Preparation and properties of composite membranes composed of non-conductive membranes and polypyrrole

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Conductive composite membrane was prepared by oxidation of pyrrole in the commercial microfiltration membrane support using ferric ions and ascorbic acid as polymerization and oxidation agents, respectively. The concentrations for pyrrole and ferric chloride solutions were optimized as 0.745 and 2 molar, respectively. An acceptable conductivity resistivity equals to 42.1 Kohm.cm was obtained in these conditions. Filtration of BSA (bovine serum albumin-charged protein) solution was carried out to investigate the properties of prepared membrane. Higher fluxes were obtained for conductive membrane, exhibiting the effect of the membrane conductivity. Both BSA and membrane are negatively charged. This results in the partial repulsion of BSA from the membrane surface or membrane matrix due to the electrostatic barrier. Repulsion means less concentration polarization and fouling i.e. lower resistivity against the passage through the membrane or higher flux. For conductive membrane higher rejection was obtained compared to non-conductive membrane. This effect is attributed to the conductivity of the membrane. The negatively charged membrane surface acts as a barrier against BSA. A part of the protein is pushed back due to the electrostatic effect. This results in higher rejection.

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In recent years, interests in the preparation and application of conducting membranes have grown. The conductive membranes exhibit unique properties including in situ alteration of transport of ionic species across the membrane by switching on and off an appropriate electrical potential which results in the control of the transport rate and the selectivity of the membrane. Wallace and co-workers reported in situ electrodynamic control.

Development of new low-price ion conductive membranes is an ongoing research. For preparation of conducting membranes, two major techniques have been introduced. The first procedure includes employment of intrinsic conducting polymers with conjugated double bonds for membrane fabrication. The natural reversible electronegativity of conductive polymers results in dynamic membranes. These materials are capable to change from an oxide state (conductive) to a reduced state (less conductive). The chemical changes that occur can be considered as an important factor for transmission of selected materials through the membrane.

The second procedure is modification of the prepared non-conductive membranes by coating the conductive materials on the surface of non-conductive membranes. Two types of conductive coatings, i.e. metal and conductive polymers are used for this purpose. The metal coatings (Au) are set as a thin layer on the surface of the membrane. The layer has a thickness of around 60 nm and can be coated without any membrane pore blockage. The water flux may somewhat be reduced. The surface of a non-conductive membrane or a support may be coated by conductive polymers via chemical polymerization of the monomers. Such a technique covers the membrane structure with conductive polymers.

Many polymers have been employed for preparation of conductive membranes including poly(vinylidene fluoride)/polyaniline blends, sulfonated polyphenylsulfone, sulfonated poly(ether ketones) and a mixture of polycarbonate-polypyrrole. Specific procedures have been used for modification of non-conductive membrane to prepare conductive membranes. The techniques include irradiation treatment of polyvinylfluoride (PVF) films, direct sulfonation of poly (vinyl fluoride) and controlled sulfonation of EPDM.

Among conducting polymers, polypyrrole is one of the most promising materials for multifunctionalized
applications due to its good environmental stability and higher conductivity compared to other conducting polymers3. Polypyrrole has a tight, rigid structure with weakly basic anion-exchangeable groups, which is easily polymerized by chemical or electrochemical oxidation17.

Polypyrrole can be used as the membrane matrix. The membrane may be prepared galvanostatically18, or by electrochemical polymerization19,20 with an excellent dynamic chemical/electrochemical properties21. Polypyrrole has been employed for preparation of organic/inorganic composite system22. The prepared polypyrrole membranes have been used for ion exchange, pervaporation, gas separation1, membrane-based sensors23, selective ion-sensitive membrane electrode22 and the release of anionic drugs20.

Polypyrrole may also be deposited as the coating medium on a wide variety of supporting materials such as microporous teflon24, filter paper25, ion exchange membranes26, microfiltration membrane27, nylon fabrics28, zeolite29, alumina30, stainless steel31 and polycarbonate membranes32. Polypyrrole may be directly synthesized on membrane9, coated by a second electrochemical deposition27 or by chemical oxidation of pyrrole in the membrane matrix17.

The polymerization of pyrrole within polymeric membranes produces composites with desirable properties. Pyrrole has been polymerized within cation exchange membranes to produce membranes with electrochemically controlled ion exchange characteristics33. For example, the combination of the electroactivity of polypyrrole and ion-exchange capacity of Nafion provides materials with novel properties34. The selectivity of ions through polypyrrole/porous polypropylene composite membrane can be highly controlled by potential application35.

In this work polypyrrole was used as the conducting agent. A procedure similar to that used by Sata and co-workers17 was adopted for preparation of conductive membrane. They selected an anion exchange support. However a non-conductive membrane was used as the support in this work. The conductivity of the prepared membrane was evaluated and the passage of charged molecules (BSA) through original and modified membranes were compared to find the effect of membrane conductivity on permeate flux and rejection of BSA.

### Experimental Procedure

#### Materials

The commercially available polyvinilidene fluoride membrane was used as the non-conductive support for the preparation of conductive membrane. The characteristics of the used membrane (GVHP) are summarized in Table 1.

Pyrrole (density, 0.97 Kg/L) was used as the conducting agent. The other chemicals used in this work include ascorbic acid, ferric chloride and hydrochloric acid (all from Merck Company).

#### Preparation of conductive membranes

The conductive composite membranes were prepared by oxidation of pyrrole in the membrane matrix i.e. coating the polypyrrole on the PVDF support which was a microfiltration membrane. Ferric ions and ascorbic acid were used as polymerization and oxidation agents, respectively.

Two different procedures are applicable: immersing the non-conductive membranes equilibrated with a ferric chloride solution into an aqueous pyrrole solution or immersing non-conductive membranes equilibrated with the pyrrole solution into the ferric chloride solution17.

#### Method I

This method results in a conductive membrane with polypyrrole spread homogeneously throughout the cross-section of the support. For preparing this type of conductive membrane, pyrrole was polymerized with ferric ions, an oxidative agent, adsorbed in the non-conductive membranes. A substantial amount of ferric ions should be adsorbed in the membrane and therefore the support was left at least for 24 h in the ferric chloride solution. After that, the membrane was taken out and washed with one molar hydrochloric acid to remove non-adsorbed ferric chloride ions. Only the absorbed ferric ions remained in the support. The membrane was blot dried with filter paper and placed in the pyrrole solution for 12 h. However, 4 h is sufficient to polymerize pyrrole in the membrane matrix17. The membrane was taken out and blot dried.

<table>
<thead>
<tr>
<th>Table 1—Characteristics of the GVHP membrane</th>
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<tr>
<td>Manufacturer</td>
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<tr>
<td>Material</td>
</tr>
<tr>
<td>Hydrophobicity</td>
</tr>
<tr>
<td>Mean pore size (µm)</td>
</tr>
<tr>
<td>Porosity (%)</td>
</tr>
<tr>
<td>Thickness (µm)</td>
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</table>
The oxidation agent plays a key role in the membrane conductivity. In this study, ascorbic acid was used as the oxidation agent. Ascorbic acid was added to the pyrrole solution and the membrane was left in the solution. The prepared conductive membrane was called the Fe-Py membrane.

**Method II**

In this method, the composite membrane is prepared with a thin layer of polypyrrole on the surface of the support. When the support is soaked in monomer medium, chemical polymerization at the interface results in the formation of a thin layer on the membrane surface. Polypyrrole film completely covers the support. The support was left in the pyrrole solution for at least 40 h to attain equilibrium. Ascorbic acid was added to the pyrrole solution. After that the membrane was taken out and immersed in the ferric chloride solution without drying. The membrane was taken out and the additional solution on the surface of the membrane was dripped. There is no need to dry the membrane again. The thickness of the deposited polymer depends on the polymerization time. The prepared membrane was called Py-Fe membrane.

**Measurement of the electrical conductivity of the prepared membrane**

To confirm the polymerization of pyrrole in the membrane matrix, the electrical conductivities of the prepared membranes were measured. A rather simple method was employed for measurement of conductivity of the prepared membranes. Metal elements were cut to the size of 2.5 × 1 cm with a thickness of 3 mm. It is necessary to reduce the contact resistance of the elements for accurate measurement tests. The prepared membranes with the dimensions of 1 × 3 cm were set on a completely non-conducting surface. Two metal elements were placed at the ends of the membrane. The distance between the two elements was 1 cm. The surface resistivity of the membrane was measured using an ohm-meter connected to the metal elements. To measure the bulk resistivity of the membrane (resistivity along the cross-section of the membrane) two elements were placed on two sides i.e. the lower and upper surfaces of the membrane and the ohm-meter was connected to the elements.

**Filtration experiments**

The performances of the prepared membranes were characterised by filtration of BSA solution through the membrane. All experiments were carried out in a 110 mL batch cell, with a membrane area of 15.2 cm². The cell (Fig. 1) consisted of a cylindrical vessel containing the test solution; two circular end pieces all were made from Perspex and a porous medium to support the membrane. The top end piece of the cell contained a feed and a gas inlet and a pressure relief valve. Stirring was achieved by an internal magnetic bar (25.4 mm long, 6.4 mm diameter) suspended 2 mm above the membrane. Nitrogen gas was used to pressurize the cell to operating pressure. The experiments were started by quickly pressurizing the cell after 100 mL of the suspension was poured into the cell. The suspension was continually fed from a reservoir connected to the cell to replenish the permeate.

**Determination of BSA concentration**

BSA was used as the feed for investigation of the properties of the prepared conductive membrane. BSA is an oblate ellipsoid charged protein with dimensions of 14 × 4 nm and the molecular weight of 67,000 D. The retention of protein was investigated for the prepared membranes by measuring the amount of BSA in the permeate using the standard Bradford method. The NaCl (0.15 M) solution was mixed with the sample. One millilitre of Bradford solution was added to 100 mL of the prepared sample. The absorption of this sample was measured at 595 nm using spectrophotometer.
Results and Discussion

Membrane conductivity

For assessment of the effect of concentration of pyrrole and ferric chloride solutions on the membrane conductivity, different solutions were prepared and tested. Three levels of pyrrole solutions i.e. 0.5, 0.7 and 1 molar and three levels of ferric chloride solutions i.e. 1, 2 and 3 molar were selected and assessed. Both Fe-Py and Py-Fe membranes were prepared with various solutions of pyrrole and ferric chloride.

The results for Fe-Py membranes are presented in Table 2. The infinite resistivity means no observed conductivity. This was the limits of the apparatus used. The electrical conductivity of the prepared membranes was measured using ohm meter. The 0.5 molar pyrrole solution did not show any pronounced result due to inadequate formation of polypyrrole on the membrane. The resistivities of the membranes prepared with 0.7 molar pyrrole solution were in a range of 45500-48.9 Kohm.cm depending on the ferric chloride concentration. Lower resistivity was obtained for higher ferric chloride concentration. For 1 molar pyrrole solution, the obtained results change from 3600 (for 1 molar ferric chloride solution) to 39.1 (for 3 molar ferric chloride solution) Kohm.cm.

The role of FeCl$_3$ is very important in this work. This is the main component for facilitating the polymerization process. The polymerization results in adequate polypyrrole to provide the conductivity. This is the reason for observing a drop in resistivity by changing the concentration of FeCl$_3$ from 1 to 2 molar. The details of the mechanism has been discussed elsewhere$^{17}$. This is a benefit of this system that a small change in the FeCl$_3$ concentration results in a steep increase in conductivity or a huge drop in resistivity.

<table>
<thead>
<tr>
<th>Pyrrole concentration (mol/L)</th>
<th>Ferric chloride concentration (mol/L)</th>
<th>Electrical resistivity (Kohm.cm)</th>
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<tbody>
<tr>
<td>0.5</td>
<td>1</td>
<td>Infinite</td>
</tr>
<tr>
<td>0.5</td>
<td>2</td>
<td>Infinite</td>
</tr>
<tr>
<td>0.5</td>
<td>3</td>
<td>Infinite</td>
</tr>
<tr>
<td>0.7</td>
<td>1</td>
<td>45500</td>
</tr>
<tr>
<td>0.7</td>
<td>2</td>
<td>49.8</td>
</tr>
<tr>
<td>0.7</td>
<td>3</td>
<td>48.9</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>3600</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>41.3</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>39.1</td>
</tr>
<tr>
<td>0.745</td>
<td>2</td>
<td>42.1</td>
</tr>
<tr>
<td>0.745</td>
<td>3</td>
<td>41.7</td>
</tr>
</tbody>
</table>

Table 2— The effect of concentration of ferric chloride and pyrrole solutions on the electrical resistivity of Fe-Py membranes

The data indicate that both 0.7 and 1 molar pyrrole solutions combined with 2 or 3 molar ferric chloride solutions result in membranes with the resistivities in the same range (49.8, 48.9, 41.3 and 39.1 Kohm.cm). These membranes exhibit acceptable conductivities. However 0.745 molar pyrrole solution was selected as the optimum concentration in accordance with the other researchers$^{17}$. Although pyrrole solutions with higher concentration exhibit slightly better conductivity (41.3 versus 49.8 for 2 molar ferric chloride solutions and 39.1 versus 48.9 for 3 molar ferric chloride solutions) a concentration close to lower concentration was selected as the optimum concentration to reduce the consumption of pyrrole which is rather expensive.

For optimum concentration of pyrrole solution (0.745 molar), the concentration of ferric solution was changed from 2 to 3 molar. The resistivity of the prepared membrane changed from 42.1 to 41.7 Kohm.cm (Table 2). This means that an increase in the concentration of ferric solution does not increase the conductivity of the membrane substantially. However due to the benefit of lower consumption of ferric chloride solution, 2 molar was selected as the optimum concentration for ferric chloride. A resistivity of 42.1 Kohm.cm was achieved with these conditions.

A similar trend was found for Py-Fe membranes (Table 3). With the optimum concentration of pyrrole and ferric chloride solutions i.e. 0.745 and 2 molar, respectively, a resistivity of 65.5 Kohm.cm was obtained.

Lower resistivity (or higher conductivity) obtained for Fe-Py compared to Py-Fe membrane (42.1 versus 65.5 Kohm.cm) indicates the superiority of the first (polypyrrole spread through membrane cross-section)
versus the second technique (polypyrrole forms a thin layer on the membrane surface) for preparation of conductive membranes composed of polypyrrole and PVDF support.

**Effect of membrane conductivity on flux and rejection of BSA**

If the non-conductive membrane is properly converted to conductive membrane, the filtration behaviour for charged particles is affected. This is due to the transport mechanism through the membrane.

Filtration of BSA (charged protein) solution was carried out to investigate the possible effect of the prepared conductive membrane. Key factors for determination of filtration behaviour are flux and rejection. Flux indicates the rate of the matter that pass through the membrane and rejection shows the percentage of the species that is rejected by the membrane. In this study, aqueous BSA solution was filtered. Water passes through the membrane and BSA is rejected by microfiltration membrane.

The results for flux of aqueous solutions of BSA using conductive and non-conductive membranes are presented in Fig. 2. Non-conductive membrane was the commercial GVHP membrane (Table 1) and conductive membrane was the Fe-Py membrane prepared in this work.

For non-conductive membrane, flux declined from 200 to 45 L/m².h in 75 min. This is a typical behaviour for microfiltration which is due to the concentration polarization and fouling. Concentration polarization means the accumulation of species available in the solution which do not pass through the membrane completely. Fouling indicates the deposition of materials on the membrane surface or in the membrane matrix which significantly blocks the membrane pores. Both phenomena provide a resistivity against the passage through the membrane.

For conductive membrane, higher fluxes were obtained for the same condition. The flux declined from 340 to 60 L/m².h in 75 min which are higher compared to the fluxes for non-conductive membranes (Fig. 2). This exhibits the effect of the membrane conductivity. Both BSA and membrane are negatively charged. This results in the partial repulsion of BSA from the membrane surface or membrane matrix due to the electrostatic barrier. Repulsion means less concentration polarization and fouling i.e. lower resistant against the passage through the membrane or higher flux.

The results for rejection of BSA using conductive and non-conductive membranes are depicted in Fig. 3. For non-conductive membrane the rejection increased from 55 to 78% during 75 min. This behaviour is expected due to accumulation of the BSA particles on the surface of the membrane or within the membrane matrix. The size of the BSA particles (14 × 4 nm) are less than membrane pores (220 nm). The reason for

![Fig. 2 — Flux versus time for BSA solution using treated and non-treated membrane](image1)

![Fig. 3 — Rejection versus time for BSA solution using treated and non-treated membrane](image2)
rejection of BSA molecules through microfiltration membrane is adsorption of BSA on the membrane. The adsorption increases during time which results in an increment in rejection.

For conductive membrane higher rejection was obtained compared to non-conductive membrane (Fig. 3). The rejection was increased from 75 to 90% during 75 min. This effect can be attributed to the conductivity of the membrane. The negatively charged membrane surface acts as a barrier against BSA. A part of the protein is pushed back due to the electrostatic effect. This results in higher rejection.

Conclusion

A commercial non-conductive microfiltration membrane can be converted to conductive composite membrane using pyrrole (0.745 molar) and ferric ions (2 molar) in the presence of ascorbic acid. The filtration of charged species such as BSA depends on the conductivity of the membrane. Higher fluxes and higher rejections were obtained for conductive membranes compared to non-conductive membrane in the same condition. The electrostatic partial repulsion of BSA from the membrane surface or membrane matrix is responsible for this behaviour.

Acknowledgement

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References