Chapter III

Materials and Methods
CHAPTER-III

3.1 Materials used

3.1.1 Equipment and instrunets

Nanofiltration pilot plant assembly, sonicator bath (Oscar ultrasonic cleaning system of Type OU-23 SPL with ultrasonic wave frequency of 34 ± 3 kHz), UV-VIS spectrophotometer, HACH DR-2010 model spectrophotometer, pH meter, TDS and conductivity meter, COD digestion apparatus, Metler Balance (Metler Toledo), Scanning electron microscope, Atomic force microscope, Fourier transform Infrared spectroscope, drop shape analyzer, Gel permeation Chromatograph, Nitrogen cylinder, heating mantle, distilled water unit, digital thermometer, water bath, hot air oven.

3.1.2 Glasswares/plasticware

Sampling bottles, volumetric flask (100 mL to 1 L), conical flask (100 mL to 500 mL), beaker (100 mL to 500 mL) measuring cylinder, cuvettes, burette, pipette, round bottom flask, condenser with standard joints, dropping bottles, specific gravity bottles, silica crucible, glass petridish.

3.1.3 Membranes and modules used

Membranes

Two types of membrane materials hydrophilized polyamide (PA-NF) and polyethersulfone (PES-NF) having different molecular weight cut-off are used in the present study. All the membranes used in the present study, are supplied by M/s Permionics Membrane Pvt. Ltd, Baroda, India. PA-NF membrane has three layers, which are fabric backed polysulfone UF support, interfacially coated with polyamide layer and then hydrophilized using Permionics proprietary layer. PES-NF is a Thin Film Composite membrane fabricated by the interfacial polymerization. The first layer consists of polyethylene terephthalate (PET), followed by a second layer of Polyether sulfone UF membrane having 50.8 micron thickness and the third layer is the Permionics proprietary layer. The average pore sizes and effective membrane area were 6±1 nm and 0.016 m² for flat sheet membrane. The key physico-chemical and performance properties of the PA-NF and PES-NF membranes are listed in Table 3.1.
Table 3.1 Key physical, chemical and performance properties of PA-NF and PES-NF membranes used in this study

<table>
<thead>
<tr>
<th>Properties</th>
<th>PA-NF 150</th>
<th>PA-NF 250</th>
<th>PA-NF 400</th>
<th>PES–NF 300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>Asymmetric</td>
<td>Asymmetric</td>
<td>Asymmetric</td>
<td>TFC</td>
</tr>
<tr>
<td>Thickness (micron)</td>
<td>125</td>
<td>125</td>
<td>125</td>
<td>140</td>
</tr>
<tr>
<td>Surface charge</td>
<td>negative to near neutral</td>
<td>negative to near neutral</td>
<td>negative to near neutral</td>
<td>neutral</td>
</tr>
<tr>
<td>MWCO (Da)</td>
<td>150</td>
<td>250</td>
<td>400</td>
<td>300</td>
</tr>
<tr>
<td>pH operating range</td>
<td>2 -11</td>
<td>2 -11</td>
<td>2 -11</td>
<td>2-13</td>
</tr>
<tr>
<td>Maximum operating pressure (psi)</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>600</td>
</tr>
<tr>
<td>Maximum operating temperature (°C)</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>70</td>
</tr>
<tr>
<td>Pure water permeability (m³/m² s Pa)&quot;</td>
<td>2.58 x 10¹¹</td>
<td>2.82 x 10¹¹</td>
<td>3.60 x 10¹¹</td>
<td>1.33 x 10¹¹</td>
</tr>
<tr>
<td>Free chlorine tolerance</td>
<td>less than 0.1 ppm continuous</td>
<td>less than 0.1 ppm continuous</td>
<td>less than 0.1 ppm continuous</td>
<td>1 ppm*</td>
</tr>
</tbody>
</table>

*: Experimental value

Table 3.2 Nanofiltration Membrane salt rejection characteristics

<table>
<thead>
<tr>
<th>Type</th>
<th>MWCO, Da</th>
<th>Flow rate, LPH</th>
<th>Minimum rejection, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>MgSO₄</td>
</tr>
<tr>
<td>PA-NF 150</td>
<td>150</td>
<td>28</td>
<td>98%</td>
</tr>
<tr>
<td>PA-NF 250</td>
<td>250</td>
<td>36</td>
<td>90%</td>
</tr>
<tr>
<td>PA-NF 400</td>
<td>400</td>
<td>45</td>
<td>85%</td>
</tr>
<tr>
<td>PES-NF 300</td>
<td>300</td>
<td>30</td>
<td>90%</td>
</tr>
</tbody>
</table>

Membrane modules

Two different types of membrane modules, namely flat sheet and spiral wound are used in the present study. The salient features of these two modules are stated below:

Flat sheet module

Test Cell Dimensions : 225 mm × 150 mm
Membrane sheet Dimensions : 300 mm × 200 mm (Approx)
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Test cell inner dimension : 160 mm x 100 mm

Effective Membrane Area : 0.016 m²

Spiral wound module

Dimension of membrane module : 2.0 inch diameter and 12 inch long.

Effective Membrane Area : 0.3 m²

The operating Pressure of the membrane was 50 psi – 200 psi (maximum) and the operating temperature was in the range of 25°C – 45°C (except mentioned otherwise).

Table 3.3 Operating Limits for spiral wound nanofiltration membrane module

<table>
<thead>
<tr>
<th>Membrane description</th>
<th>Hydrophilized Polyamide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum operating pressure</td>
<td>200 psi</td>
</tr>
<tr>
<td>Feed spacer thickness</td>
<td>30 mils- standard</td>
</tr>
<tr>
<td>Membrane filtration area</td>
<td>0.3 m²</td>
</tr>
<tr>
<td>Operating Temperature</td>
<td>Max. 45°C</td>
</tr>
<tr>
<td>Operating pH range</td>
<td>2-11 pH</td>
</tr>
<tr>
<td>Cleaning pH range</td>
<td>1.5-12 pH</td>
</tr>
<tr>
<td>Free chlorine tolerance</td>
<td>&lt;0.1 ppm continuous</td>
</tr>
<tr>
<td>Outer wrap</td>
<td>Tape wrap</td>
</tr>
<tr>
<td>Maximum feed flow rate</td>
<td>0.54 m³/h</td>
</tr>
<tr>
<td>Minimum concentrate flow rate</td>
<td>0.36 m³/h</td>
</tr>
<tr>
<td>Maximum pressure drop per element</td>
<td>20 psi</td>
</tr>
</tbody>
</table>

Compaction of membrane

Before using a fresh membrane, it was compacted at a pressure of 980 kPa for 3 h using distilled water. During compaction of the membrane, water flux was measured continuously until a constant flux was achieved. During operation of NF systems, membrane material is exposed to high pressure of the feed water. Exposure of membranes to high pressure may result in an increase in the density of membrane material (called compaction), which decreases the rate of diffusion of water and dissolved constituents through the membrane. As a result of compaction, higher pressure has to be applied to maintain the design permeate flow. In parallel, a lower rate of salt diffusion will result in lower permeate salinity. The effect of compaction is more significant in asymmetric cellulose membranes than in composite polyamide membranes. In seawater RO, where the feed pressure is much higher than in brackish
applications, the compaction process will be more significant. Higher feed water temperature will also result in a higher compaction rate. Usually membrane compaction results in few percent flux decline, and has strongest effect during the initial operating period.

3.1.4 Chemicals

Reactive dyes

Three different reactive dyes *C.I. Reactive Black 5*, *C.I. Reactive yellow 160* and *C.I. Reactive Red 198* are used in the present study. These dyes are largely used in dyeing of cotton knits wear in a winch machine at various hosiery dye houses locally. The characteristics of these dyes are presented in Table 3.5.

Molasses

Molasses was collected from a local sugar factory and was stored at 5-6°C in the refrigerator. It was diluted with distilled water and three different concentrations namely 1000 mg L\(^{-1}\), 2000 mg L\(^{-1}\) and 4000 mg L\(^{-1}\) were used in the present study. Some physico-chemical characteristics of the molasses used in the present study are summarized in Table 3.4

Table 3.4 Physical and Chemical Characteristics of molasses used in the present study

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.2- 5.4</td>
</tr>
<tr>
<td>Total dissolved solid (mg/L)</td>
<td>1430</td>
</tr>
<tr>
<td>Water content</td>
<td>15-20%</td>
</tr>
<tr>
<td>Ash content</td>
<td>10-15%</td>
</tr>
<tr>
<td>Color intensity at 475 nm</td>
<td>35 ± 3</td>
</tr>
<tr>
<td>Density (g/L)</td>
<td>1.292</td>
</tr>
<tr>
<td>Color</td>
<td>Dark brown</td>
</tr>
</tbody>
</table>
Table. 3.5 Characteristics of the dyes used in the study.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Reactive Black 5</th>
<th>Reactive Yellow 160</th>
<th>Reactive Red198</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.I. (Color · Index) name</td>
<td>C.I. Reactive Black 5</td>
<td>C.I. Reactive Yellow 160</td>
<td>C.I. Reactive Red 198</td>
</tr>
<tr>
<td>CAS No</td>
<td>17095-24-8</td>
<td>129898-77-7</td>
<td>145017-98-7</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>991.82 Da</td>
<td>818.13 Da</td>
<td>968.21</td>
</tr>
<tr>
<td>Melting point</td>
<td>&gt; 260°C</td>
<td>&gt; 240°C</td>
<td>&gt; 260°C</td>
</tr>
<tr>
<td>Application class</td>
<td>Cotton</td>
<td>Cotton</td>
<td>Cotton</td>
</tr>
<tr>
<td>Chemical Class</td>
<td>Azo</td>
<td>Azo</td>
<td>Azo</td>
</tr>
<tr>
<td>Absorption max (water) (^a)</td>
<td>595 nm</td>
<td>430 nm</td>
<td>520 nm</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>(C_{26}H_{31}N_3NaO_{18}S_6)</td>
<td>(C_{25}H_{23}ClIN_9Na_2O_{12}S_3)</td>
<td>(C_{27}H_{18}ClN_3Na_4O_{13}S_5)</td>
</tr>
<tr>
<td>Molecular structure</td>
<td><img src="image1" alt="Molecular structure" /></td>
<td><img src="image2" alt="Molecular structure" /></td>
<td><img src="image3" alt="Molecular structure" /></td>
</tr>
<tr>
<td>UV spectra</td>
<td><img src="image4" alt="UV spectrum" /></td>
<td><img src="image5" alt="UV spectrum" /></td>
<td><img src="image6" alt="UV spectrum" /></td>
</tr>
</tbody>
</table>

\(^a\): Experimental value

Waste water was procured from Deo Piyu industry, a manufacturer of reactive dye at Ahmedabad, India. The waste water samples were analyzed on ‘as received basis’ to evaluate its characteristics. The general parameters of the effluent used for the experiments are presented in Table 3.6.
Table 3.6 General Parameters of the effluents used for the experiments

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Obtained value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye concentration (mg/L)</td>
<td>320</td>
</tr>
<tr>
<td>Alkalinity, (mg/L)</td>
<td>00</td>
</tr>
<tr>
<td>Acidity, (mg/L)</td>
<td>46</td>
</tr>
<tr>
<td>Nitrate (mg/L)</td>
<td>18.49</td>
</tr>
<tr>
<td>Sulphate, (mg/L)</td>
<td>987.22</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>4240</td>
</tr>
<tr>
<td>Total solids (mg/L)</td>
<td>22.2</td>
</tr>
<tr>
<td>Total dissolved solids, (mg/L)</td>
<td>14600</td>
</tr>
<tr>
<td>Chlorides, (mg/L)</td>
<td>1316</td>
</tr>
<tr>
<td>Hardness, (mg/L)</td>
<td>1934</td>
</tr>
<tr>
<td>Conductivity, (µs/cm)</td>
<td>1030</td>
</tr>
<tr>
<td>pH</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Other chemicals used:
Sodium chloride (NaCl), potassium dichromate (K₂Cr₂O₇), Ferrous ammonium sulphate, [Fe(NH₄)₂(SO₄)₂·6H₂O], ferroin indicator, hydrochloric acid (HCl), sulphuric acid (H₂SO₄) Mercuric sulphate (HgSO₄), Sodium metabisulphite, hydrogen peroxide (H₂O₂), sodium dodecyl sulphate, potassium permanganate (KMnO₄), Ammonium chloride and ammonium hydroxide, EDTA (Mg salt), Eriochrome Black T indicator, Calcium carbonate (CaCO₃), Sodium carbonate (Na₂CO₃), Phenolphthalein indicator, potassium nitrate (KNO₃), Magnesium chloride, (MgCl₂·6H₂O), Sodium acetate (CH₃COONa·3H₂O), Potassium nitrate (KNO₃), acetic acid (CH₃COOH), Barium chloride (BaCl₂), Silver nitrate (AgNO₃), Potassium chromate indicator (K₂CrO₄), sodium dodecyl sulfonate (SDS), cetyltrimethyl ammonium bromide (CTAB). All the chemicals used in this experiment were of AR grade supplied by Merck, India and were used without further purification.

3.1.5 Software used
MATLAB-7 was used for the computational analysis of the membrane surface concentration and various resistances during gas-sparged nanofiltration. D-plot graphing software was used for construction of several plots of the experimental data points.
3.2 Analytical methodologies

3.2.1 Measurement of Total Dissolved Solids (TDS)

Total Dissolved Solids (TDS) are the solids which are dissolved in the water. Total dissolved solids may be present in the water due to different salt of NaCl, etc. The high content of TDS leads to change in aesthetic as well as quality of water for different purpose. Also high TDS leads to affecting the water transparency which will affect to the aquatic life and also decreases the sunlight transparency. Also, high TDS value increases the conductivity of water and hardness. The conductivities and total dissolved solids (TDS) of all the streams were measured by an auto-ranging conductivity/TDS meter (Hanna Instruments, Taiwan) with automatic temperature compensation (Fig. 3.1).

![TDS meter](image)

**Fig 3.1** Photograph of the TDS meter used in the present study

3.2.2 Measurement of Chemical Oxygen Demand (COD)

The COD is the measurement of oxygen consumed during the oxidation of the oxidizable organic matter by a strong oxidizing agent. The sample (feed and permeate) was refluxed (at 150 °C) with the potassium dichromate and sulphuric acid in presence of mercuric sulphate (to neutralize the effect of chlorides). The excess of potassium dichromate is titrated against ferrous ammonium sulphate (FAS) using ferroin as an indicator. The amount of potassium dichromate used is proportional to the oxidizable organic matter present in the sample.
Reagents

1. Standard Potassium dichromate digestion solution (0.0166 M):
   Add to about 500 ml distilled water 4.903 g K$_2$Cr$_2$O$_7$, primary standard grade, previously dried at 150° C for 2 h, 167 mL conc. H$_2$SO$_4$ and 33.3 gm HgSO$_4$. Dissolve, cool to room temperature and dilute to 1000 mL.

2. Sulphuric acid reagent.

3. Ferroin indicator.

4. Standard ferrous ammonium sulphate titrant (FAS) (0.10 M):
   Dissolve 98 g Fe(NH$_4$)$_2$(SO$_4$)$_2$.6H$_2$O in distilled water. Add 20 mL conc. H$_2$SO$_4$, cool and dilute to 1000 mL. Standardize solution daily against std. K$_2$Cr$_2$O$_7$ digestion solution as follows:
   Pipette 5 mL digestion solution into a small beaker. Add 10 mL reagent water to substitute for sample. Cool to room temperature. Add 1-2 drops of ferroin indicator and titrate with FAS titrant.

   Molarity of FAS solution (M) = Volume of 0.0166m K$_2$Cr$_2$O$_7$ digestion solution titrated × 0.1 Volume of FAS used in titration, mL

Procedure:
The closed refluxed COD titrimetric method is used for COD measurement. Wash the culture tubes and condensation tubes with 20% H$_2$SO$_4$ before first use to prevent contamination. Make volumetric measurements as accurate as possible. Place sample in culture tubes as shown in Fig 3.2. and add digestion solution. Carefully run sulphuric acid reagent down inside of vessel so an acid layer is formed under the sample digestion solution layer. Tightly cap the condensation tubes and mix the sample and reagent well before keeping for reflux. Prepare blank as same using distilled water instead of sample. Place tubes in block digester preheated to 150°C and reflux for 2 h.

After 2 h of reflux, cool the culture tubes and place them in test tube rack. Some mercuric sulphate may precipitate out but this will not affect the analysis. Wash down the condensation tubes by distillate water and remove it after cooling. Add 1-2 drops ferroin indicator and titrate against 0.1 M FAS. The different shades of green-blue
color will be appeared. The end point will be sharp color change from bluish-green to red wine.

![Photograph of COD digestion apparatus](image)

**Fig 3.2.** Photograph of COD digestion apparatus

Calculation:

\[
\text{COD (ppm)} = (b - a) \times (M) \times 1000 \times 8/\text{Volume (in mL) of Sample}
\]

Where,  
\( b = \text{mL of FAS used for blank} \)
\( a = \text{mL of FAS used for the sample} \)
\( M = \text{Molarity of FAS used} \)
\( 8 = \text{Miliequivalent weight of oxygen} \)

3.2.3 Estimation of Color

The feed, permeate and the reject concentration are measured by using UV-VIS Spectrophotometer 117 supplied by Systronics, Ahmedabad, Gujarat. Initially the samples of dye solution are scanned to find out absorbance at maximum wavelength. The feed, permeate and reject concentration are checked with reference to distilled water and concentration is measured with help of standard graph plotted at different known concentration of the same dye at same wavelength.
Fig 3.3 Photograph of UV-VIS spectrophotometer (Model 117, Systronics)

Fig 3.4 Standard calibration chart of Reactive Red-198 dye at the wavelength 520nm
Fig 3.5 Standard calibration chart of Reactive Yellow-160 dye at the wavelength 430 nm

Fig 3.6 Standard calibration chart of Reactive Black-5 dye at the wavelength of 595 nm
Color intensity of the permeate and reject streams of molasses wastewater was measured by a HACH DR-2010 model spectrophotometer following USEPA approved HACH method # 8000 (APHA, 2005). For color measurements, this device was calibrated at a wavelength of 455 nm with Pt-Co standard solution.

### 3.2.4 Estimation of conductivity

Conductivity is the numerical expression of the ability of a sample to carry an electrical current and it varies with number and types of ions present in the solution. Most dissolved inorganic substances in water are in the ionised form and hence contribute to conductance. Conductivity was measured by conductivity meter provided by an auto-ranging conductivity/TDS meter (Hanna Instruments, Taiwan) with automatic temperature compensation.

### 3.2.5 Estimation of total hardness

Total hardness of the water samples was determined by EDTA (Ethylene diamine tetra acetate) titrimetric method using Eriochrome Black T sodium salt indicator. 25 mL of sample water was diluted to 50 mL. It was added with 1 to 2 mL of buffer solution to give a pH of 10.0 to 10.1. Indicator solution was added and titrated with EDTA titrant to change in color from reddish tinge to blue. EDTA titrant was standardized using standard calcium solution (Calcium carbonate).
Total hardness (EDTA), mg CaCO₃/L = \( \frac{A \times B \times 1000}{mL \text{ sample}} \)

where \( A = mL \) EDTA titrated for sample; \( B = mg \) CaCO₃ equivalent to 1.00 mL EDTA titrant

3.2.6 Estimation of alkalinity

Alkalinity was determined by the titrimetric method using phenolphthalein indicator. 25 mL of water sample was taken in a conical flask. 2 to 3 drops of phenolphthalein indicator was added into it. If it turned pink (pH > 8.3), it was titrated with 0.02 N \( H₂SO₄ \) to disappearance of the colour. mL of titrant used was recorded.

Phenolphthalein alkalinity, mg CaCO₃/L = \( \frac{A \times N \times 5000}{mL \text{ sample}} \)

where \( A = mL \) titrant used to phenolphthalein end point and \( N = \) normality of titrant.

3.2.7 Estimation of nitrate

Nitrate content in the waste water was determined by an UV spectrophotometric method. Calibration standards were prepared by diluting 50 mL of the nitrate standard solution (prepared by diluting 100 mL of \( KNO₃ \) stock solution to 100 mL with distilled water) and was added with 1 mL of 1 N \( HCl \). Absorbance was measured in a spectrophotometer at an wave length of 220 nm.

3.2.8 Estimation of sulphate

Sulphate content of the waste water sample was determined by using a Nephelometric turbidity meter. After standardizing the nephelometer following the manual, the turbidity of the blank sample with no \( BaCl₂ \) added. 100 mL sample was measured into a 250 mL conical flask, added with 20 mL buffer solution (30 g of \( MgCl₂.6H₂O \), 5 g of \( CH₃COONa.3H₂O \), 1 g of \( KNO₃ \) and 20 mL acetic acid in 500 mL distilled water with volume making up to 1000 mL) and mixed. While stirring a spoonful of \( BaCl₂ \) was added. The turbidity was measured at 5 min after stirring ended. Sulphate standards at 5 mg/L increments in the range of 0 to 40 mg/L sulphate were prepared. \( BaSO₄ \) turbidity for the standards was developed. The turbidity of the standards was determined using the same procedure and calibration curve was drawn between the turbidity and sulphate concentration, mg/L.
3.2.9 Estimation of Chlorides

Amount of chlorides in the water samples was estimated by argentometric titration method using potassium chromate (K₂CrO₄) as indicator. 100 mL of sample was used. For colored or turbid samples 3 mL of aluminium hydroxide suspension was added, it was mixed, allowed to settle and filtered. 1 mL of K₂CrO₄ indicator solution was added, and it was titrated against standard AgNO₃ solution to a pinkish yellow end point. The blank titration was done with distilled water.

3.2.10 Estimation of pH

pH of the feed and permeate solutions were measured using a pH meter (Systronics make, India). pH sensors used for the analyses allowed automatic and continuous correction of the values by taking into account the sample temperature. Freshly prepared 1(N) NaOH and HCl solutions were used for pH adjustment during pH study.

3.2.11 Estimation of membrane permeability

Membrane permeability was measured by conducting experiments using pure distilled water. Flux values at various operating pressures were measured and the slope of the volumetric flux versus pressure gave the membrane permeability. Once a set of runs were over membrane was thoroughly washed by distilled water for 15 mins applying maximum pressure of 980 kPa. It was followed by soaking the membrane sheet in 1% surfactant (Sodium dodecyl sulphate) solution for about an hour. After that it was washed again with distilled water to remove the traces of adhered surfactants. Membrane permeability was once again measured with distilled water. It was observed that the membrane permeability remained almost constant between successive runs.

3.2.12 Estimation of volumetric flux and membrane rejection coefficient

Volumetric flux (Jₜ) of the membrane was determined using following relation

\[ J_w = \frac{Q_p}{A}, \]

where \( Q_p \) is the permeate flow per h and ‘A’ is the active surface area of the membrane (m²). Membrane rejection coefficient was estimated by
\[ R = (1 - \frac{C_p}{C_b}) \times 100 \] (3.2)

Where \( C_p \) is the concentration of the permeate and \( C_b \) is the bulk concentration.

The effect of pH was found to be marginal for the feed, permeate and reject concentration in the present study. Therefore, pH variation was not considered in the parametric study of nanofiltration.

The increase in bulk concentration in the batch cell was marginal over the duration of experiments (1.5 h). For example, for the operating pressure of 490 kPa and initial bulk concentration of 25 ppm, the bulk concentration increased to 26.4 ppm at the end of the experiment.

3.2.13 Determination of trans-membrane pressure (TMP) drop

The trans-membrane pressure driving force is given by

\[ \text{Driving force} = (\Delta P - \Delta \pi) \] (3.3)

Where \( \Delta P \) is the applied pressure difference between the upstream (feed side) and the downstream (permeate side) pressure. Downstream pressure is essentially atmospheric. \( \Delta \pi \) is the osmotic pressure difference across the membrane. The osmotic pressure is expressed as a linear function of concentration according to Vant Hoff's law.

\[ \pi = cRT \] (3.4)

Where 'c' is the concentration of the solutes in g/L, 'R' ideal gas constant and 'T' temperature (K). Since in the present study a very dilute solution of reactive dye was used, the value of \( \pi \) was negligibly small (Belkhouche et al., 2009).

3.2.14 Determination of flux decline and fouling index

The fouling index was obtained by using the following equation:

\[ J = J_p V_p^{-b} \] (3.5)

where \( J \) is the initial flux, \( V_p \) is the cumulative permeate volume, and \( b \) is the fouling index.

The decrease in the flux \( F_d \) was determined by using Eq. (3.6)
where $J_w$ is the pure water flux, $J_p$ is the flux of the solution.

The irreversible fouling ($F_{irr}$) was determined by using Eq. (3.7)

$$F_{irr} = \frac{J_w - J_{w1}}{J_w}$$  \hspace{1cm} (3.7)

Where $J_{w1}$ is the pure water flux measured after membrane cleaning

The flux recovery $F_r$ was determined by using Eq. (3.8):

$$F_r = \frac{J_{w1}}{J_w}$$  \hspace{1cm} (3.8)

3.2.15 Scanning Electron Microscopy (SEM)

The cross-section and surface morphologies of the membrane was examined by a scanning electron microscope (SEM) using a JEOL/JSM-633F-INCA instrument with an accelerating voltage of 10.0 kV. All membrane samples were dried overnight at 40°C before preparing 3 mm×3 mm strips for silver sputter coating. The silver-coated strips were used for recording the SEM images.

3.2.16 Fourier transform infrared spectroscopy (FTIR)

FT-IR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy.

The surface organic functional groups of the membranes were studied by the Fourier transform infrared spectroscopy (Perkin Elmer Spectrum GX). The spectra were recorded from a wave number of 400 – 4000 cm$^{-1}$.

In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. Infrared absorption spectra are usually obtained by placing the sample in one beam of a double-beam infrared spectrophotometer and measuring the relative intensity of transmitted (and
therefore absorbed) light energy versus wavelength (or wave number). A common light source for infrared radiation is the Nemst glower, a molded rod containing a mixture of zirconium oxide, yttrium oxide and erbium oxide that is heated to around 1500°C by electrical means (Dyer, 2012).

3.2.17 Atomic force microscopy (AFM)
Quantitative surface roughness analysis of the HPA nanofiltration membrane before and after use was measured using atomic force microscopy (AFM) imaging and analysis (Park Instrument Auto Probe CT). Membrane samples, being dried under vacuum at 40°C for 24 h, were fixed on a specimen holder and 10μm×10 μm areas were scanned by tapping mode in air. The surface roughness was reported in terms of the root mean square roughness (Rms).

Atomic force microscopy (AFM) was carried out using a NT-MDT NTEGRA Aura Autoprobe CP atomic force microscope. Measurements were performed on the dry membrane samples under ambient atmospheric conditions. Silicon cantilevers with integrated pyramidal tips were used to image membrane surface topography. The membrane surfaces were imaged in tapping mode. Differences in the membrane surface morphology can be expressed in terms of various roughness parameters such as the average roughness and the root mean square (RMS) roughness. The average roughness is defined as the average deviation of peaks and valleys from the mean plane, and the RMS roughness is the deviation of peaks and valleys from the mean plane. At least three separate scans, each covering an area of 100 μm², were acquired on each membrane to determine the mean roughness values. The surface roughness was reported in terms of the root mean square roughness (RMS) and calculated by using Eq. (3.9)

\[ \text{RMS} = \sqrt{\frac{\sum (Z_{\text{cu}} - Z_{\text{av}})^2}{p}} \]  

(3.9)

where \( Z_{\text{av}} \) is the average of the z values within the given area; \( Z_{\text{cu}} \) is the current z value; and \( p \) is the number of points within a given area. The surface roughness parameter was calculated from the AFM images using an AFM software program.
3.2.18 Estimation of contact angle

The hydrophobicity of clean and fouled membranes was analyzed by contact angle measurements using drop shape analyzer (model no DSA 100). The membranes were initially washed twice with pure water and then dried at room temperature. After drying, 2 μL of distilled water with a tight syringe was placed on the membrane surface. Each equilibrium contact angle was the average of the left and right contact angles, and the reported values are the average of three equilibrium contact angles.

3.2.19 Test for transient cavitation activity

The introduction of a strong acoustic field to an aqueous solution results in the generation of cavitation microbubbles. The growth and cavitation collapse of these microbubbles in an ultrasonic field generates highly reactive free radicals. In particular, sonication in water can result in hydroxyl radicals that react to form hydrogen peroxide (H$_2$O$_2$). The yield of H$_2$O$_2$ after sonication can thus be used as an indicator of transient cavitation activity. Following sonication for 60 min the bath water was analyzed for Hydrogen peroxide by permanganometric titration (Alegria et al., 1989).

To observe the effect of transient cavitation impingement a new piece of household aluminium foil (15 x 8 cm$^2$) (1 x w) was placed inside the bath during sonication cycle. After a lapse of one sonication cycle the foil was examined to observe the presence of holes and crevices, if any.

3.2.20 Estimation of Power and specific energy consumption

Power consumption for the high pressure plunger pump can be calculated at every operating condition using Eq. (3.10)

$$ P = \sqrt{3}VI \cos \Phi $$  \hspace{1cm} (3.10)

Where, $V$ is the voltage, $I$ is the average current for a particular set of conditions (average of R, Y and B phase), $\cos \Phi$ is the power factor.

The ultrasonic power transferred to the medium can be calculated calorimetrically from the increase in temperature of the liquid medium. A digital thermometer was used to measure the increase in water temperature over time. The power ($P$) delivered was then calculated using Eq. (3.11),
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\[ P = \left( \frac{\Delta T}{t} \right) c_p M \]  
(3.11)

where, \( t \) is the duration of sonication; \( c_p \) heat capacity of water \((4.18 \times 10^3 \text{ J kg}^{-1}\text{K}^{-1})\); 
\( M \) the mass of water in the ultrasonic bath (kg).

Specific energy consumption (SEC) is defined as the energy consumed for every \( \text{m}^3 \) of feed water processed, then the SEC (kW h/m\(^3\)) can be calculated at every operating condition using Eq. (3.12)

\[ SEC = \frac{\sqrt{3VI \cos \phi}}{1000Q} \]  
(3.12)

where \( V \) is the voltage, \( I \) is the average current for a particular set of conditions, \( \cos \phi \) is the power factor (cosine of the phase angle between voltage and current), \( Q \) is the feed flow rate (m\(^3\)/h).

3.2.21. Determination of critical and limiting flux

The critical and limiting fluxes were determined by a ‘step-by-step’ technique (Chiu and Jame, 2005). The initial TMP was 196 kPa and TMP was increased at fixed intervals of 98 kPa in time step of 20 min. This was done prior to the onset of non-linearity in the increase of the volumetric flux, which indicates the critical flux, thereafter the time step of 20 min were used. The definition of critical flux here is a variation of critical flux concept used widely during microfiltration. It indicates that critical flux is considered to be the onset of effect of concentration polarization on the flux where it deviates from pure water flux data. The limiting flux is the flux which is independent on the pressure. Three different cross-flow velocities (CFV) 0.2, 0.35 and 0.45 ms\(^{-1}\) were used in this study.

3.2.22. Determination of shear stress number

It is known that an increase in cross flow velocity and/or gas injection leads to an increase in wall shear stress on the membrane surface. A dimensionless shear stress number \( (N_s) \) was introduced to compare the shear stress at the membrane wall and the driving force (trans-membrane pressure (Chiu and Jame, 2006). In the absence of gas sparging (single-phase flow), the dimensionless shear stress number is:

\[ N_s = \frac{\rho_{\text{liq}} u_{\text{liq}}^2}{\text{TMP}} \]  
(3.13)
If gas sparging is applied (two-phase flow), the generalized shear stress number is

\[ N_s' = \frac{\rho_{\text{mixture}} u_{\text{mixture}}^2}{\text{TMP}} \]  

(3.14)

where \( \rho_{\text{liquid}} \) and \( \rho_{\text{mixture}} \) are the liquid density and mixture density \((\text{kg m}^{-3})\) respectively, \( u_{\text{liquid}} \) and \( u_{\text{mixture}} \) are the superficial liquid velocity and mixture velocity \((\text{m s}^{-1})\), respectively, and \( \text{TMP} \) is the trans-membrane pressure \((\text{Pa})\). The \( \text{TMP} \) at specified condition (for example at critical flux or at limiting flux) is used to calculate the corresponding shear stress number.

The mixture velocity can be taken as:

\[ u_{\text{mixture}} = u_{\text{liq}} + u_{\text{gas}} \]  

(3.15)

The mixture density can be calculated as follows

\[ \rho_{\text{mixture}} = \frac{\rho_{\text{gas}} u_{\text{gas}} + \rho_{\text{liq}} u_{\text{liq}}}{u_{\text{mixture}}} \]  

(3.16)

3.2.23. Determination of mass transfer coefficient

In general, the Sherwood \((Sh)\) number is related to the Schmidt \((Sc)\) and Reynolds \((Re)\) numbers for laminar flow as follows

\[ Sh = \frac{k d_x}{D} = 1.85 (Re Sc d_x / L)^{1/3} \]  

(3.17)

The Leveque’s equation is valid for flow in impervious conduits. However, the effect of wall porosity (or suction) is important only in the cases of relatively open membranes, e.g., UF and MF membranes as was shown by De and Bhattacharya (1997) and Minnikati et al.(1999). Therefore, the equation in its present form can safely be used in the nanofiltration for the present system.

For turbulent flow conditions \((Re > 2000 - 4000)\) Harriott- Hamilton correlation was used to calculate (van der Berg, et.al .1989).

\[ Sh = 0.0096 Re^{0.91} Sc^{0.35} \]  

(3.18)

For the determination of diffusivity \( D \), the correlation of Wilke and Chang (Treybal, 1981) was used.

\[ D = \frac{(117.3 \times 10^{-18}) (\varphi M)^{0.5} T}{\mu^{0.6}} \]  

(3.19)
Where $M$ is the molecular weight of the solvent, $\mu$ solution viscosity, $v$ solute molar volume and $\varphi$ association factor for solvent.

### 3.2.24 Membrane cleaning and maintenance

The membrane was maintained by water flushing and chemical flushing once in a week and acid–alkaline–acid flushing once in a month. Chemical flushing was carried out by 1 wt% sodium metabisulphite solution in distilled water for about 15 min. prior to restarting the system. Once again, water flushing was done until the bisulphate was washed off. This can be identified by smelling the concentrate water, which should not have any smell of bisulphate. In acid–alkaline flushing, 0.5% solution of hydrochloric acid and 0.1N caustic soda were flushed one after another for a period of 15 min each. This was again followed by water flushing. The life of a HPA module can be anywhere between 1 and 3 years depending on the aggressiveness of the feed.

### 3.3 Experimental Set-up and operating conditions

#### 3.3.1 Set-up for nanofiltration with two different modules

The schematic diagram and photograph of the experimental set-up of nanofiltration pilot plant with two different modules are presented in Fig. 3.8 and Fig. 3.9 respectively. Feed solution from the feed tank after pressurizing by high pressure plunger pump (50-400 psi) was taken to the test cell, made of stainless steel (dimension: 225 × 150 × 50 mm). The test cell housed the flat sheet HPA membrane. The top half of the cell contained the flow distribution chamber and the bottom half was used as the membrane support system. The upper half of the test cell contained a groove for the arrangement of HDPE ‘O’ ring to prevent leakage at high pressure operation. Reject stream was collected and recycled to the feed tank routed through a rotameter, while the permeate samples were collected and analyzed for various parameters such as pH, TDS, conductivity, COD etc. The flow rates of permeate and reject streams were measured by rotameters, the combined value of which gave the feed flow rate. The feed solution was also passed through the spiral wound module (having 50.8 mm diameter and 304.8 mm length) made of SS-316 and the same procedure was repeated. A quick release interconnecting coupling of SS 316 was used for changeover of feed line from flat sheet module to spiral wound and the vice versa.
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In both the cases volumetric flux was calculated under various pressure conditions. The pilot plant assembly was equipped with variable frequency drive (VFD) for flow control, inlet and outlet pressure gauge and high pressure switch.

Fig 3.8 Schematic of experimental set-up of nanofiltration (VFD: variable frequency device; HPS: high pressure switch; PG: pressure gauge; CV: control valve; PR: permeate rotameter; RR: reject rotameter)
Fig 3.9 Photograph of the experimental setup of the nanofiltration pilot plant with two different modules.
Three different feed concentrations of 12.5, 25, and 50 ppm (mg/L) and operating pressures of 5, 7 and 10 kg/cm² (i.e. 490, 686, 980 kPa respectively) were selected for the nanofiltration experiments using two different modules. The volume of feed solution was 25 L in the feed tank. Permeate samples were collected at fixed time intervals and concentration of the same were measured. Duration of each run was 1.5 h in both flat sheet and spiral wound module. All the experiments were conducted at the prevailing ambient temperature of 32±2°C.

3.3.2 Set-up for nanofiltration with ultrasonic irradiation

The schematic diagram and the photograph of the experimental set up with ultrasound irradiation are schematically illustrated in Fig.3.10 and Fig.3.11 respectively. It consists of a cross flow nanofiltration unit with flat sheet membrane module. The test cell, made of stainless steel (dimension: 225 × 150 × 50 mm³) was immersed in the water bath of sonicator (Oscar ultrasonic cleaning system of Type OU-23 SPL with ultrasonic wave frequency of 34 ± 3 kHz). The inner dimension of the test cell was 160 mm × 100 mm × 2 mm. A perforated 1 mm thick stainless steel plate was laid over with a stainless steel gauge of 350 mesh size, which was topped by a Whatman filter paper and followed by the actual membrane with its active thin layer exposed to the high pressure feed. This arrangement provided sufficient mechanical support to the test membrane at high pressures. The top half of the cell contained the flow distribution chamber and the bottom half was used as the membrane support system. The upper half of the test cell had a groove for the arrangement of HDPE ‘O’ ring to prevent leakage at high pressure operation. The effective tank size of the water bath of sonicator was 300×300×200 mm³ (l × w × h). The membrane unit was completely immersed in the water of ultrasonic bath and kept 5 cm above the bottom to keep it away from the transducers of sonicator. The dense skin layer of the membrane faced the transmission direction of ultrasound wave, such that the sound waves transmitted through the slurry impinged on to the surface of any deposit formed at the septum. During the experiments, the temperature increase of water bath was checked as less than 5°C. Hence, this temperature increase through the experiment is negligible in measurement. Experiments were carried out in the total recycle mode of filtration (TRMF). Feed solution from the feed tank was pressurized by high pressure plunger pump (50-400 psi) and introduced in to the test cell. Reject stream was collected and...
recycled to the feed tank routed through a rotameter. The permeate stream was also recycled to maintain a constant concentration in the feed tank since the feed volume was kept constant throughout the experiment. The cross flow velocity was maintained at 0.3 m/s. The permeate samples were collected and analyzed for various parameters such as pH, TDS, conductivity, COD etc. The flow rates of permeate and reject streams were measured by rotameters, the combined value of which gave the feed flow rate. The pilot plant assembly was equipped with variable frequency drive (VFD) for flow control, inlet and outlet pressure gauge and high pressure switch. Nanofiltration was carried out for 2.5 h duration with the cumulative filtrate volume monitored throughout the experiment. All the experiments were carried out at the full nominal input supply of 230 V unless otherwise specified.

Fig 3.10 Schematic of the experimental setup for nanofiltration unit with ultrasonic irradiation bath (VFD: variable frequency device; HPS: high pressure switch; PG: pressure gauge; CV: control valve; PR: permeate rotameter.)

NF experiments were designed to observe the variation of operating conditions on the steady state volumetric flux, different membrane resistances and rejection. Four combinations of dye mixtures having different ratios of dye 1 (reactive black) and dye 2 (reactive yellow) were examined. These combinations were 50
(30:20); 100 (50:50), 125(70:55) and 150 (60:90) mg/L. NaCl concentration was fixed at 500 mg/l for all dye combinations. Four different trans-membrane pressures (294, 490, 686 and 980kPa) were selected. While one parameter was varied, the others were held constant to get an exact picture of dependence. The dye and salt were analytically weighed to the desired concentrations, depending on the set parameters. It is noteworthy to mention that the increase in bulk concentration in the batch cell was marginal over the duration of experiments (160 min). For example, for the operating pressure of 490 kPa and initial bulk concentration of 50 mg/L, the bulk concentration increased to 53.2 mg/L at the end of the experiment.

![Fig 3.11](image.png)

**Fig 3.11** Photograph of the experimental setup of the nanofiltration unit with ultrasonic irradiation bath

### 3.3.3 Set-up for nanofiltration with gas sparging

The experimental set up is schematically illustrated in Fig.3.12. It consists of a cross flow nanofiltration unit with a flat sheet membrane module. The test cell, made of stainless steel has the dimension: $225 \times 150 \times 50 \text{ mm}^3$. The top half of the cell contained the flow distribution chamber and the bottom half was used as the membrane support system. The upper half of the test cell had a groove for the arrangement of HDPE ‘O’ ring to prevent leakage at high pressure operation. Feed
solution from the feed tank was pressurized by high pressure plunger pump (50-400 psi) and entered into the test cell. Nitrogen gas from a cylinder was introduced to the inlet of the flat sheet module, via the buffer tank (to reduce the pressure fluctuation of the incoming gas) through a T-piece connector having ID of 4 mm. The gas was injected with the feed in co-current flow manner. The gas flow rate was controlled by means of a gas rotameter. Two non-return valves (NRV) were provided, one at the gas inlet and the other at the feed inlet line in order to prevent the back flow of air or liquid as the case may be.

![Fig 3.12. Schematic of experimental set-up of gas-sparged nanofiltration unit](image)

(VFD: variable frequency device; HPS: high pressure switch; PG: pressure gauge; RR: reject rotameter, GR: gas rotameter; NRV-A: non return valve for air; NRV-L: non return valve for liquid)

Experiments were carried out in the total recycle mode of filtration (TRMF). Reject stream was collected and recycled to the feed tank routed through a rotameter. The
permeate stream was also recycled to maintain a constant concentration in the feed tank since the feed volume was kept constant throughout the experiment. The permeate samples were collected and analyzed for various parameters such as TDS, conductivity, COD etc. The flow rates of permeate and reject streams were measured by rotameters, the combined value of which gave the feed flow rate. The pilot plant assembly was equipped with variable frequency drive (VFD) for flow control, inlet and outlet pressure gauge and high pressure switch. Nanofiltration was carried out for 1 h duration with the cumulative filtrate volume monitored throughout the experiment. All the experiments were carried out at the full nominal input supply of 230 V unless otherwise specified.

Fig 3.13. Photograph of the experimental set-up of gas-sparged nanofiltration system