CHAPTER-V

MEMBRANE-BASED MF/ED HYBRID PROCESS FOR THE TREATMENT OF PAPER INDUSTRY WASTEWATER

ABSTRACT
In this research, the pilot plant of a hybrid microfiltration (MF) and electrodialysis (ED) system was designed, constructed and employed successfully to remove the color and contaminants of paper industry wastewater. Microfiltration module comprising of ceramic membrane was used at constant pressure as a pretreatment step for the ED pilot scale unit operation. The ED stack consisted of 11 cation-exchange and 10 anion-exchange membrane pairs. Tubular ceramic module was employed to pre-filter the wastewater at 60°C and ambient temperature. Electrodialysis was successfully applied for the treatment of paper industry effluent for the first time with MF as a pretreatment step. The combined hybrid process at the applied potential of 50 V showed a low content of total dissolved solids (TDS) of 546 mg/L, conductivity of 0.61 mS/cm, and chemical oxygen demand (COD) of less than 20 mg/L. The hybrid MF/ED module used in this research gave a recovery and reuse of more than 90% of original wastewater. The proposed pilot plant was found to be more advantageous, since the ceramic membrane module used could withstand higher temperature of the discharged effluent and given the permeate that is free from the suspended particles of colloidal nature. It is also evident from the results that the hybrid process is more efficient than the single unit process.

Results of this chapter are published in Separation and Purification Technology (in Press, 2007)
V.1. INTRODUCTION

Water is the key component in paper production industry. It is used in nearly every cycle of the pulping and papermaking process, which inevitably picks up unwanted and sometimes hazardous pollutant. Paper industries are considered to be the major pollution threats in India with regard to wastewater regulation, since these generate large volumes of wastes that are harmful to the environment. The freshwater consumption in pulp and paper industry used during the manufacturing process are all taken from the external sources [1]. Recently, the Central Pollution Control Board of India (CPCB) [2] and the United States Environmental Protection Agency (USEPA) [3] have suggested the safe/effective alternative treatment methods from pulp and paper industry effluent. According to the European Integrated Pollution Prevention and Control Bureau (EIPPCB) directive, the officially allowed effluent loads are extremely rigorous and are aimed at minimizing the freshwater consumption [4]. There is thus a greater need to reduce the level of pollutants from pulp and paper waste streams utilizing newer technologies for their safe and clean manufacturing processes.

Among the many methods employed, the membrane-based separation techniques like microfiltration (MF), nanofiltration (NF), ultrafiltration (UF) and reverse osmosis (RO) have been most widely used for treating a variety of industrial effluents [5-10], but the purification technologies used in pulp and paper making processes include flotation [11], evaporation [12,13], etc. These processes are used to concentrate and fractionate the spent liquor [14,15] to remove color [16] and treat the effluents [17]. However, the membrane-based techniques are known to offer high level of purification coupled with relatively low energy consumption. The present growing trend in many countries has been to reuse the municipal effluent to provide safe water supply and to avoid the discharge of wastewater to the green environment. Recently, Pizzichini et al [18] studied the performance of
different ceramic MF, polymeric MF, UF and RO modules for purification of pulp and paper wastewater for water reuse in a closed loop, with an end objective of generating good permeate stream, minimize the energy consumption and consequently, promote a practical process application. The experimental results [19,20] from a pilot-scale paper mill filtration were examined with the multivariate methods using different ultrafiltration membranes in a paper mill application and these authors have concluded cellulose membranes were most optimal membranes for the studied application.

In our earlier report, we have employed the NF and RO hybrid process for the treatment of distillery-spent wash [21]. In continuation of this work, we present here the research results on the application of a hybrid microfiltration (MF) combined with electrodialysis (ED) process for the effective treatment of effluent wastewater collected from the local paper industry (Dandeli, India). The recirculation of process water was studied using the indigenously built MF and ED hybrid pilot plant under various process variables such as feed pressures, initial feed concentrations, applied voltage and flow rates.

V.2. RESULTS AND DISCUSSION

V.2.1. Effect of Operating Pressure and Feed Temperature on MF

Membrane characteristics influence its performance in terms of flow rate, rejection and resistance to fouling; hence, these parameters can be used to foresee the economical feasibility of the implementation of the present hybrid pilot module for large-scale operations. Separation tests were performed in specific pilot plants under different hydraulic pressure conditions. In a concentration mode, permeate stream was continuously collected during the filtration. In the recycle mode, in which permeate and concentrate were remixed in the feed tank. Process parameters such as trans-
membrane pressure and flow rate were continuously monitored during the filtration process. The temperature was automatically controlled by a thermostatic system.

A comparison of pure water flux over that of wastewater through MF ceramic membrane module between the pressure range of 4 to 12 bar with an increment of 2 bar is presented in Figure V.1. The flux is lower than that of pure water over the studied pressure range, indicating no jamming of the system at pre-filter cartridge or housing. However, a steady state is reached between pressures of 8 and 10 bar, indicating the fouling affect on membrane surface. Possibly, shear rates generated at the membrane surface tend to shear off the deposited material and thus, reduce hydraulic resistivity of the fouling layer. However, this may not always happen if the trans-membrane pressure is high enough in relation to permeation flow. Differences between initial pure water fluxes for the same membrane type reflect the variation of membrane properties (permeabilities), which is not unusual when different sheets of the same membrane are used. However, it was found in this study that there was a considerable increase in pure water flux from 100 to 180 L/m².h, whereas the flux for wastewater varied from 90 to 125 L/m².h. Such a slow increase in flow rate is due to the possible cake formation on the membrane surface. The decrease in flux values can be explained by a combination of osmotic pressure and adsorption/pore blocking mechanism. Water flow rate increases linearly with the driving pressure when the pressure is higher than that of the feed osmotic pressure. It is commonly assumed that there is no permeate production when driving pressure is lower than that of the feed osmotic pressure.

The bleach plant is the major producer of effluent, even though the volume of the wood room effluent, that is from debarking, is only about 5 % of the total volume. It is the most toxic effluent, which constitutes 10 % of color load in the total effluent. Organic lignin compounds with spent white
liquor, which contains mainly Na₂S and NaOH at the pH of around 14 can form the black liquor that is removed from the washing stage.

![Graph showing comparison of pure water and wastewater fluxes in MF process.](image)

**Figure V.1.** Comparison of pure water (-■-) and wastewater (-○-) fluxes in MF process.

In this study, MF experiments were carried out mainly to remove the suspended particles and color of the paper effluent. MF module effectively removed the particles of colloidal size range. As wastewater has a very dark brown color, the pre-treated effluent samples free from suspended particle were used as feed for the ED experiment with their characteristics shown in Table V.1.

As the large amount of water is consumed in the digestion step, discharged effluent at this stage will be around 60°C. Effect of this temperature and operation time on permeate flux was evaluated for MF pre-filtration for the effluent at 25° and 60°C as shown in Figure V.2. The temperature was automatically controlled by a thermostatic system. Temperature operated was as that of born temperature for the effluent at the bleaching section. Process parameters such as trans-membrane pressure and flux were continuously monitored during the filtration process. The ceramic membrane was tested for 120 min in the recycle mode and for about 75 min in the concentration mode reaching a (VCR) of 12. The ceramic MF module
in the batch mode gave a stable flux with a clear permeate of 113 L/m².h at 25°C and 121 L/m².h at 60°C under a constant pressure of 4 bar. Permeate collected for the applied pressure of 4 bar was used as feed for all ED runs.

Table V.1. Characteristics of paper industry effluent collected from West Coast Paper Mill, Dandeli, India

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.92</td>
</tr>
<tr>
<td>Conductivity (mS/cm)</td>
<td>10.78</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>6046</td>
</tr>
<tr>
<td>Na⁺ (mg/L)</td>
<td>864</td>
</tr>
<tr>
<td>Lignin (mg/L)</td>
<td>50</td>
</tr>
<tr>
<td>Cl⁻ (mg/L)</td>
<td>1600</td>
</tr>
<tr>
<td>Ca²⁺ (mg/L)</td>
<td>293</td>
</tr>
<tr>
<td>DOM (mg/L)</td>
<td>9.166</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>390</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>35</td>
</tr>
</tbody>
</table>

TDS-Total Dissolved Solids
COD-Chemical Oxygen Demand
DOM-Dissolved Organic Matters
BOD-Biological Oxygen Demand
Figure V.2. Comparison of clarified wastewater flux obtained for born of 60°C (–o–) and at (–■–) 25°C.

V.2.2. Electrodialysis

V.2.2.1. Limiting Current Density (LCD)

For different potentials, the results of minimum found for the reciprocal electrical current (1/\(I\)), limiting current (\(I_{\text{lim}}\)) and limiting current density (\(i_{\text{lim}}\)) (current divided by the effective membrane area gives LCD) are given in Table V.2. A minimum limiting value of 9.8 mA/cm² was found for an electrical potential of 50 V. However, as noted before, LCD is not a constant value; it will change with the working conditions and operating time of the ED system.

Changes in electrical conductivity of the diluate stream (feed, Tank 1) as a function of time under three constant applied voltages is shown in Figure V.3. Electrical conductivity of the diluate solution decreased exponentially with time. A continuous decrease in electrical conductivity was mainly due to the deionization of diluate solution. A significant difference is observed in the electrical conductivity of the diluate when operating the ED stack at different applied voltages; a higher transfer rate of ion is observed at 50 Volts.
Table V.2. Limiting current density for different applied voltages

<table>
<thead>
<tr>
<th>Voltage (volts)</th>
<th>1/I (1/A)</th>
<th>$I_{lim}$ (A)</th>
<th>$i_{lim}$ (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1.0</td>
<td>1.11</td>
<td>11.1</td>
</tr>
<tr>
<td>50</td>
<td>1.1</td>
<td>0.9</td>
<td>9.8</td>
</tr>
<tr>
<td>60</td>
<td>1.0</td>
<td>1.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Figure V.3. Plot of conductivity vs time.

As shown in Figure V.4, shows color change was observed in the diluate after 120 min of operation. Specific ion transfer depends upon the equivalent fraction of the corresponding ion in wastewater, the mobility of the ion as well as the type of the membrane.
Figure V.4. Photograph of MF clarified ED feed samples before and after ED experiment.

Figure V.5 shows the results of a comparative study for the separation of monovalent (Na\(^+\)) and divalent (Ca\(^{2+}\)) ions by the ED process. From Figure V.6, the molar ratio of Ca\(^{2+}/Na^+\) clearly indicates that the selectivity of the membrane shifted from Ca\(^{2+}\) to Na\(^+\) after 90 min of ED operation. Even though the operational time for both monovalent and divalent ions was the same, the monovalent ions were removed at a higher rate than the divalent ions. The permeation rate of Na\(^+\) across the cation-exchange membrane is larger than that of Ca\(^{2+}\) ion because the hydrated ionic radius of Na\(^+\) is small. The equilibrium constant of ion exchange process is large for ions of a small hydrated radius or for multivalent ions, and the permeation rate across the ion exchange membrane is also large for ions of a large equilibrium constant. However, the difference in the permeation rates of two ions is smaller than that of the equilibrium constants, especially between multivalent ions and monovalent ions, because the release rate of multivalent ions from the ion exchange site is small due to a strong interaction with the exchange sites.
Figure V.5. Comparison of Na$^+$ (-o-) and Ca$^{2+}$ (-■-) concentration at 50V.

Figure V.6. Molar ratio of the Ca$^{2+}$/Na$^+$ against time for electrodialysis at 50 V.

The efficiency of the ED process depends upon the permselectivity of the membrane, back diffusion of salts from brine to diluate, and the leakage of current through the distribution system of the concentrate solution to the cells. Maintenance of the permselectivity of an ion-exchange membrane
depends upon the counterion conducting most of the electrical current and on a low concentration of diffused electrolytes in the pores of the membrane, i.e., on low concentrations of the concentrate solution. When the solution concentration is increased, the high concentration of diffused electrolytes in the membrane will sharply decrease the membrane permselectivity.

Figure V.7 displays the results of a comparative study for the separation of TDS and chloride, respectively. The effect of flow rate on the separation performance was not so apparent. For different flow rates of 0.4,
0.8 and 1.2 L/min studied, separation was almost the same as documented for most of the selected concentrations and applied potentials. Energy consumption calculations were made for the final concentrations of TDS in the diluate solution at an optimal voltage of 50 V. With this, the pollutant levels in the diluate are below the maximum contaminant level specifications for the effluent discharge. For paper industry effluent treatment earlier [18, 19] several membrane modules were employed; however, in our case study, microfiltration with ceramic membrane was used as a pretreatment step for a successful ED operation.

V.3. CONCLUSIONS

The results of this study show that 80 % of wastewater could be recovered by the use of MF/ED hybrid process, while the remaining 20 % of flow (concentrate) can be used as a biomass. These include wood residues, residues from forestry operations, bark, black liquor and production residues. Pulp and paper mills also recover the energy from their waste streams using the biomass as a primary energy source in the manufacturing process [29]. However, employing the membranes for effluent treatment to obtain purified water is potentially the large single application of membrane technology today. Almost every pulp and paper manufacturing industries generates a large quantity of wastewater on a daily basis. However, the need for stringent pollution control (by legislation) provides tremendous opportunity for membrane technology in many aspects of water pollution control, from end-off-pipe treatment to treatment and reduction of wastes from the effluents. It should be emphasized that the membrane merely serves to separate or purify the wastewater into more useful and/or less polluting streams. The combined MF/ED process developed in this study reveals that the pilot plant module would be quite useful in treating wastewater effluents from the paper
industry. However, the presently developed indigenously built pilot plant module was able to reduce the contaminated ion concentrations to the level set by WHO from the polluted water out of the paper industry. In summary, the method proposed in this research is quite satisfactory in producing good quality reusable water from the effluent mixture by removing the unwanted ions. At any rate, it may be noted here that the pilot scale results of this study would be useful as a good indicator of the scale up operations that deal with large volumes of wastewater from paper industries.
V.4. REFERENCES


[2] Central Pollution Control Board (CPCB), New Delhi, India Annual Report, 2002-03.


