Preparation of PVA membrane on hydrolyzed polyester fabric to be used as ultrafiltration in water treatment.

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Abstract

The preparation of polyvinyl alcohol (PVA) membrane on hydrolyzed polyester fabric was investigated. Cross-linking of PVA was conducted by using two kinds of aldehydes namely formaldehyde and acetaldehyde in the presence of H₂SO₄, as catalyst, in the room temperature range of 25-30 °C. The using of polyvinyl alcohol with high degree of polymerization 250,000 MW produced good thin-film membranes on polyester fabric. Scanning electron microscope (SEM) study revealed that the produced membranes have homogeneous surface with no significant change in the surface morphology of the prepared film coated polyester membrane using formaldehyde and acetaldehyde solutions. Also the produced film coated membranes application for filtration of raw and industrial waste water was investigated with different applied pressure for ultrafiltration technique.

Key word: PVA membrane, Ultrafiltration, water treatment and hydrolyzed polyester.

1- Introduction:

Poly (vinyl alcohol) (PVA) is human and environmental safe material, has always seemed an attractive material for producing membranes. It is a very important membrane material. PVA Produced by the polymerization of vinyl acetate is an odorless and tasteless, translucent, white or cream colored granular powder with high swollen and high tendency to attract water and it can be even dissolved in water at room temperature. PVA has been widely used in PV dehydration of organic liquids due to its good hydrophilicity. The swelling of the PVA membrane was reduced by crosslinking with a variety of chemical and physical methods (Gohil et al, 2006; Kumar and D’Souza, 2008). Normally, the inherent hydrophilicity of PVA makes it a very useful polymer for dehydration applications using membranes. To create a stable membrane with good mechanical
properties and permeabilities to water, many modification methods have been studied by researchers, such as cross-linking (Xie et al, 2011; Das et al, 2011; Singha et al, 2009), blending (Hong et al, 2011; Magadal et al, 2010), filling (Lin et al, 2012; Teli et al, 2011; Khoonsap and Amnuaypanich, 2011) and surface modification (Meng et al, 2010; Ma et al, 2010; Rachipudi et al, 2011; Zhang et al, 2012; Zhang et al, 2012). PVA is known to be truly biodegradable, biocompatible, and of excellent film-forming properties and toughness (Lyoo and Ha, 1996). PVA is a non-toxic and biocompatible synthetic polymer with good chemical and thermal stability (Kumar and D’Souza, 2008), facile film-forming film ability, hydrophilic nature, and chemical Mechanical stability (Smitha et al, 2005; Mustafa et al, 2016). PVA used as a very important membrane material due to its good hydrophilicity, has a very important advantages of chemical and thermal resistance, high anti-fouling potential, and high water permeability superior membrane-forming properties and good resistance to organic mixtures (Mandal and Sant, 2011; Razavi et al, 2011; Hu et al, 2012). Its excellent tensile strength and flexibility make PVA ideal for fiber strength improvements and modifications, chemically stable and non-toxic, good antimicrobial polymers (Kenawy et al, 2007; Pal et al, 2009). The presence of –OH functional groups be effectively in cross-linked by aldehydes, resulting in remarkable improvements in their thermal and mechanical stabilities (Kang, 2005; Smitha, 2005), improving membrane physicochemical properties, such as hydrophobicity, crystallinity, and mechanical strength (Guo et al, 2007; Muhammed et al, 2012). Studied the kinetics of the formation of the formal of PVA. It was reported that the rate was proportional to the product of the stoichiometric concentrations of formaldehyde and the hydroxyl group of PVA. (Kim et al, 1994).

In this paper, the crosslinking reaction of PVA membrane on hydrolyzed polyester fabric using formaldehyde or acetaldehyde as a crosslinking agents are investigated. Also the produced film coated membranes application for filtration of raw and industrial waste water was investigated with different applied pressure for ultrafiltration technique.

2- Material and Methods:
2-1. Materials:

Polyvinyl alcohol M.W app. (250,000) with degrees of hydrolysis (88%) supplied by Rassayan.SD-Fin-Chemical ltd. Boisar., formaldehyde supplied by Horizon Chemical For Special Chemicals Company, acetaldehyde supplied by Almotaheda for trading and general supplies, Sodium sulphate supplied by ADWIC, sulphuric acid, hydrochloric acid and other chemicals were of pure grad.
2-2. Preparation of hydrolyzed polyester:

The polyester fabrics were cut to prepare short pieces approximately (16 x 12.5) cm in length and width. The pieces were immersed in trays containing 200 cc of 10% aqueous NaOH. The trays were kept in a constant temperature 30°C for 2 hours. At the end of the designated time the polyester fabrics were removed and rinsed with distilled water several times and dried at room temperature.

2-3. Preparation of (PVA) film coated polyester:

The air dried polyvinyl alcohol films about 100 to 150 micrometers thick at room temperature, were thermally compressed on partially wet hydrolyzed polyester fabrics to produce will stuck PVA/polyester fabric. The product was cut into suitable test specimens (16 x 12.5) cm. The PVA/polyester membranes were treated with the following solutions at 25-30 °C for 1 hour. A three different concentrations 3, 6 and 9% of formaldehyde or acetaldehyde in a solution contained 1 liter water, 20 ml concentrated H₂SO₄, and 200 grams Na₂SO₄ as salting out agent to decrease solubility of the PVA film during the reaction. The sulfuric acid used as a catalyst, and sodium sulfate inhibits the solubility of the polyvinyl alcohol film. The treated films and PVA coated polyester were washed with water and treated with 1 percent aqueous HCl at 30 °C for 1/2 hour to complete the reaction. At this time the film has lost its water solubility. After the HCl treatment, the films were immersed for several minutes in water and then in dilute sodium bicarbonate solution to neutralize acid residues. This is an important step if dried films are to be stored for long time periods because acid remaining in the film causes decomposition of the acetalized polymer. The film was again immersed in water several times to remove salts and then air dried at room temperature. The dried PVA film coated polyester membrane stored in 45 percent KOH for at least 24 hours prior to the taking of investigation measurements.

2-2. Testing and Analysis:

The produced film coated polyester fabrics were examined in the following manner:

2-2-1. PVA membranes Inspection by (SEM):

PVA film coated polyester membranes surface was inspected by Scanning Electron Microscope FEI-Inspect S50.

2.2.1.1 Estimation of permeability and water permeation:

The water permeation and membrane characteristic was estimating using Osmonics Membrane Test Cell (C).
2.2.2 Water analysis:

The following series of water examination and chemical analysis were carried out according to the standard method of ASTM Book of Standards (Audrey et al., 1997a and Audrey et al., 1997b).

2.2.2.1 Atomic absorption for determination of heavy metal in water:

The heavy metals were determined by using atomic absorption spectrometer Solaar S-4S Series Thermo Electron Corporation UK.

2.2.2.2 Turbidity:

Turbidity was measured in Nephelometric Turbidity Units (N.T.U.) using HANNA LP200-H, turbidimeter according to ASTM D 1889-81.

2.2.2.3 pH test:

pH was determined by using pH meter HI 120, according to ASTM(D1293-04).

2.2.2.4 Colloidal silica:

- The Colloidal silica was determined by deducting the dissolved silica from the total silica.
- The total silica was measured according to ASTM (D859-04) using spectrophotometer using Baush & lamb, spectronic 2000 spectrophotometer.

2.2.2.5 Organic matter test:

The organic matter expressed as KMnO₄ was measured according to Degremont (Degremont, ,1991)

3- Results and discussion:

3.1 PVA Cross-linking with aldehyde:

In general polyvinyl alcohol reacts with aldehydes such as formaldehyde or acetaldehyde in acidic media to form water insoluble poly-formals or poly-acetals (Sorenson and Campbell, 2001). Reaction with aldehydes is expected to form formal or acetal cross-linked structure.

3.2 Representation of film coated polyester membrane:

A schematic diagram was made to illustrate the structure of PVA film-coated polyester membrane, assuming that film coated membrane can be roughly illustrated as in figure (1).
3.3 Investigation of film coated polyester membrane:

PVA film coated polyester fabric membrane has not yet been reported. In order to make an investigation of these unique membranes for long-term operational stability during ultrafiltration, the effect of aldehydes concentration was investigated in case of using formaldehyde and acetaldehyde.

As mentioned above treatment of PVA film coated polyester with aldehyde solution in the presence of sulphuric acid as a catalyst renders the PVA insoluble in water due to intramolecular blocking of tow OH- groups, the blocking in the 1, 3 position of PVA , few cross-links occurs between OH -groups of two or more neighboring chains (Gohil et al., 2006). This treatment of PVA gave higher water absorption, and also found to possess excellent dimensional stability, resistance to abrasion, remarkable tensile strength, and elongation (Muhammad et al., 2015; Rajaeian, 2012; Das et al., 2010).

The following equation represents the blocking of two intramolecular blocking of tow OH- groups in the 1, 3 position of PVA in case of using formaldehyde for explanation:

\[
\text{OH - OH} + \text{CH}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4} \text{O - O}
\]

3.3.1 Finishing of PVA film on hydrolyzed polyester fabric:

Alkaline hydrolysis is one of the most classic fiber finishing methods, however, its potential as tuning surface super hydrophobicity in mass scale has not been studied much. In this research, fine roughness was formed on the polyester fiber surfaces by alkaline hydrolysis at room temperature. As alkaline hydrolysis treatment time increased, surface roughness was increased as a lot of nano-craters were generated with the decrease of fabrics weight and tensile strength as
well. As air pockets formed through nano-craters on the fiber surfaces, static contact angle increased, and shedding angle tended to decrease (Mi et al., 2016).

In the present study, Wet partially hydrolyzed polyester fabric is compressed on PVA film, in presence of formaldehyde or acetaldehyde solution to form PVA polyester mixed phase via chemical and physical bonds.

The reaction may occur at this phase as suggested as the following schema:

![Chemical Reaction Schema](image1)

To avoid complicated chemical formula, the units of partially hydrolyzed polyester are represented by the symbol PET-OH, while polyvinyl alcohol chains are shown by wavy lines. The functional groups only are indicated by the chemical formula.

The treatment of polyvinyl alcohol with aldehyde solution may also form crosslinking structure via acetylation that can be explained as follow:

![Chemical Reaction Schema](image2)

In addition acetylation may also occur between two OH End groups of partially hydrolyzed polyester chains as suggested in the following scheme:

![Chemical Reaction Schema](image3)
Figure (2) show the schematic representation of the structure of film coated PVA/ polyester fabric in case of using formaldehyde (A) and acetaldehyde (B) as cross-linking agents. Also the physical and chemical bond are represented.

3.3.2 Surface morphology of PVA / polyester fabric:

Figure (3) shows SEM images of PVA film coated membranes prepared from PVA film and polyester fabric at different concentration of aldehyde.
As seen in Figure (3) there is no significant change in the surface morphology of the prepared film coated polyester membrane using formaldehyde and acetaldehyde solutions.

Figure (4) shows the SEM images of PVA/polyester fabric membrane at the polyester fabric side.

Figure (5) shows the SEM image of the PVA film alone in case of using formaldehyde and acetaldehyde solution.
Figure (6) shows the Photomicrograph of cross section film coated PVA/Polyester fabric membrane. The figure illustrates each of polyester side, PVA film side and interfacial area between them.

3.3.3 Typical photograph of the prepared PVA film coated polyester membranes:

Figure (7) Show the typical photograph of film coated polyester membrane in both PVA film and polyester side. It clearly seen that the PVA film was completely stuck on the polyester fabric and apiaries as shiny layer in in both case of treatment using formaldehyde or acetaldehyde. On the other
hand the other side (polyester fabric) does not deteriorate by such treatment as can be seen from figure (7).

![Figure 7](image)

**Figure (7)** Show the typical photograph of film coated polyester membrane in both PVA film and polyester side.

### 2-4. Application of the prepared PVA film coated polyester membranes for filtration:

The comparison of filtration characteristics of the prepared PVA membrane and other membranes using micro, ultra and nano filtration techniques was investigated in this part. The performances of the two different prepared membrane using 9% formaldehyde or acetaldehyde solution were chosen. Also some general conclusion is given and reported.

The membrane performance was evaluated by determining the reduction of certain measurable parameters in the feed water such as turbidity, total organic matter (T.O.M), colloid silica, total
solids (T.S), conductivity, residual aluminum and some metal ions. Also the water fluxes and pressure differences for all membranes under test were studied in case of turbulent flow.

3.3.3.1 Evaluation of the prepared membrane in the filtration of water:

The investigated raw and industrial waste water having high turbidity, solid content, organic matter and some elements, were tested by using clarification and membrane filtration. This part mainly includes the results of the laboratory trials in order to evaluate the previously tested membranes of (MF, UF and NF) and to compare the corresponding trial results of the laboratory with the conventional clarification.

A comparison was made between the different types of membranes MF, UF, NF and the two prepared membrane PVA I and II, where Micro, Ultra and Nano filtration membranes were used as a controls and were supplied by Osmonics Inc., having the following characteristics:

— Microfiltration membrane, SEPA CF Cell, RHO2 part No 55411.
— Ultrafiltration membrane, SEPA CF Cell, RHO2 part No 55410.
— Nanofiltration membrane, SEPA CF Cell, MXO7, part No. 55409.

The comparison was deducted as the following:

3.3.3.2 Permeate flux:

The membranes were tested by using SEPA CF membrane cell as a lab scale cross flow membrane filtration unit. The turbulent flow of water was parallel and carried out by changing the feed water spacer. The data produced when studying the effect of pressure and time of operation, are given.

The data obtained were collected in figures (10-12). These results show a significant change in the specification of the produced water had occurred, by membrane filtrations. These results signified that the quality of the water produced from PVA (I and II) have approximately the same as that produced form ultrafiltration (UF) membrane for both raw and industrial waste water as can be seen from figures (10-12).

The above finding indicates that the PVA (I and II) membranes prepared by formaldehyde and that by acetaldehyde respectively, act as an ultrafiltration (UF) membranes. Therefore PVA (I and II) can be used as ultrafiltration technique.
Figure (10): Effect of increasing applied pressure and time on the permeate flux of raw water, of the different membranes.

Figure (11): Effect of increasing applied pressure and time on the permeate flux of raw water, of the different membranes.
Figure (12): Effect of increasing applied pressure and time on the permeate flux of raw water, of the different membranes

3.3.5 Characteristics of filtered raw and industrial waste water:

Characteristics of filtered raw and industrial waste water by using MF, UF and NF membranes supplied by Osmonics Inc., were evaluated, with respect to that obtained from PVA (I and II).

The obtained data of pure water produced by using PVA membrane (I and II) were as that obtained in case of using ultrafiltration UF membrane.

Table (1): Variation of raw water constituents by membrane filtration

- *T.O.M = Total organic matter*
- *Membranes was tested on one stage at a temperature = 25 °C and operating time 15 minutes.*

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Raw water</th>
<th>MF</th>
<th>UF</th>
<th>NF</th>
<th>PVA I</th>
<th>PVA II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity (N.T.U)</td>
<td>13.000</td>
<td>1.200</td>
<td>0.800</td>
<td>0.600</td>
<td>0.800</td>
<td>0.700</td>
</tr>
<tr>
<td>Conductivity (µS)</td>
<td>375.000</td>
<td>358.000</td>
<td>348.000</td>
<td>300.000</td>
<td>345.000</td>
<td>343.000</td>
</tr>
<tr>
<td>pH</td>
<td>7.700</td>
<td>7.600</td>
<td>7.600</td>
<td>7.500</td>
<td>7.500</td>
<td>7.500</td>
</tr>
<tr>
<td>Total Solid mg/L</td>
<td>272.000</td>
<td>248.000</td>
<td>232.000</td>
<td>200.000</td>
<td>231.000</td>
<td>230.000</td>
</tr>
<tr>
<td>T.O.M mg/L</td>
<td>22.000</td>
<td>13.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Colloidal silica mg/L</td>
<td>3.600</td>
<td>2.200</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Pb mg/L</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>Mn mg/L</td>
<td>0.050</td>
<td>0.030</td>
<td>0.020</td>
<td>0.010</td>
<td>0.020</td>
<td>0.015</td>
</tr>
<tr>
<td>Cu mg/L</td>
<td>0.043</td>
<td>0.033</td>
<td>0.008</td>
<td>0.002</td>
<td>0.007</td>
<td>0.006</td>
</tr>
<tr>
<td>Cr mg/L</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>Zn mg/L</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>Fe mg/L</td>
<td>0.130</td>
<td>0.100</td>
<td>0.050</td>
<td>0.010</td>
<td>0.040</td>
<td>0.020</td>
</tr>
</tbody>
</table>
Table (2): Variation of industrial waste water constituents by membrane filtration:

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Industrial waste water</th>
<th>Filtered water using different membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MF</td>
<td>UF</td>
</tr>
<tr>
<td>Turbidity (N.T.U)</td>
<td>14.000</td>
<td>1.400</td>
</tr>
<tr>
<td>Conductivity (µS)</td>
<td>675.000</td>
<td>872.000</td>
</tr>
<tr>
<td>PH</td>
<td>7.600</td>
<td>7.200</td>
</tr>
<tr>
<td>Total Solid mg/L</td>
<td>620.000</td>
<td>575.000</td>
</tr>
<tr>
<td>T.O.M mg/L</td>
<td>35.000</td>
<td>15.000</td>
</tr>
<tr>
<td>Colloidal silica mg/L</td>
<td>4.800</td>
<td>2.300</td>
</tr>
<tr>
<td>Pb mg/L</td>
<td>0.180</td>
<td>0.030</td>
</tr>
<tr>
<td>Mn mg/L</td>
<td>0.159</td>
<td>0.084</td>
</tr>
<tr>
<td>CU mg/L</td>
<td>0.100</td>
<td>0.050</td>
</tr>
<tr>
<td>Cr mg/L</td>
<td>0.090</td>
<td>0.010</td>
</tr>
<tr>
<td>Zn mg/L</td>
<td>0.859</td>
<td>0.310</td>
</tr>
<tr>
<td>Fe mg/L</td>
<td>18.000</td>
<td>3.500</td>
</tr>
<tr>
<td>Al mg/L</td>
<td>12.000</td>
<td>1.400</td>
</tr>
<tr>
<td>Si mg/L</td>
<td>5.800</td>
<td>2.400</td>
</tr>
</tbody>
</table>

- T.O.M = Total organic matter
- Membranes was tested on one stage at a temperature = 25°C and operating time 15 minutes.

4- Conclusion:

A new kind of high flux ultrafiltration membrane containing a cross-linked PVA fabricated on hydrolyzed polyester fabrics was demonstrated in this study. The optimization of physical properties of the PVA with degrees of hydrolysis (88%) and molecular weights (250.000 M.W) were tested, where the cross linking reaction was carried out with two kind of aldehydes namely formaldehyde and acetaldehyde. The PVA coating layer on the hydrolyzed polyester was cross-linked by using aldehyde at varying concentrations. Although the PVA film coating layer was macroscopically non-porous, it acted microscopically as a mesh of hydrophilic chains connected by crosslinking points. The mesh size could be controlled by the degree of crosslinking. The best permeation rate and filtration efficiency was achieved by using 6% formaldehyde solution. Scanning electron microscope (SEM) study revealed that the produced membranes have homogeneous surface with no significant change in the surface morphology of the prepared film coated polyester membrane using formaldehyde and acetaldehyde solutions. Also the produced film coated membranes application for filtration of raw and industrial waste water was investigated with different applied pressure for ultrafiltration technique.
Reference


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