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COMBINATION OF REVERSE OSMOSIS AND ELECTRODEIONIZATION FOR SIMULTANEOUS SUGAR RECOVERY AND SALTS REMOVAL FROM SUGARY WASTEWATER

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Abstract

An integrated membrane system combining reverse osmosis (RO) and electrodeionization (EDI) is used for simultaneous sugar concentration and salts removal from a synthetic dilute sugar solution as a model of sugar-containing wastewater. The RO system uses a thin film composite RO membrane (Saehan CSM, RE1812-60). Meanwhile, the EDI stack has two diluted compartments, one concentrated compartment, one anode compartment, and one cathode compartment. Commercially available cation exchange membrane (MC-3470) and anion exchange membrane (MA-3475) are used as ionic selective barriers of the EDI stack. Both diluate and concentrate compartments are filled with mixed ion exchange resins (purolite strong acid cation exchange, C-100E and strong base type I anion resins, A-400). Two different operation modes, i.e. RO-EDI and EDI-RO, were assessed. The experimental results show that the observed sugar rejection of RO membrane is more than 99.9% and there is no sugar loss in the EDI stack. This indicates that the hybrid process allows almost total sugar recovery. In addition, significant reduction of salts content from the concentrated sugar solution is obtained. From permeate flux and permeate purity points of view, however, the EDI-RO configuration seems superior to the RO-EDI configuration. It should be emphasized that scale formation on the membrane surface of the concentrate compartment side has to be controlled.

Key words: *electrodeionization; reverse osmosis; sugar recovery; sugary wastewater*

Introduction

In the confectionery and beverage industries, sugar (in the form of sucrose, maltose, fructose, glucose, etc.) is the main constituent in most of the process streams. Inevitably, the effluent streams arising from these industries exhibits a high COD (chemical oxygen demand) due to the presence of sugar within the waste stream. Effluent having sugar concentration of 1% w/w produces a COD of about 10,000 mg/L. In addition to reduce the COD level, therefore, it is considerably interesting to optimize process economics through sugar recovery. Recently, a number of studies have been carried out to study the conversion of carbohydrates-containing solutions to hydrogen gas (Taguchi, et al., 1992; Ueno, et al., 1996; Mizuno, et al., 2000; Fang and Liu, 2002; Zang, et al., 2003)

Today, reverse osmosis (RO) is used for desalination of sea and brackish water and for various industrial purposes. Generally, RO membranes capable of retaining most of dissolved solutes, including sugars and salts. To move water from the concentrated stream toward the permeate stream, the operating pressure of the RO system must exceed the osmotic pressure of the solution. A number of studies (Prasetyo, et al., 2005; Pepper, et al., 1985; Rektor, et al., 2004; Hayakawa, 2001; Shimanskaya and Shimansky, 2002) have shown the RO feasibility for concentrating sugar-containing solutions, e.g. for concentrating fruits juice. Compared to conventional evaporation technology, RO offers some advantages: (i) sugar degradation by heat effect can be avoided so that the concentrated sugar solution may be reused directly within the process, provided the feed stream is not contaminated; (ii) RO requires a relatively low energy, using electrical power to run pumps; and (iii) being modular, small plant can be installed close to the source of effluent stream.

In most circumstances the sugary wastewater contains various inorganic salts and/or organic acids generated by micro-organism present in the effluent stream. As the water is removed from the solution, concentration of such impurities increases, depending on the volumetric concentration ratio (VCR). VCR is a measure to express the degree of concentration of the rejected solutes in the feed relative to the initial

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condition. By using average salts rejection of 97% (Shimanskaya and Shimansky, 2002), for example, VCR of 10 to 20, giving concentrated volume of 10% to 5% of the initial value, results in the increase of impurities concentration about 9.7 to 19.3 times. Without a further treatment, therefore, it may not be appropriate to reuse the recovered sugar within the process.

Experimental results using laboratory scale electrodeionization (EDI) unit to remove ionic component from sugar solutions (Widiasa, et al., 2002; Widiasa and Wenten, 2003; Widiasa, et al., 2004) and to recover citric acid (Widiasa, et al., 2004) have been reported. In this study, an integrated system combining RO and EDI is used for simultaneous sugar concentration and salts removal from a synthetic dilute sugar solution as a model of sugar-containing wastewater. Two different operation modes, i.e. RO-EDI and EDI-RO, were assessed. Performance of the integrated system is evaluated in term of water removal rate (permeate flux) and conductivity and pH of the concentrated sugar solution.

Experimental

Feed solution

A synthetic sugar solution was prepared for the experiments by diluting 200 g technical grade sucrose crystals within 20 L tap water at room temperature. For every experiment, a fresh solution was prepared. The solutions had a pH of 7.2 ± 0.3 and a conductivity of 250 ± 10 μS/cm. The solution was filtered by cartridge filter (10 μm) to remove insoluble matters prior to be treated by the integrated systems.

Experimental Set up

Figure 1 shows the schematic representation of the experimental setup used in this study, which consisted of a stirred feed tank, a RO module, a high pressure pump connected to a panel control, an EDI stack, a main adjustable DC power supply to generate a potential field in the EDI stack, three diaphragm pumps (Puricom UP-8000, maximum flow rate of 3 lpm, maximum pressure of 80 psi, motor 48VDC/2A/50hz) connected to a three output adjustable DC power supply, a concentrate tank and an electrodes rinse tank. The system is also equipped with a three way valve to switch the fluid flow either through the RO module or through the EDI stack. For simplicity, a number of such components is not depicted in Fig. 1. The RO unit used a thin film composite RO membrane (Saehan CSM, RE1812-60). The permeate channel of the module was little modified to be suited for the housing. The characteristics of the membrane are shown in Table 1. Meanwhile, the EDI stack consisted of two diluted compartments, one concentrated compartment, one anode compartment, and one cathode compartment. Commercially available cation exchange membrane (MC-3470) and anion exchange membrane (MA-3475) were used as the ionic selective barriers of the EDI stack. Typical characteristics of the Ionac® ion exchange membranes are shown in Table 2.The effective area of the ion exchange membranes is 140 cm^2 (10 cm x 14 cm). Both diluate and concentrate compartments were filled with mixed ion exchange resins (purolite strong acid cation exchange, C-100E and strong base type I anion resins, A-400).

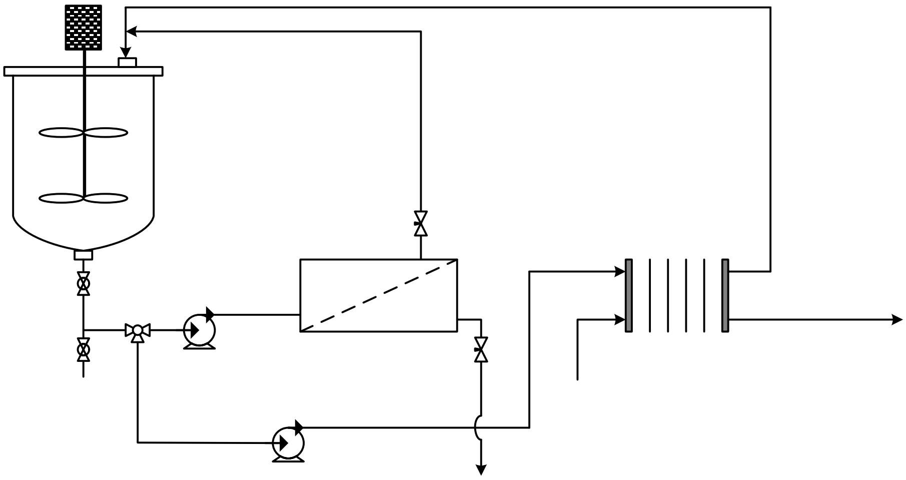

Figure 1. Schematic representation of the experimental set-up

Procedure

The system (Fig. 1) was operated in a discontinuous way according to two operation modes, i.e. RO-EDI and EDI-RO. In the RO-EDI operation mode the RO permeate was continuously withdrawn whereas the RO retentate was totally recycled to the feed tank until reaching a desired volume concentration ratio (VCR):

$$VCR = \frac{V_0}{V_c} \qquad (1)$$

where V_0 is the initial volume of the sugar solution and V_c is the final volume of the concentrate. Subsequently, the concentrate having high salts concentration was deionized in the EDI stack. In the latter operation mode, the feed solution was firstly deionized in the EDI stack until reaching a desired conductivity. The deionized sugar solution is further fed to the RO module where the RO permeate was continuously withdrawal whereas the RO retentate was totally recycled to the feed tank until reaching a desired VCR. The feed solution with sugar and salt contents 10 g/L and 200 mg/L, respectively was concentrated gradually up to VCR 20. After each run the setup was cleaned and sterilized to avoid the bacterial growth by using 0.5% (w/w) NaOH solution.

Both RO-EDI and EDI-RO configurations were operated as follows. For the concentration step, the solution flow rate through the RO membrane was controlled in the range of 250 to 300 L/h. A transmembrane pressure of 30 bar was maintained in all runs. The transmembrane pressure, TMP, is given as:

$$TMP = \frac{P_{in} + P_{out}}{2} - P_p \qquad (2)$$

where P_{in} and P_{out} are the hydrostatic pressures before and after the membrane module, respectively; P_p is the hydrostatic pressure of permeate. For the salt removal step, however, the solution flow rate through the EDI stack was maintained at 5 L/h. The temperature of the circulating solution was maintained at 30±2^{o}C.

Table 1. Saehan CSM membrane characteristics (Catalogue of Saehan CSM membrane)

Element type	RE1812-60
Permeate flow (GPD)	60
Typical salt rejection (%)	96.0
Test condition	Pressure : 60 psig NaCl : 250 ppm Temperature : 25^{o}C pH : 6.5 – 7 Recovery : 15%

Tabel 2. Typical characteristics of the Ionac® ion exchange membranes (Ionac® Ion Exchange Membranes)

			Cation, MC-3470	Anion, MA-3475
Thickness	mils		15	16
Exchange capacity	meq/g		1.4	0.9
Mullen burst tes, min	Bar		10.3	10.3
Area resistance	Ohm/cm	0.1 N NaCl	25	50
		1.0 N NaCl	10	25
Perselectivity	0.5 N NaCl/1.0 N NaCl		96	99
Water permeability	ml/h/ft2 @ 5 psi		25	25
Temperature stability, max	^{o}C		80	80
Chemical stability, pH			1 to 10	1 to 10
Current density, max	Ampere/ft^2		50	50

Analysis

Several parameters such as permeate flux, conductivity, refractive index, and pH were observed to evaluate the performance of both RO-EDI and EDI-RO operation modes. Flux measurements were carried out by measuring the volume of permeate received per time at the specific test conditions. In order to express the flux in term of L/m^2/h the effective membrane area was assumed to be 0.5 m^2. Moreover, refractive index, conductivity, and pH were directly measured by means of refractrometer, conductimeter, and pHmeter, respectively. The refractive index can be correlated to the amount of total solids whereas the conductivity is a measure for the amount of ionic substances present.

Results and Discussion

Stability test of the RO module

The Saehan CSM, RE1812-60, is household membrane for producing drinking water from tap water that is usually operated at room temperature and pressure in the range of 60 – 90 psig. Since the membrane would be used at moderate pressure, a stability test of the RO module using deionized water was performed. The RO module was exposed to a deionized water under pressure and temperature up to 30 bar and 40^{o}C, respectively. In this stability test, both retentate and permeate returned to the feed vessel. As can be seen in Fig.2, the membrane has a high permeability of approximately 3.3–3.6 L/m^2.h.bar depending on the deionized water temperature. The increase of temperature up to 40^{o}C resulted in a proper increase of flux. Moreover, the flux of pure water was directly proportional to the applied transmembrane pressure indicating that the RO module is pressure stable. Thus, all further fluxes data to reach VCR up to 20 (i.e. sugar concentration of 200 g/L) were taken at pressure 30 bar.

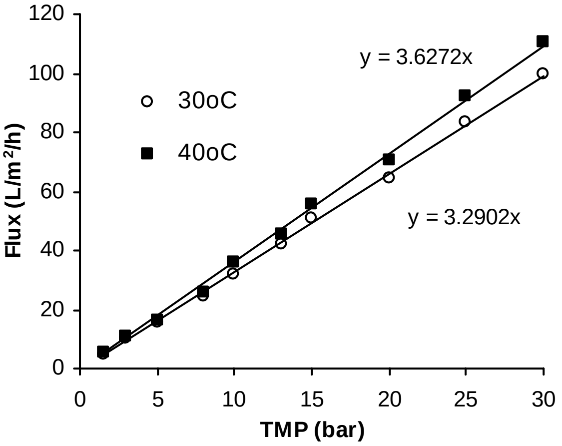

Fig. 2. Flux of pure water as a function of transmembrane pressure and temperature

Permeate fluxes

After the membrane stability test, discontinuous operations of the simultaneous sugar recovery and salt removal from a sugary wastewater model were performed with initial sugar and salt concentrations 10 g/L and 200 mg/L, respectively. During these experiments, RO was operated at pressure of 30 bar and temperature of 30±3 ^{o}C whereas EDI was operated at current density of 10 A/m^2. The solutions were concentrated gradually to reach VCR up to 20. Fig. 3 shows the permeate fluxes of the two operation modes as a function of VCR according to the procedure discussed above. As can be seen that permeate flux of the EDI-RO operation mode is considerably higher than that of the RO-EDI operation mode due to the great difference of their salt concentrations (Fig. 4). This means that the EDI-RO operation mode requires smaller area of RO membrane as well as installation cost for achieving the same concentration level compared to the other one. From this point of view, the EDI-RO operation mode is obviously superior to the RO-EDI operation mode.

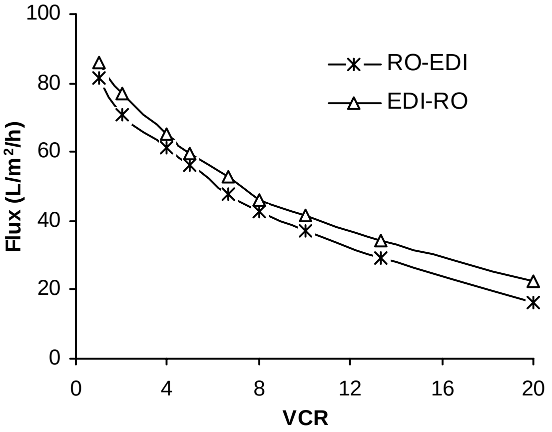

Fig . 3. Permeate flux vs. VCR of both RO-EDI and EDI-RO operation modes. T = 30±3^{o}C, P = 30 bar

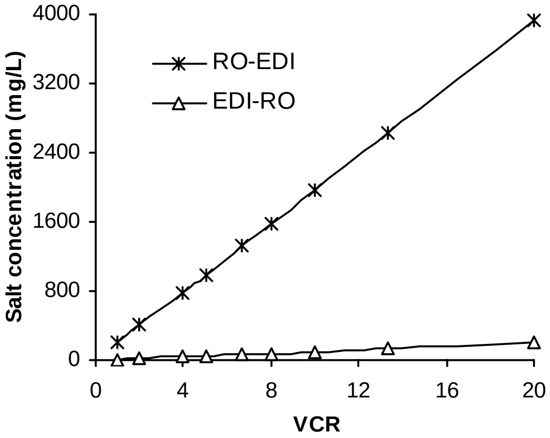

Fig. 4. Salt concentration of RO retentate vs. VCR of both RO-EDI and EDI-RO operation modes

Sugar recovery

Fig. 5 shows the results of refractive index measurements for both permeate and concentrated sugar solution. It can be seen that the observed refractive index of permeate is closed to the refractive index of water. On the other hand, the refractive index of the concentrated sugar solution is proportional to the VCR. The same performance was showed by either RO-EDI or by EDI-RO operation mode. Furthermore, using Somogyi-Nelson method [16] where sucrose was previously hydrolyzed to glucose and fructose, the sugar quantity of permeate was observed to be less than 10 mg/L. In other words, the observed sugar rejection of RO membrane is more than 99.9%. Meanwhile, there was no considerable sugar loss in the EDI stack. These results confirm that the hybrid process, either RO-EDI or EDI-RO configuration, allows almost total sugar recovery.

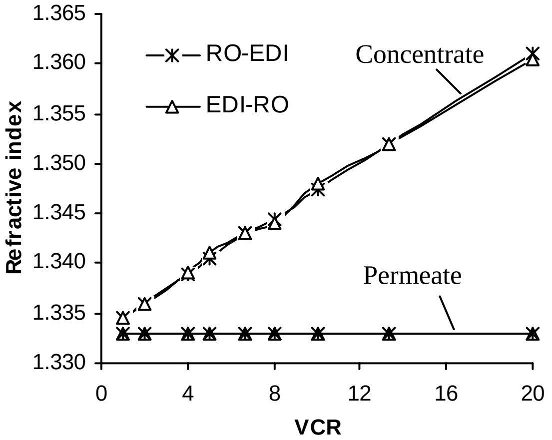

Fig. 5. Refractive index of the permeate and concentrated sugar solution vs. VCR of both RO-EDI and EDI-RO operation modes

Conductivity of the RO permeate

In addition to increase sugar concentration, the water removal from the feed solution results in the increase of salt concentration. The effect of VCR on the permeate conductivity is shown in Fig. 6. It can be seen that permeate conductivity of the RO-EDI operation mode is much higher than that of the EDI-RO operation mode. At VCR 20, for example, permeate conductivity of the RO-EDI configuration is about 35 μS/cm whereas permeate conductivity of the EDI-RO configuration is only about 4 μS/cm. This is due to the difference of the salt concentration during the concentration step by the RO unit. As a result of higher salt concentration, the produced permeate will also have a higher conductivity. It should be emphasized that permeate of the two operation modes can be reused. Nevertheless, the higher permeate purity of the EDI-RO configuration is important when a high water quality is required, e.g. for boiler feed water make-up.

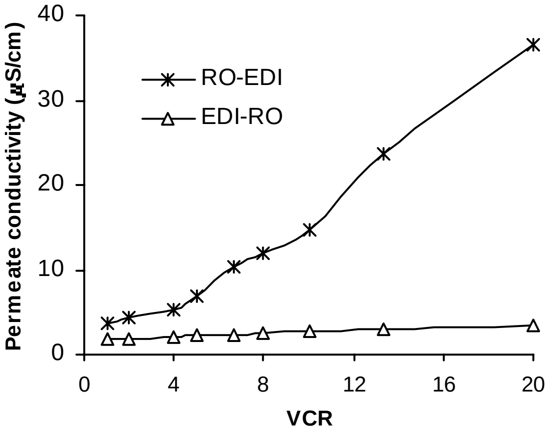

Fig. 6. Permeate conductivity vs. VCR of both RO-EDI and EDI-RO operation modes

pH of the concentrated sugar solution

Sucrose hydrolysis can occur at all pH levels, being fastest at pH 5 (Chuy and Bell, 2003). As the sucrose hydrolysis produces reducing sugars in sufficient amounts, it can cause a negative effect on food quality. For this reason, the control of pH solution is important to reduce the rate of sucrose hydrolysis. Fig. 7 shows the pH of solution treated by either RO-EDI or by EDI-RO operation modes. It can be seen that the pH of the concentrated sugar solution of the RO-EDI operation mode is around 7.

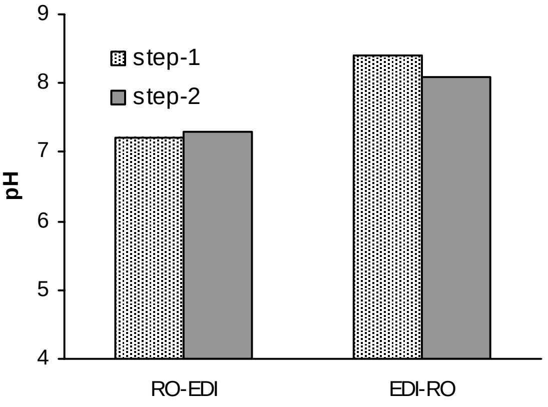

Fig. 7. pH of sugar solution after each step of both RO-EDI and EDI-RO operation modes (TMP = 30 bar, current density = 10 A/m^2)

In the RO-EDI operation mode, the sugar solution flowing through the diluate compartments of the EDI stack has a relatively high salt concentration. Under such condition, the salt transfer rate from the bulk stream to the ion exchange bed is similar to from the ion exchange bed to the concentrate compartments via ion exchange membranes. The increase of current density up to 25 A/m^2 has inconsiderable effect on the pH of solution. In the RO-EDI operation mode, however, salt removal was carried out at low salt concentration and as a result the overall ion transfer rate is controlled by the ion transfer from the bulk solution to the mixed-bed resins. For a typical current density, the sugar solution after processed in the EDI stack generally had pH higher than 8. Moreover, the decrease of pH value with increasing current density was observed (Fig. 8).

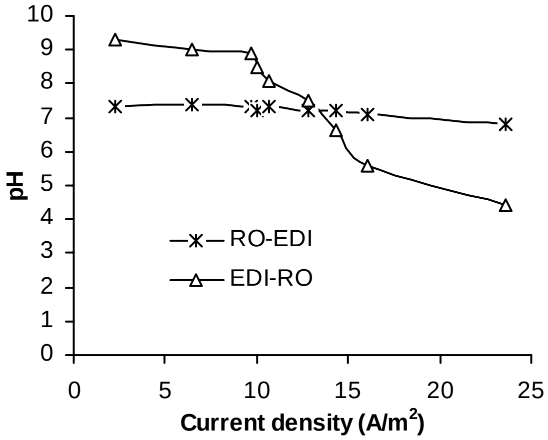

Fig. 8. Final pH of the sugar solution concentrated by RO-EDI and by EDI-RO operation modes (TMP = 30 bar)

Membranes Scaling

Scaling of EDI equipment is of particular concern as it reduces membrane efficiency and fouls the surface of electrodes. Scaling has been found to occur in localized regions of EDI equipment in where high pH is typically present (Tessier, et al., 2000). Such regions include those on the membrane surface of the concentrate compartment side and on the chatode surface. As can be seen in Fig. 9 and 10, severe scaling occurs on the surface of both anion and cation membranes. This mechanism of scale formation is basically due to the migration of hydroxyl ions from water splitting in the diluate compartments.

Fig. 9. scaled anion membrane

Fig. 10. Scaled cation membrane.

Various techniques have been proposed for reducing scaling in EDI system (Tessier, et al., 2000; Mir, 2001). The scale formation in EDI system can be minimized by either reducing the concentration of calcium and magnesium or by lowering pH level of the concentrate stream. The addition of antiscalants into the concentrate stream to form complexes with the calcium and magnesium ions may also be used. In this study, scaling is controlled by pH adjustment of concentrate stream with HCl solution. As shown in Fig. 11, scale on the membrane surface is completely reduced.

Fig 11. Scaling control by pH adjustment of concentrate stream with HCl solution

Conclusions

An integrated membrane system combining reverse osmosis (RO) and electrodeionization (EDI) was used for simultaneous sugar concentration and salts removal from a synthetic dilute sugar solution as a model of sugar-containing wastewater. The system was operated in a discontinuous way according to two operation modes, i.e. RO-EDI and EDI-RO. Several parameters such as permeate flux, conductivity, refractive index, and pH were observed to evaluate the performance of both operation modes. The results show that simultaneous sugar recovery and salts removal from sugary wastewater can be achieved. Either RO-EDI or EDI-RO operation mode allows almost total sugar recovery. In addition, significant reduction of salts content from the concentrated sugar solution is obtained. From permeate flux and permeate purity points of view, however, the EDI-RO configuration seems superior to the RO-EDI configuration. It should be emphasized that scale formation on the membrane surface of the concentrate compartment side has to be controlled.

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