulphate salts of lead, copper, sodium and iron (all purchased from Sigma Aldrich). All retentions were studied by UV-Vis method [12, 13] using a Camspec instrument.

3 RESULTS AND DISCUSSIONS

All obtained materials were characterised by FT-IR (using a Bruker Tensor 27 with ATR diamond annex) and NMR (using a Bruker 400 MHz instrument). In FT-IR spectra no interactions were observed between carbon nanotubes and polysulfone. After functionalization with

cyanuric chloride a band at 1490 cm^{-1} appear due to formation of $=\text{NH}$ group. Also, chemical shifts from 2.975 and 2.977 in NMR spectrum are attributed to formation of this functional group.

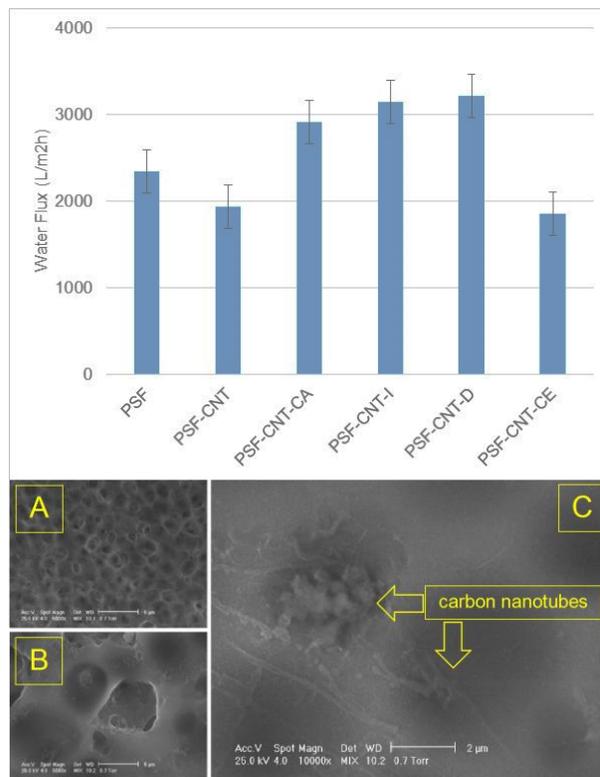


Figure 2: Top - water fluxes for polysulfone membrane (PSF), polysulfone-carbon nanotubes composite membranes (PSF-CNT) and polysulfone-carbon nanotubes functionalized with carbonic anhydrase (PSA-CNT-CA), invertase (PSF-CNT-I), diastase (PSF-CNT-D), and crown ethers (PSF-CNT-CE); bottom - SEM images of PSF membrane (A) and PSF-CNT membrane (B and C)

Water fluxes (Figure 2) were studied in order to evaluate hydrodynamic characteristics of synthesized membranes and also to predict the access of reagents to reaction centres at the surface of carbon nanotubes inside membrane pores. For composite membrane with carbon nanotubes, the decrease of water flow can be explained by the crosslinking effect of carbon nanotubes with consequence in the decrease of total porosity of membrane [14, 15]. After the derivatization with enzymes, the increase of water flows can be explained by the presence of hydrophilic groups from proteins at the surface of enzymes, the differences between the used three enzymes being a consequence of enzyme dimensions (which increase in order carbonic anhydrase<invertase<diastase). The immobilization of crown ethers, due to their hydrophobic character does not improve water fluxes. From SEM images, changes in membrane porosity can be observed, correlated with data obtained at water fluxes. These values

of fluxes recommend the synthesized membrane materials for biomedical applications like haemodialysis or proteins concentration. Single restriction that can be applied is the presence of carbon nanotubes, but using long nanotubes (>10 μm length) this limitation can be avoided (a part of carbon nanotube will be trapped in polymeric structure of membrane and another one will be free in membrane pore). In order to study this potential application, Bovine Serum Albumin and Haemoglobin retention were studied. Obtained data are presented in Table 1. Best obtained retention for composite membranes with diastase derivatized carbon nanotubes are attributed to high surface area of this enzyme which allows protein-protein interaction and aggregation inside membrane pore. Higher value for Bovine Serum Albumin is explained only by dimensional discrimination (lower protein volume lead to a higher aggregation of proteins inside membrane pores and surface).

PSF-CNT derivatized with	Retention (%) for	
	Bovine Serum Albumin	Haemoglobin
Carbonic anhydrase	79 ± 3	72 ± 4
Invertase	86 ± 8	79 ± 6
Diastase	91 ± 6	88 ± 1

Table 1: Retention of Bovine Serum Albumin and Haemoglobin for synthesized membranes.

Based on these data, for potential use in haemodialysis, the only parameter of membrane that must be adjusted is membrane surface, in order to substitute the kidney function. More than that, the use of composite membrane with crown ethers derivatized carbon nanotubes open a new possibility for removal of cations or heavy metals after possible intoxications and accumulation in biological fluids. Crown ethers are widely used molecules for removal of cations being very well known their ability to form stable complexes with cations.

Cations retentions were studied also for composite membrane with carbon nanotubes and on composite membrane with derivatized carbon nanotubes in order to see the differences between adsorption capacity of carbon nanotubes at their surface and complex capacity of crown ethers immobilized at the surface of carbon nanotubes. As it can be observed from Figure 3 higher rejection degrees were obtained from Na^+ due to its small dimension and high solubility in water (18-crown-6 ether presents higher complexation yield for sodium and potassium). Copper and lead have a large cation volume and equilibrium in complexation reaction with crown ethers is heavy to achieved due to steric spatial conformation. Differences in rejection degrees between composite membranes with carbon nanotubes and derivatized carbon nanotubes can be attributed exclusively to crown ethers (approximately 5%). Membranes can be also used for decontamination techniques where small amounts of heavy elements must be retained (wastes from electronic industry), or any

application where classical separation methods are inefficient.

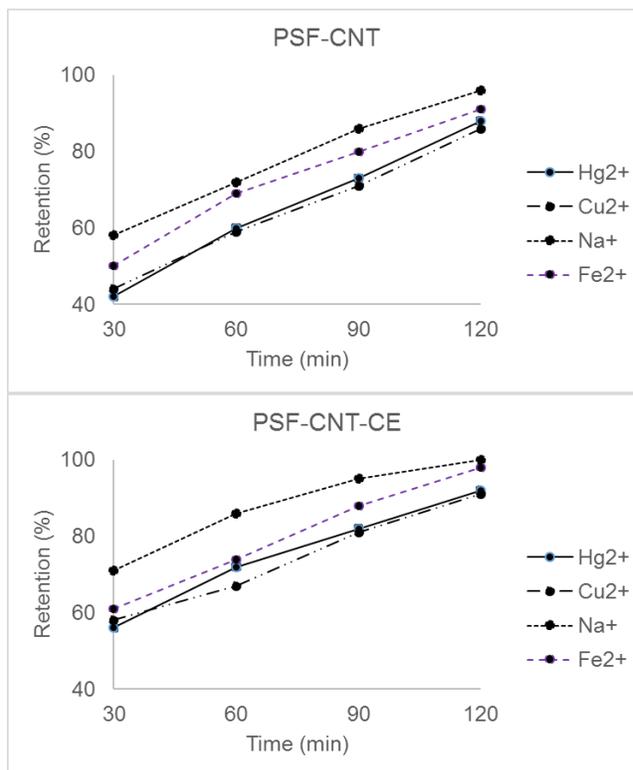


Figure 3: Cations retention for composite membranes with carbon nanotubes (PSF-CNT) and composite membranes with derivatized carbon nanotubes with crown ethers (PSF-CNT-CE).

Proposed method for derivatization of carbon nanotubes inside membrane pores allows the recovery of derivatized carbon nanotubes by dissolving the composite membrane in a proper solvent for polymer. Using this method, future researches will study the possibility to functionalize carbon nanotubes inside membrane pores by treatment in plasma, for inducing different functional groups at carbon nanotubes surface, like amino or carboxyl [16].

4 CONCLUSIONS

A new approach and concept for derivatization of carbon nanotubes using a polymeric membrane reactor was presented. The principle of method consists in the synthesis of polysulfone-amino carbon nanotubes composite membranes (by phase inversion) with controlled porosity, the access of reagents to reactive centres being favoured by diffusion through membrane pores. On this way, a part of carbon nanotubes will be trapped and fixed in polymeric structure of membrane and a part will be free in membrane pore (which will allow the access of reagents to reactions centres). Amino carbon nanotubes were derivatized with

enzymes (carbonic anhydrase, invertase, diastase) and amino-benzo-18-crown-6. Membranes were characterised by FT-IR, NMR and SEM. In terms of process application, Bovine Serum Albumin and Haemoglobin retentions were studied (best values for composite membranes with diastase derivatized carbon nanotubes, respectively 91±6% for Bovine Serum Albumin and 88±1% for Haemoglobin). Best rejection degree was achieved for Na⁺ (retained on composite membranes with crown ether derivatized carbon nanotubes), almost 99%.

5 ACKNOWLEDGEMENT

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