Removal of total dissolved solids with simultaneous recovery of acid and alkali using bipolar membrane electrodialysis–Application to RO reject of textile effluent

M Nisha Priya & K Palanivelu*
Centre for Environmental Studies, Anna University, Chennai 600 025, India
Email: kpvelu@hotmail.com

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The present paper focuses on the application of electrodialysis process with bipolar membranes (EDBPM) for the treatment of reverse osmosis (RO) reject. The purpose of this work includes investigation on the reduction of total dissolved solids (TDS) of the RO reject process with the recovery of acids and bases. Preliminary studies were conducted with sodium chloride solutions in batch recirculation mode. The effect of process parameters such as electrolyte concentration in the electrode compartments (sulphuric acid and NaOH in anode and cathode compartments respectively), current density, flow rate, feed concentration on the process efficiency such as acid and alkali production, current efficiency and energy consumption were evaluated. The transport of co-ions to the electrode compartments was also studied. The optimum conditions of the process were found to be with electrolytes of 0.05 N concentration in electrode compartments (sulphuric acid and sodium hydroxide in anode and cathode compartments, respectively), with current density of 0.83A/dm² at 10,000 mL/h flow rate. At these conditions the treatment was applied to a RO reject of textile effluent for the removal of TDS with acid and alkali recovery. On treatment the conductivity of the solution decreased to about 99.6% with recovery of acid and alkali concentrations of 0.274 N and 0.258 N, respectively. The energy consumption and current efficiency of the process were found to be 0.310 KWh/L and 56.8%, respectively. The transport number of chloride and sodium ions during the treatment of RO reject was found to be 0.0389 and 0.0161, respectively.

Keywords: Electrodialysis, Bipolar membranes, Textile dye effluent, RO reject, TDS removal, Acid/alkali recovery
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Textile dyeing industries is one among the largest number of industries in India. The most difficult environmental issue for the textile dyeing and finishing industry is the management of the generated wastewaters. Salts are important constituents of the textile dyeing industry wastewater. Common salts are required in a number of dyeing systems–particularly for cotton dyeing where reactive dyes are used. The low cost of salts makes them a poor target for recovery and the small nature of the ions comprising salts makes them difficult to remove by conventional effluent treatment methods. They are not removed by biological treatments and require advanced physical or chemical separation techniques such as reverse osmosis, evaporation and electrolysis.

Contamination of groundwater, surface water and soil in the areas of textile dyeing industries occurs due to the discharge of improperly treated wastewater into waterways. The usual method of treatment for textile dyeing waste involves coagulation and precipitation using ferrous sulphate for the removal of colour. But this method though removes colour from the effluent produces sludge that requires further treatment processing. In addition, the treated water still contains high TDS that is left untreated. Now-a-days the effluent that is treated for colour is processed using a reverse osmosis unit (preceded by filtration) for the removal of TDS. This combined method of treatment using coagulation and reverse osmosis is gaining increased interests for application in Tiruppur dyeing industries. The reverse osmosis process though removes TDS from the effluent effectively, concentrates the TDS on the other side, which again requires further processing. Currently, two membrane processes that are competing in the market for domineering positions for desalination purposes are: (i) reverse osmosis (RO) and (ii) electrodialysis (ED). For over two decades of operation experience, RO showed its strong properties, but euphoria of the first success passed away and the time has come for a matter-of-fact attitude to both methods in order to choose the most optimal concept of membrane desalination.
A bipolar membrane (BPM) is composed of three parts—an anion exchange layer (AEL), a cation exchange layer (CEL) and a hydrophilic interphase at their junction. When a current is passed across this kind of membrane, electrical conduction is achieved by the transport of $H^+$ and $OH^-$ ions generated by the electro dissociation of water. The illustration of water splitting and acid base generation using electrodialysis with bipolar membranes (EDBPM) is given in Fig. 1. When a BPM is introduced in an ED stack, the fluxes of $H^+$ and $OH^-$ ions enable the salt $M^+X^-$ to be transformed into both acid ($HX$) and base ($MOH$). The separation or better production of acid and base is possible with only one pair of working electrodes and many repeat units in between, reducing the cost of electrodes and reducing the influence of the electrode reactions on the energy efficiency and membrane transport compared to electrolysis. However, ion exchange membranes are not perfectly selective due to the incomplete exclusion of co-ions, i.e. the ions that carry the same charge as the membrane fixed charge. In the cation and anion exchange membranes, the co-ions are mainly hydroxide ions and protons, respectively. Their transport limits the overall current efficiency and the maximum base or acid concentration. However, the product purity is mainly influenced by the salt ion transport across the bipolar membrane.

The electrodialytic water-dissociation process employing bipolar membrane has been successfully used for obtaining acids and bases from salt solutions. The process has been used to convert sodium acetate solution to sodium hydroxide and acetic acid. Electrodialysis using bipolar membranes has been used for recovery of acids and alkali from etching solutions. Bipolar electrodialysis, in combination with a two-stage monopolar electro-dialysis process, yielded the recovery of two valuable components of etching rinse: high-quality water and acid. The process of base purification yielded a NaOH solution concentrated nine-fold as compared to the feeding solution for the bipolar electrodialysis process. A process developed for sodium lactate purification based on mono-polar and bi-polar electrodialysis was also successfully reported. Current efficiency for bipolar electrodialysis was in excess of 90%. Lee et al. also have reported the recovery of lactic acid from sodium lactate solutions. Tongwen et al. conducted the recovery of citric acid from sodium citrate and sodium sulphate solutions using EDBPM. Electrodialysis with BPM has also been used to recover glycerin from dieter wastes. Thus, it can be seen that electrodialysis using bipolar membranes has been widely studied for the recovery and concentration of acid and alkali solutions. The present investigations using EDBPM process were carried out to study the feasibility of reducing the TDS and recovering acid and alkali from the reject solutions emanated from reverse osmosis plant during the treatment of textile dyeing effluents. The RO reject was chosen for study in the present work because of its high TDS content, which remains a problem for treatment and disposal, and has high potential for the generation of acid and alkali.

**Experimental Procedure**

The laboratory electrodialysis system was supplied by Arun Electrochemicals, Chennai, India. It consisted of a DC power supply and an electrodialysis stack. The general scheme of the electrodialysis stack is shown in Fig. 1. It is composed of two electrodes between which five identical compartments of 1 cm thickness were inserted. The anode was Ti based metal coated with Ti-Ru-Pd oxides and the cathode was made of stainless steel. The cation-exchange membrane and the anion-exchange membrane were made up of polystyrene and DVB quaternary ammonium ion and polystyrene and DVB sulphonic acid group, respectively. The bipolar membrane was a combination of both. The effective electrode and membrane area was 120 cm$^2$. The total exchange capacity of the membrane was 1.3 (meq/g). The membranes were separated with polypropylene spacers each of 1 m thick which determines the chamber.
The volume of each chamber was about 160 cm$^3$, which varied slightly with the bending of membranes. In all the compartments solutions were circulated in a batch mode using recirculation pumps. The power for the process was provided by a DC power supply (current range 0–1.5 A, voltage 0–50 V). The experiments were carried out under galvanostatic conditions and the temperature of the solutions was maintained at 30°C.

The solution to be treated was circulated in the central compartment. For this purpose, sodium chloride was used. Dilute hydrochloric acid (0.005 N) and dilute sodium hydroxide (0.005 N) solutions were taken in the acid and base compartments, whereas higher concentration of acid (sulphuric acid) and alkali (sodium hydroxide) were used in the anode and cathode compartments (0.05 N), respectively to minimize cell voltage in the initial stages of experiments. All the chemicals (AR) were obtained from Merck, India and used without further purification.

The depletion of the TDS in the process water was analysed by measuring the conductivity of the solution using conductivity meter (WTW LF 197). The TDS value of the solution was obtained from the conductivity of the solution using TDS versus conductivity curves plotted with known concentration of NaCl. The pH of the solution was measured using pH meter (Elico pH meter, LI 120, India). Acid and base concentrations of the solutions were determined by titrimetric method. The chloride and sodium ion concentrations were measured by argentometric method and using flame photometer (Sherwood, Model 410), respectively. All the experimental analyses were carried out as per standard methods used for water and wastewater examination$^{11}$. The transports of sodium and chloride ions were determined using the relation$^{12}$.

$$t_{BPM} = \frac{(N_o - N_f)}{N_e} \quad \ldots (1)$$

where $N_o$ and $N_f$ are the equivalents of ions before and after electrolysis, respectively and $N_e$ is the amount of electrical charges carried by the current expressed in Faraday.

The current efficiency of the process was analysed using the relation

$$\text{Current efficiency} \ (\%) = \frac{W \times F \times 100 \%}{E \times N \times I} \quad \ldots (2)$$

where $W$ = weight of the salt removed, $F$= Faraday (26.8 Ah), $E$ = equivalent weight of the salt removed (g), $N$= number of cell compartments and $I$ = current (A).

The energy consumption of the process was analysed by

$$\text{Energy consumption (Wh/L)} = \frac{\text{Voltage (V)} \times \text{Time (h)}}{\text{Volume of the solution treated (L)}} \quad \ldots (3)$$

**Results and Discussion**

The experiments were carried out to study the effect of variable operating parameters on the removal of TDS and production of acids and alkali from salt solutions.

**Effect of concentration of electrolytes on the EDBPM process**

In order to find out the effect of concentration of the electrolytes in the electrode compartments on the EDBPM process, experiments were carried out with various concentrations of sulphuric acid and sodium hydroxide solutions. The treatment was carried out with solutions of 10 g/L sodium chloride which had a corresponding conductivity of 17 mS/cm. The treatment was conducted until the conductivity of the solution dropped below 100 μS/cm. Results obtained were analyzed based on the acid/alkali production, sodium and chloride ion leakage, time required and energy consumption. The acid and alkali concentrations were expressed in terms of normality for acid and alkali compartments, respectively. The results obtained show that though not much difference was observed in production of acid and base, higher amount of sodium and chloride ion migration towards the cathode and anode compartments, respectively were observed at higher concentrations of electrolytes in the electrode compartments. The transport of chloride and sodium ions towards anode and cathode compartments through bipolar membranes as a function of electrolyte concentration is given in Fig. 2. Variation of concentration of electrolytes also influenced the treatment time and energy consumption as evident from Fig. 3, which shows that both the energy consumption and treatment time...
decreased with increase in electrolyte concentration. Based on the results obtained, an electrolyte concentration of 0.05 N was chosen in the electrode compartments for further studies which showed better performance in terms of treatment time and energy consumption.

**Effect of current density**

Influence of operating current density on the electrodialytic process was studied in the range of 0.2 to 0.83 A/dm². Higher current densities resulted in increased co-ion transport to the electrode compartments. Also at higher current densities evolution of chlorine was observed. The effect of current density on the process in terms of current efficiency, energy consumption and treatment time required is presented in Table 1. The process requires 26.8 Ah/L of the solution for the removal of one-gram equivalent weight of the salt (which is 58.44 for NaCl). The pH of the treated solution was ~ 4 at all current densities studied. Therefore, a charge of 0.83 A/dm² is considered optimum for the process with 10 g/L of the salt where the feed volume is 200 mL and further studies were carried out at this current density. However, the required current density for the process is dependent upon the feed concentration.

<table>
<thead>
<tr>
<th>Current density (A/dm²)</th>
<th>Energy consumption (KWh/L)</th>
<th>Current efficiency (%)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>0.063</td>
<td>91</td>
<td>240</td>
</tr>
<tr>
<td>0.41</td>
<td>0.143</td>
<td>91</td>
<td>120</td>
</tr>
<tr>
<td>0.62</td>
<td>0.240</td>
<td>74</td>
<td>100</td>
</tr>
<tr>
<td>0.83</td>
<td>0.264</td>
<td>67</td>
<td>70</td>
</tr>
</tbody>
</table>

**Effect of flow rate**

The flow rate was varied in the range of 500 - 10,000 mL/h for the treatment of 10 g/L NaCl, at constant current of 0.88 A/dm². Production of acid and base was not affected by the variation of flow rate, however the energy consumption and treatment time were reduced at higher flow rates (Fig. 4).

**Effect of feed concentration on the process**

The influence of feed concentration was studied on the process with NaCl concentration ranging from 1 to 75 g/L. As expected, the acid and base formation increased with increased concentration of the feed (Fig. 5 a, b). But increase in the concentration of both the acid and base leveled off after a certain limit, which could be due to the leakage of H⁺ and OH⁻ to the feed compartments. In case of acid production, the concentration of H⁺ ions leveled off, whereas in case of OH⁻ ions the concentration initially increased which decreased later. This is evident from Fig. 6,
which shows the variation of $pH$ of the feed solution with time. During all experiments with various feed concentrations, the $pH$ of the salt solution increased initially, which reflects the leakage of OH$^{-}$ ions from alkali compartment predominating in the initial stage to the feed compartment, followed by the decrease of $pH$ during the end of electrolysis. This is due to the predominating concentration of H$^{+}$ ions in the feed compartment transported from acid compartment during the later stage of experiments. Consequently, the OH$^{-}$ ions from the alkali compartment pass to the feed compartment to balance the concentration of H$^{+}$ ions in the feed solution. However, for all experiments the final $pH$ of the salt solutions was always in acidic range of approximately 4.

The transport of co-ions to the electrode compartments increased with increased current density. Conversion of chloride and evolution of chlorine from anode compartments increased with HCl concentration in acid compartments as a result of higher feed concentrations. Treatment time for feed solutions increased linearly with feed concentrations (Fig. 7). The energy consumption and current efficiency of the process for various concentrations of feed solutions are furnished in Table 2.

**Application of the EDBPM process for the treatment of RO rejects of textile dyeing effluent**

In order to evaluate the technical feasibility of the process in practical application, the treatment was applied to a textile RO reject obtained from a textile-dyeing unit, located in Tiruppur. The reject solution was obtained from a RO unit where processing for TDS removal was done for a dyeing effluent (pretreated for the removal of colour and suspended solids using coagulation and filtration methods).
characteristics of the RO reject used for the study are presented in Table 3. Higher amounts of suspended solids were observed to be present in the effluent, which exceeds the prescribed 25 mg/L of suspended solids as fixed by the manufacturer of the membranes. The level of suspended solids had to be brought down prior to the treatment using EDBPM process. Hence the effluent was passed through a sand filter at a flow rate of 60 mL/min, contained in a glass column of 30 cm length with a cross sectional area of 706 cm². This effluent was then subjected to the EDBPM treatment. The feed solution with conductivity value 27.0 mS/cm was fed into the middle compartment with mild acid and alkali solution of 0.005 N in acid and alkali compartments. The electrode compartments were filled with 0.05 N sulphuric acid and sodium hydroxide solutions in anode and cathode compartments, respectively. The treatment process lasted for 115 min when operated at 0.83 A/dm² current density and the decrease of conductivity of the solution versus time is plotted in Fig. 8. The acid and alkali concentrations were 0.274 and 0.258 N, respectively with the energy consumption and the current efficiency of the process were found to be 0.310 KWh/L and 56.8%, respectively. The transport number of chloride and sodium ions was 0.0389 and 0.0161, respectively. The process was successfully found to decrease the TDS of the solution with simultaneous recovery of acid and alkali from the RO reject.

**Conclusion**

The study shows that the process using electrodialysis with bipolar membranes will prove to be an effective solution for the removal of TDS from effluents. The method can successfully recover the salt present in the effluents in the form of acids and bases. The study revealed the evolution of chlorine gas from anode compartments at high feed concentrations as a result of co-ion migration. However, this can be prevented if a cation exchange membrane is placed next to the anode that prevents the movement of chloride towards the anode compartment. The method removed more than 99% TDS with recovery of acid and alkali of 0.274 and 0.258 N respectively within 115 min of the tested textile RO reject solution. Thus, this method has promising future in the treatment of RO rejects where problems of further treatment and disposal problems are eliminated.

**Acknowledgement**

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**References**