



# Modification of PVDF membrane by chitosan solution for reducing protein fouling

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## ABSTRACT

This work studied modification of hydrophobic membrane by chitosan solution for the purpose of reducing protein fouling. The membrane used was flat sheet polyvinylidene fluoride (PVDF) of 0.22  $\mu\text{m}$  pore size. The membranes were modified by 3 different methods, i.e. immersion method, flow through method and the combined flow through and surface flow method. Chitosan solution concentration and modification time were varied. The modified membranes were then neutralized with NaOH solution. The results of scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) study of modified membranes compared to unmodified membranes confirmed that there was chitosan coated on the membrane surfaces. The water contact angles and water fluxes decreased with increasing chitosan concentration and modification time. The result also indicated that modified membranes had higher hydrophilicity than unmodified membrane. In protein fouling experiment, bovine serum albumin (BSA) was used as a protein model solution. Modified membranes exhibited good anti-fouling properties in reducing the irreversible membrane fouling. The membrane modified by a combined flow through and surface flow method showed the best anti-fouling properties compared with other methods. Protein adsorption on the modified membrane was highest at the isoelectric point (IEP) of BSA solution and decreased as the solution pH was far from the IEP.

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## 1. Introduction

Poly(vinylidene fluoride) (PVDF) membrane is widely used in microfiltration, ultrafiltration and nanofiltration due to its excellent chemical resistance, good thermal and mechanical properties [1–3]. However, in the application involving protein solution, the protein adsorption on the membrane surface and in the membrane pores due to the inherent hydrophobic characteristic of PVDF often causes serious membrane fouling and a rapid decline of permeation flux.

Protein fouling in membrane processes is a complicated mechanism due to many factors affecting fouling formation. It is known that the electrostatic force and the hydrophobic interaction between certain domains in protein molecules and the hydrophobic membrane surfaces as well as between protein molecules are the main factors affecting membrane fouling [4,5]. Huisman et al. [6] reported that membrane–protein interactions influenced the fouling behavior in the initial stage of filtration and in the later stage of filtration, protein–protein interactions dictated the overall performance. The interactions also depend on other parameters such as membrane materials, solution type and operating conditions.

Solution pH is an important factor which can strongly affect membrane fouling and filtration performance. It was reported that change in pH could cause fouling in protein filtration. Zhao et al. [7] found that BSA adsorption on chitosan/PES (polyethersulfone) composite MF membrane was highest at the IEP (isoelectric point) and at low pH (3.0–4.7), the MF composite membranes had higher adsorption capacities of BSA than at higher pH range (6.0–8.0). Mo et al. [8] emphasized the effect of pH on BSA fouling in RO process. The study found that the most severe BSA fouling occurred at pH near IEP of BSA, where the electrostatic repulsion between BSA molecules was weakest.

To obtain a hydrophilic surface with anti-fouling property, several techniques have been studied. The modification by adsorbing suitable hydrophilic polymer on the membrane surface can introduce the repulsive force between membrane surface and protein molecules. Previous works reported that increasing membrane surface hydrophilicity such as modification by hydrophilic polymer through blending, coating and surface grafting could effectively reduce irreversible membrane fouling [9,10]. Many hydrophilic polymers have been coated on different base membranes, for examples, chitosan/poly(acrylonitrile) [11], carboxymethyl chitosan/poly(ethersulfone) [7], chitosan/polystyrene [12] and polyvinyl alcohol/polypropylene [13]. The hydrophilic polymers may be casted onto the membrane surfaces [14] or the membranes were immersed in the hydrophilic polymer solution

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[7]. These methods are limited by the fact that the hydrophilic modification occurs only on the membrane surface, while internal pores remain susceptible to fouling. A promising method to modify surface of internal pores is to force the hydrophilic polymer solution to flow through the membrane pores.

Chitosan is the hydrophilic polymer of interest for modifying the membrane in this work. Chitosan has been identified as hydrophilic, non-toxic, biodegradable, antibacterial, and biocompatible. It has been widely used for coating on hydrophobic membranes to increase hydrophilicity [11,12].

Only a few studies of coating hydrophilic polymer on PVDF membrane have been reported [15]. It may be because PVDF membranes are highly hydrophobic which make them difficult to be coated by hydrophilic polymers. The complicated methods are often applied in PVDF membranes modification such as UV-modification and grafting [15].

The present work focuses on modification of hydrophobic micro-filtration PVDF membrane to obtain the hydrophilic ultrafiltration membrane with anti-fouling properties. In this work, the PVDF commercial membrane was modified by chitosan solution using 3 different methods, i.e. (1) an immersion method, (2) a flow through method and (3) a combined flow through and surface flow method. The effects of chitosan concentration, modification time were investigated. In addition, protein fouling and adsorption behavior of the modified membranes at various pH were also reported.

## 2. Methodology

### 2.1. Materials

PVDF flat sheet membrane with reported pore size of 0.22  $\mu\text{m}$  was purchased from the Millipore Co. Ltd. Chitosan ( $M_n = 50,000$  Da, 85% deacetylation) was procured from NNC Production Co. Ltd., Thailand. Polyethylene glycols (PEG) with molecular weights 4, 15, 35, 100 and 400 kDa were supplied by Fluka. Dextran with molecular weight of 162 kDa was obtained from Sigma. Bovine serum albumin (BSA) was purchased from Fluka. Its molecular weight and IEP were 67,000 Da and 4.7, respectively. All chemicals were analytical grade. Deionized (DI) water was used for preparing all solutions.

### 2.2. Experimental setup

The schematic diagram for the filtration experiments is displayed in Fig. 1. The feed solution was supplied from the feed tank (2 l in volume) by a peristaltic pump (Masterflex, Model 77201-

62) through the flow meter and a pressure gauge before entering the membrane module. The module was a radial cross flow type that can be equipped with a circular flat sheet membrane with an effective area of 19.638  $\text{cm}^2$ . When the experimental setup was applied for membrane modification, both permeate and retentate were returned to the feed tank. For filtration experiments, the permeate was collected at different time intervals (to determine flux) and was then returned to the feed tank. The feed flow rate was fixed to 0.877 l/min for all experiments.

### 2.3. Membrane modification

Prior to modification, the water flux of the original membrane was determined at fixed conditions (flow rate of 0.877 l/min, applied pressure 1.5 bar, temperature 25 °C). We noticed variation in water flux for different pieces of membrane. Therefore, the membranes with water flux in range of  $1510 \pm 100$  l/m<sup>2</sup> h were selected for further modification. Before modification process, the membranes were wetted by filtering DI water for 5 min.

The chitosan was dissolved in 2 wt% aqueous acetic solution. The amount of chitosan was varied to obtain the chitosan solution with concentrations between 0.1 and 2.5 wt%. Three methods of modification were studied. For each method, chitosan concentration and time were varied.

- Method 1: Immersion method. The membrane was immersed in the chitosan solution with specific concentration and time.
- Method 2: A flow through method. The chitosan solution was fed at an applied pressure of 2 bar, through the membrane module.
- Method 3: A combined flow through and surface flow method. This method involved 2 steps of modification, each with equal time. The chitosan was fed through the membrane at an applied pressure of 2 bar. The operation was then switched to a surface flow mode in which the chitosan solution flowed (without applying any pressure) tangentially over the membrane surface.

The modified membranes from methods 1, 2 and 3 were dried by annealing in a vacuum oven at 60 °C for 45 min. After that the dried membranes were neutralized by filtering NaOH solution (1.0 M in 50%v water–ethanol mixture) for 30 min to ensure that all chitosan acetate was converted to chitosan. Then the membranes were cleaned by filtering 50%v ethanol solution for 10 min to remove the remaining NaOH and to prevent the osmotic crack, and followed by washing with DI water for 30 min. Finally, the membranes were dried at 25 °C.

### 2.4. Analysis

The concentrations of PEG and dextran were analyzed by Gel Permeation Chromatography (GPC) column (Polysep 4000) with HPLC [16,17]. UV–vis spectrometer (HP 8433) was used for analyzing BSA concentration.

### 2.5. Membrane characterizations

#### 2.5.1. Fourier transform infrared spectroscopy (FTIR) study

To investigate the chemical structures of PVDF membrane, chitosan and modified membranes, Thermo-Nicolet Magna 550 FTIR was used with 50° angle of incidence. Each spectrum was collected by cumulating 32 scans at a resolution of 4  $\text{cm}^{-1}$ .

#### 2.5.2. Membrane morphology study

The surface and the cross-sectional morphology of the membranes were characterized by scanning electron microscopy (SEM, LEO model 1455VP). All samples were dried in vacuum for 12 h at

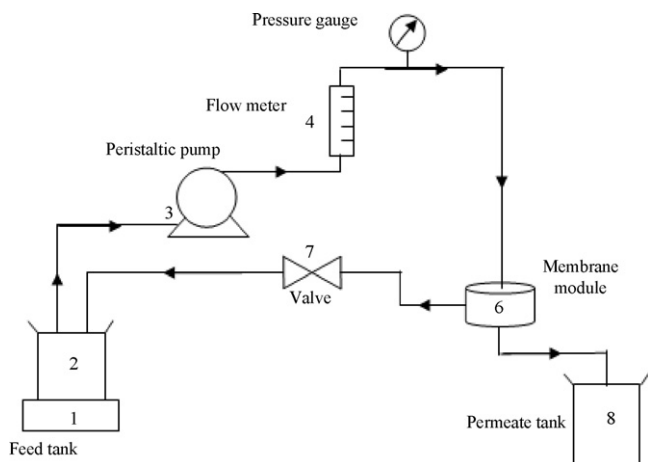


Fig. 1. Schematic diagram of the radial cross flow ultrafiltration (UF) unit.

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