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Membrane treatment options for wastewater from cellulosic ethanol biorefineries

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ABSTRACT

Ethanol production from cellulose is technically feasible. However, treatment of the resultant wastewater can account for 20–33% of the total process cost and thus potentially hold back commercialisation. Wastewater from dilute acid processes has high levels of organic material, colour, sulphate and ammonium. Two approaches were considered to reduce treatment costs by selectively separating the ammonium and sulphate from the remaining organics in the wastewater. Using ultrafiltration, ammonium and sulphate retentions (68 and 57%, respectively) were similar to COD retention (67%). The second approach used was electrodialysis. This proved far more selective and was able to regenerate solutions of sulphuric acid and ammonium hydroxide with little evidence of sugar, COD or colour migrating across the ion-exchange membranes. These preliminary results thus confirm previous findings that sulphuric acid can be recovered from aqueous streams containing high concentrations of sugars with little sugar loss—resulting in a saving in the amount of ammonia required for neutralisation and indeed for the overall process.

Keywords: Ultrafiltration; Ion exchange; Electrodialysis; Lignocellulosic ethanol; Wastewater

1. Introduction

Lignocellulose feedstocks (typically sugar cane bagasse, cornstover and grasses) are an alternative source of renewable substrate for large ethanol production from biorefineries. The National Renewable Energy Laboratory (NREL) process appears promising with an estimated production costs of ≈\$2.15 per gallon [1]. This process (see Fig. 1) consists of breaking down the cellulose with 1% H_2SO_4 at 130–160˚C which is neutralised later by the addition of ammonia. Then, enzymes are used to convert cellulose into sugars and fermentation is carried out by a micro-organism such as *Zymomonas mobilis*. Ethanol is recovered by distillation followed by molecular sieve drying.

The latest NREL estimate for the production cost of cellulosic ethanol is a minimum ethanol selling price (MESP in 2007 US dollars) of \$2.15 per gallon (\$0.57 per litre) [1]. A more recent estimate, using a similar process but with actual pilot-plant data, is a MESP of \$1.97–\$2.50 per gallon (\$0.52–\$0.66 per litre)

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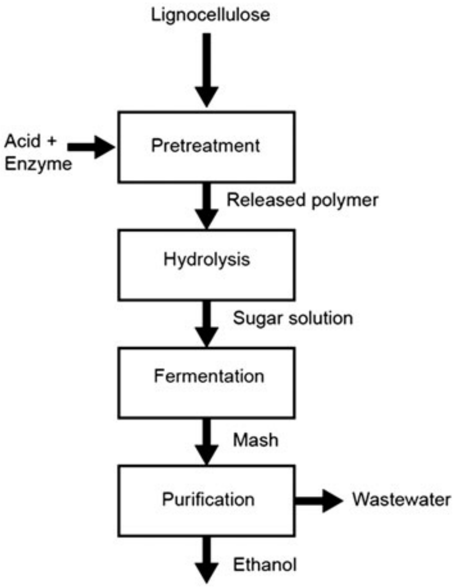

Fig. 1. Process diagram of conversion of lignocellulose to ethanol.

[2]. The NREL estimate uses a wastewater treatment cost of \$0.34 per gallon (\$0.09 per litre) of ethanol produced. However, using the necessary capital costs as reported by Steinwinder et al. [3] increases treatment costs to \$0.42–\$0.77 per gallon (\$0.11–\$0.20 per litre) of ethanol produced which results in a target MESP to \$2.20–\$2.48 per gallon (\$0.58–\$0.66 per litre). Thus, wastewater treatment represents a significant proportion of the total cost of producing cellulosic ethanol, and remains an unresolved challenge for the widespread adoption of this technology. Much of the recent cost increases arise due to a change from over-liming to ammonia neutralisation so as to reduce sugar losses. This increases the ammonium and sulphate levels in the wastewater to a point where direct evaporation is impractical while anaerobic digestion is difficult and/or costly.

Given the recent increase in cost estimates due to the presence of high levels of ammonium and sulphate in the waste stream, a means of separating these components preferentially from the organics and either treating them (e.g. to produce a fertilizer of saleable value), or recycling them internally within the process, would be highly beneficial in reducing the cost of cellulosic ethanol technology. For processes where the solids are concentrated by pressing after the sulphuric acid pretreatment stage, electrodialysis may have the potential to recover the acid directly from the aqueous sugar stream, reducing the amount of ammonia necessary for pH neutralisation. The potential for the cost-effective use of electrodialysis is the focus of this paper.

Relative to the pre-treatment, enzymatic hydrolysis and fermentation stages or similar wastewater problems such as those associated with molasses distillery wastes where there are numerous reviews such as those by Satyawali and Balakrishnan [4] and Mohana et al. [5], there is a relatively scant literature on the treatment of lignocellulosic wastewater, with most papers focussing on anaerobic digestion for COD reduction and the production of biogas. For example, Merrick et al. [6] in laboratory trials achieved up to a 73% reduction in COD, and hence proposed a design for treating effluent arising from the NREL acid hydrolysis process, while Torry-Smith et al. [7] investigated the use of a pilot-scale UASB on wet-oxidised wheat straw effluent to enable water recycling after achieving a better than 80% COD reduction. More recently, Twumasi [8] focussed on sulphur mass balances and the relationship between COD and TOC in a softwood-to-ethanol process, Kaparaju et al. [9] studied the anaerobic digestion of hydrolysate and stillage, while Qiu et al. [10] achieved very considerable COD reductions (31,200–65 mg/L) through the sequential use of thermophilic anaerobic digestion in a fluidized bed reactor, an aerobic airlift loop reactor, and a biological aerated filter. Moreover, Sun et al. [11] reported colour removals in excess of 90% by the addition of 5 g/L of activated carbon to their hydrolysate, though the economics of the process weren't considered.

Kavanagh et al. [12] used stillage produced from a dilute sulphuric acid process, achieving COD reductions of 45–67% by anaerobic digestion and 28–38% by aerobic treatment. Colour removal followed a similar trend with 25–34% being achieved anaerobically but only 4–31% achieved aerobically. However, when aerobic treatment was combined with coagulation via alum dosing, colour removal levels of close to 90% were possible. In a subsequent study, Handelsman et al. [13] investigated the use of ultrafiltration (UF) and nanofiltration (NF) membranes for the treatment of various biorefinery effluents. A COD reduction of 37% was achieved with a 2000 MWCO UF membrane, increasing to a 75% reduction with an NF membrane. The colour removals in these two cases were 75 and ~100%, respectively. Negaresh et al. [14] have demonstrated that NF membranes can preferentially segregate organics from salts in post-treatment paper-mill effluents, however, the effluents here are relatively low strength (around 57 mg/L DOC) compared to those arising from the production of cellulosic ethanol. Given the relative size of the ammonium and sulphate ions, it was postulated that the use of such membranes could result in the fractionation of the COD from the ionic species. However, the data in Handelsman et al. [13] indicates this may be difficult.

The literature on cellulosic ethanol production has repeatedly mentioned the need for a reduction in both capital expenditure and operating costs so as to make the process economically viable. The recovery and/or recycling of processing material are an option that could be employed to improve the process economics. In this latter vein, Goldstein et al. [15] investigated the use of electrodialysis for acid recovery from concentrated hydrochloric (60%) and sulphuric (20%) acid hydrolysis processes. Their findings were encouraging in that electrodialysis was more cost-effective than pure diffusion, that little sugar was lost through the membrane, and that current efficiency increased as the concentration decreased. In this 1989 paper, it was estimated that the cost of recovering the acid was $0.02 per lb of glucose. This equates to $0.46 per gallon ($0.12 per litre) of ethanol which is at the lower end of the estimated cost range for treating wastewater from dilute acid hydrolysis ethanol which is similar to the estimate of $0.42–$0.77 per gallon ($0.11–$0.20 per litre) given by Steinwinder et al. [3]. Due to the low selling price for ethanol from 1990 to 2000 after this seminal study, research has since largely focussed on the use of ion-exchange resins for acid recovery (e.g. Sun et al. [11] and US Patent [16]), or been supplanted by dilute acid hydrolysis. Lee et al. [17] explored the recovery and separation of ammonium sulphate from fermentation waste, with particular emphasis on the potential of "pulsed power" as an effective fouling mitigation strategy. Different power modes gave removals of ammonium and sulphate ions in the ranges 52–63% and 65–86%, respectively. However, the energy inputs required (~100 kWh/m^3) were very high compared to reverse osmosis or evaporation. The exact nature of their experimental apparatus is unclear but if (as seems likely) a batch process were used, then more energy would be required than for a counter-current process where the electrical field can be used to augment the concentration gradient. More recently, Grzenia et al. [18] showed how a combination of membrane and solvent extraction technologies could be used to detoxify dilute acid pre-treatment streams, resulted in a beneficial rise in pH and hence a potential reduction in ammonia requirements for neutralisation with concomitant cost savings.

In summary then, the modest literature available indicates that electrodialysis may be a viable method to recover salts, acids and alkalis, provided that the electrical power is used efficiently. Further, given the high estimated costs of treating cellulosic biorefinery effluent, it was felt timely to revisit the feasibility of electrodialysis for acid recovery. Certainly, it would seem that considerable benefits may be obtained by the employment of counter-current flow devices where both diffusion and the applied electric field are working in conjunction. Considering that Goldstein et al. [15] were investigating the recovery of 20% sulphuric acid, and that ion-exchange membrane costs have dropped by more than 75% (in absolute terms) in the intervening decades, the cost-effective recovery of low strength sulphuric acid (~1%) via electrodialysis seems a real possibility. Thus, in this context, the remainder of this paper presents preliminary data on ammonium and sulphate recovery obtained from laboratory-scale membrane and electrodialysis units that will be compared to UF fractionation results.

2. Materials and methods

The waste material used was provided by NREL (Golden Co, USA) and Microbiogen (Lane Cove, NSW, Australia), with the effluent to be treated coming from Microbiogen's pilot-scale fuel and food process, as described in Kollaras et al. [2]. In summary, sugar cane bagasse was milled and pre-treated by NREL before being used for both fermentation to ethanol and the growth of a xylose fermenting yeast. Effluent pH and conductivity were measured by a Hanna HI 255 combined meter; COD was determined by either a PeCOD$^{\text{TM}}$ analyser or a COD Merck test cell; colour was determined by spectrometry using Aquanal plus Spectro Hazen; osmolality was measured by an Advanced Instruments Model 3320 Osmometer; ammonium was evaluated by a Hanna HI 4101 probe. Other chemical species (including sulphur) were evaluated by Inductively Coupled Plasma, a Varian ICP-OES model 720, using high-purity standards. TS, TSS, VS and VSS were measured by Australian Laboratory Services (Wetherill Park, NSW). A representative composition of the wastewater is given in Table 1.

3. Experimental

A LabUnit M20 from Alfa Laval (Nakskov, Denmark) UF system was used, operating between 5 and 20 bar. 1,000 and 2,000 molecular weight UF (ETNA 01PP and GR95 PP) membranes in a spiral wound configuration (65 mm in diameter; 432 mm in length) were obtained from the manufacturer. A heat exchanger connected to a Julabo FL1201 chiller unit was used to maintain a constant feed temperature.

The electrodialysis unit consisted of a DC Power Supply control unit (adjustable output voltage from 0 to 35 V), three (Fig. 2a) or two (Fig. 2b) independent compartments (23 mL each) depending on the experimental mode, with two carbon electrodes (2 × 6 × 70 mm) as

Table 1
Wastewater parameters compared to previous studies

Parameter	Present study	Handelsman et al. [13]	Steinwinder et al. design basis [3]	Qiu et al. [10]	Torry Smith et al. [7]	Twumasi [8]	Kaparaju et al. [9]	Uellendahl and Ahring [23]
pH	3.9–4.3	4	5.2	4.0–4.6	5.8–6.0	4.7	3.6	
Conductivity (mS/cm)	17.35–18.50	6.7						
Osmolality (mOsm/kg)	430–475	199						
TS (g/L)	33		68		29	41	120	41–73
VS (g/L)			58		19		102	34–42
TSS (g/L)	0. 17		1.5	5.7–6.2		0.004	1.2–1.6	18–22
TDS (g/L)			67					10–15
COD (mg/L)	38,000–43,000	15,530	87,400	29,000–33,000	26,000–28,600	54,000	150,000	
Color (Pt/Co)	43,000–45,000	2,712						
B (ppm)	20–80							
Ca (ppm)	225–290		6.79					
Cr (ppm)	0–5		0.177					
Cu (ppm)	0–5		0.005					
Fe (ppm)	100–125		0.814					
K (ppm)	280–330		498					
Mg (ppm)	95–120		4.63					
Na (ppm)	695–800		15.8					
Ni (ppm)	0–5							
NH_4^+ (ppm)	2,400- 2,620		1,060	50–61			160	
P (ppm)	40–65		262					
SO_4^{2-} (ppm)	8,120–9,570		4,400			570		
Zn (ppm)	0–5							

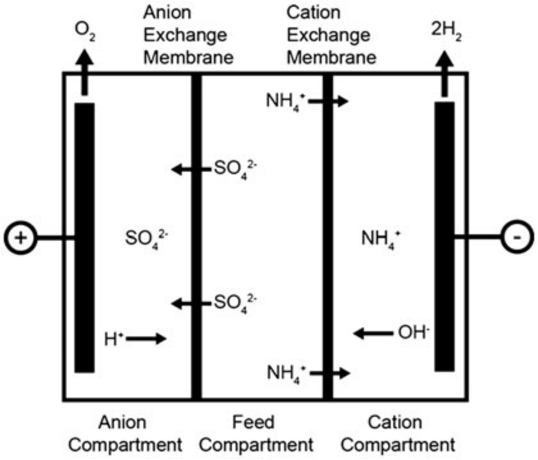

Fig. 2a. Configuration of the three-compartment electrodialysis unit, showing the anion, feed and cation compartments.

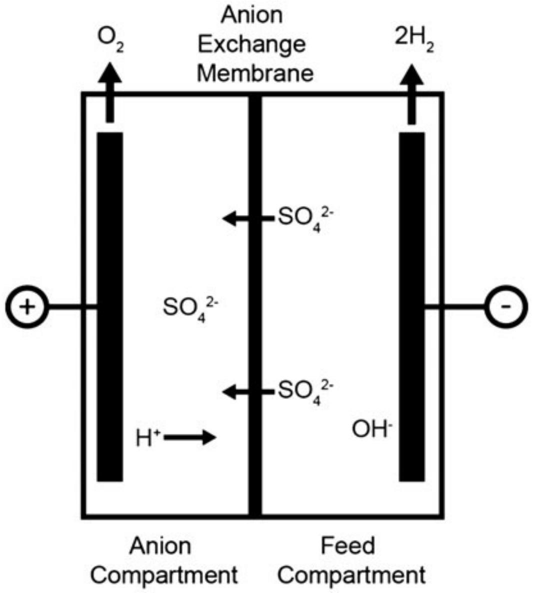

Fig. 2b. Anion configuration of the two-compartment electrodialysis unit.

anode and cathode. Silicone gaskets between the compartments were used to prevent solution leakage. The current flowing was measured using a Digitech QM-1324 multimeter.

AMX anion and CMX cation Neosepta membranes (Tokuyama Soda Company) were used. They were prepared with a Cl^- fixed ion for the cation-exchange membrane and Na^+ for the anion-exchange membrane. These membranes were chosen as being specified for electrodialysis separation processes and/or water desalination. The membrane surface area in each case was 1,960 mm. Before each experimental run, membranes were soaked in a KCl solution (~100 mM) for at least 24 h, after which they were soaked in deionised water for another 24 h [19].

3.1. Efficiency and recovery calculations

The separation performance for the Alfa-Laval membrane rig was defined as the percentage rejection (% R) of each feed component, calculated as:

$$\% R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{1}$$

where C_p represents the component concentration in the permeate stream and C_f the corresponding feed concentration.

The separation performance for the ion-exchange rig was defined by the current efficiency determined as follows:

$$\% \text{ efficiency} = \frac{n_{\text{experiment}}}{n_{\text{theory}}} \tag{2}$$

where the theoretical current efficiency was estimated using Faraday's Law:

$$n\text{SO}_4^{2-}{}_{\text{theory}} = \frac{I \cdot \Delta t}{2 \cdot F} \tag{3}$$

$$n\text{NH}_4^{+}{}_{\text{theory}} = \frac{I \cdot \Delta t}{F} \tag{4}$$

$$n_{\text{component experiment}} = \frac{(C_{\text{initial, component}} - C_{\text{final, component}}) \cdot V}{M_{\text{component}}} \tag{5}$$

Here I (A) is the current passing between compartments; Δt (s) is the run time; F (96,485 C.eq^{-1}) is the Faraday constant; n is the number of moles; M (g/mol) is the molar mass of the component; and V(L) is the volume of the feed compartment. C_{initial} and C_{final} (mg/L) are the initial and final concentrations in the feed compartment.

4. Results and discussion

4.1. Wastewater composition

The composition of the wastewater used in this study is given in Table 1, together with a comparison to previous studies conducted over the last decade.

This wastewater originated from dilute acid-treated bagasse from Florida (USA), Handelsman et al. [13] used dilute acid- and alkali-treated cane trash from Queensland (Australia), while Steinwinder et al. [3] used effluent from dilute acid-treated cornstover. As expected, the waste used in this present study was more concentrated than that of Handelsman et al. [13], whilst the COD was lower than that of Steinwinder et al. [3] due to the aerobic growth of a xylose fermenting *Saccharomyces cerevisiae* strain [2]. It is noteworthy that there are also considerable differences in dissolved metal concentrations between the various effluents.

4.2. Ultrafiltration

Table 2 shows the results from using a 1000 MWCO membrane on a 1 g/L $(NH_4)_2SO_4$ solution. This experiment was conducted to serve as a baseline for later runs with cellulosic wastewater. Experiments were run at 25°C and at pressures of 5 and 10 bars.

There is a modest rejection of both ammonium and sulphate ions which are to be expected as such a "tight" membrane is bordering on being classified as NF. However, when compared with the results of Handelsman et al. [13], who obtained COD rejections of 37% for UF and 91% for NF and conductivity rejections of 27% for UF and 91% for NF, these present results indicate that UF and NF membranes seem unable to preferentially separate dissolved ionic species from COD. In order to confirm these results, cellulosic effluent was treated using a 2000 MWCO UF membrane that had similar separation performance to the 1000 MWCO membrane for the pure ammonium sulphate solution.

Despite pre-filtering with a fine cloth to remove residual fibres (which caused fouling problems in earlier unpublished UF runs by blocking the spacers in the spiral wound membrane), the permeate flux declined rapidly, essentially ceasing after 10 min, due to membrane fouling. Thus, both membrane fouling and effluent pre-treatment are issues that need active consideration in any cellulosic wastewater treatment design, with a cost-effective role for spiral wound membranes being uncertain.

The effluent treated by the UF membrane was analysed and results are given in Table 3. The reduction of COD (67%) and colour (98%) are better than those of Handelsman et al. [13] who obtained corresponding removals of 37% and 75%. It is highly likely that the improved COD removal is due to the aerobic growth of a xylose-fermenting yeast as part of the Microbiogen pilot-scale process, leaving a reduced level of "small" carbohydrate material in the feed, and a lower solubilisation of lignin in the NREL pre-treatment due to the absence of the alkali pre-treatment step that was used by Handelsman et al. [13].

As seen with Handeslman's et al. [13] results with lignocellulose effluent, all dissolved ionic species experienced high rejection. The 2000 MWCO UF membrane removed around 57% of the sulphate and 68% of the ammonium ions, levels that were considerably higher than those observed for a pure solution of ammonium sulphate. These removal levels are quite similar across all ionic species (e.g. 51% for sodium and 60% for potassium), suggesting that possibly

Table 2
1,000 MWCO UF membrane results using a feed of 1 g/L $(NH_4)_2SO_4$ with a feed pressure of 5–10 bar

Pressure (bar)	Flux (L/m/h)	Ammonium (% rejection)	Sulphate (% rejection)
5	30.2	10.6	9.8
10	43.6	18.4	18

Table 3
2,000 MWCO Ultrafiltration of Cellulosic Ethanol Wastewater at 10 bar

	COD (ppm)	Colour (PtCo)	SO_4^{2-} (ppm)	NH_4^+ (ppm)	Ca^{2+} (ppm)	K^+ (ppm)	Mg^{2+} (ppm)	Na^+ (ppm)
Initial concentration	46,900	41,100	8,100	2,400	230	280	95	700
Final concentration	15,500	760	3,510	770	85	110	35	340
% Rejection	67	98	57	68	62	60	63	51

membrane fouling is enhancing ion rejection, either due to some form of electrostatic attraction to the larger coloured lignin compounds or the build-up of a lignin-rich layer on the surface of the membrane. Whatever the reason, the conclusion would seem to be that spiral wound UF is unlikely to offer a viable route to preferentially separate ionic material from COD.

4.3. Electrodialysis

A series of small-scale runs were next conducted as part of a preliminary investigation into the recovery of H_2SO_4, $(NH_4)_2SO_4$ and NH_4OH from both "model" and actual cellulosic ethanol process streams. These experiments were motivated by the encouraging results obtained by Goldstein et al. [15] and examined (i) the effects of concentration difference on anion and cation fluxes in two and three cell configurations and (ii) a comparison of pure diffusion and electrodialysis (where diffusion and the applied electric filed act in conjunction with each other) for the same compartmental configurations.

4.4. Runs employing ammonium sulphate at different feed concentrations

One means of improving current utilisation over previous studies is to use a counter-current system, where the ionic concentration is lower in the "draw solution". To examine the significance of this effect, runs were first conducted by varying the feed concentrations (of anions and cations) in a two-compartment configuration. All runs were carried out at an applied voltage of 5 V, and for a duration of 60 min. For sulphate ion recovery, the anion compartment contained a solution of sulphuric acid in the range 86–95 ppm [average 0.92 mmol/L]. For ammonium ion recovery, the cation compartment was filled with a solution of ammonium hydroxide with a cation concentration of 98 ppm [average 5.4 mmol/L]. The effect of feed concentration on the efficiency of sulphate recovery is shown in Fig. 3a, and for ammonium in Fig. 3b.

Sulphate current efficiency has some scatter in the data, but shows an increase in performance with higher concentrations, reaching 160% at 30,000 ppm SO_4^{2-}. Efficiencies higher than 100% can be explained by the concentration ratio used for this experiment. The current efficiency for ammonium ion recovery is also far greater than 100% indicating a significant level of "assistance" by ionic diffusion. This can occur due to the equilibrium between ammonia and the ammonium and hydrogen ions, with the back-diffusion of hydrogen ions through the cation-exchange membrane preventing any charge imbalance.

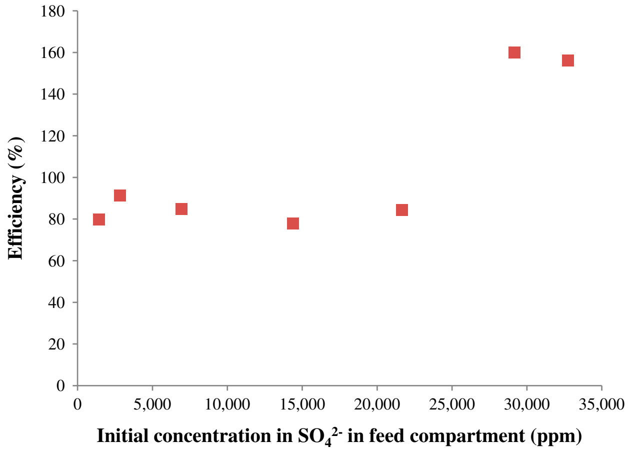

Fig. 3a. Variation of SO_4^{2-} recovery efficiency with feed concentration.

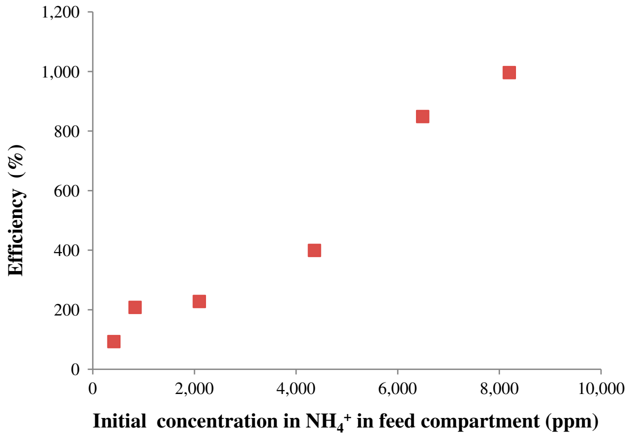

Fig. 3b. Variation of NH_4^+ recovery efficiency with feed concentration.

4.5. Runs employing variations in concentration ratios

A series of three-compartment runs were carried out to look at the effects of draw solution concentration on current efficiency for the recovery of sulphuric acid and ammonium hydroxide from both a pure ammonium hydroxide solution and from a cellulosic ethanol effluent. In all runs, both Neosepta AMX anion and Neosepta CMX membranes were used. Sulphuric acid was used in the anion compartment with ammonium hydroxide in the cation compartment. The concentrations in each compartment are given as mass percentages in Table 4.

Table 4
Conditions used for three-compartment runs to determine the impact of concentration ratio on sulphate and ammonium ion recoveries

Anion compartment	Feed compartment		Cation compartment
Salt model			
H_2SO_4	$(NH_4)_2SO_4$		NH_4OH
$[SO_4^{2-}]$ ppm	$[SO_4^{2-}]$ ppm	$[NH_4^+]$ ppm	$[NH_4^+]$ ppm
300	3,000	1,000	100
1,500	1,500	500	500
3,000	300	100	1,000
Lignocellulosic effluent			
H_2SO_4	Lignocellulosic Effluent		NH_4OH
$[SO_4^{2-}]$ ppm	$[SO_4^{2-}]$ ppm	$[NH_4^+]$ ppm	$[NH_4^+]$ ppm
3,00	3,000	1,000	100
1,500	1,500	500	500
3,000	300	100	1,000

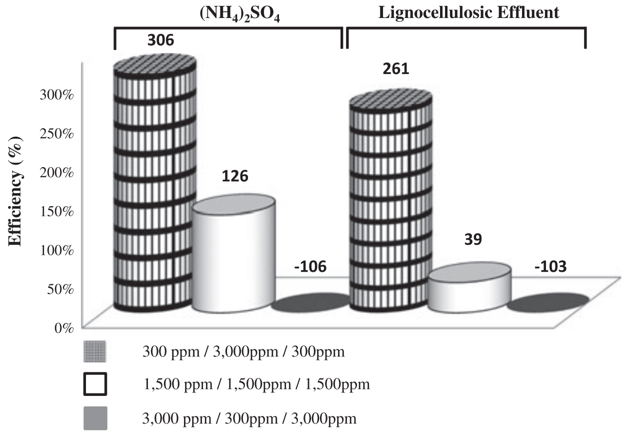

Fig. 4a. Variation of SO_4^{2-} current efficiency with concentration ratio.

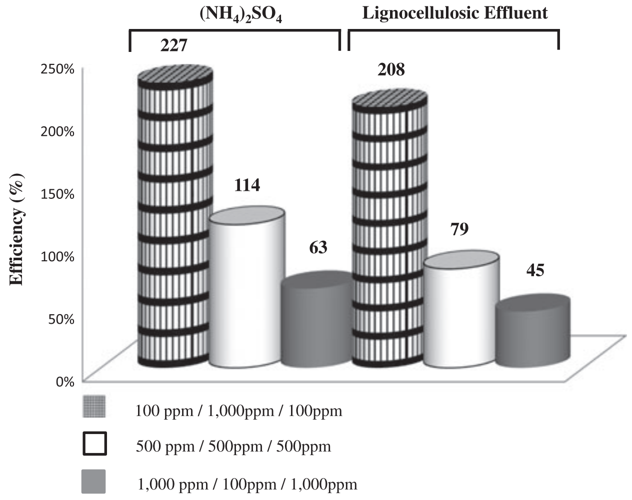

Fig. 4b. Variation of NH_4^+ current efficiency with concentration ratio.

Figs. 4a and 4b reveal several relevant points. Firstly, efficiencies of both ammonium and sulphate recovery are similar. However, based on these results, sulphate ions may diffuse more readily than ammonium ions. Secondly, there is a slight decrease when moving from an ammonium sulphate solution to an actual cellulosic ethanol solution, most likely due to the presence of other ions. Lastly, in both scenarios (i.e. pure solution and cellulosic solution) the efficiency declines significantly with decreasing concentration ratio between the feed and the draw solution. The last point is most evident when looking at sulphate recovery where diffusion can be more significant than the movement of ions due to the applied electric field, and hence a negative efficiency for sulphate recovery is actually possible. However, ammonium efficiencies for the following condition; 1,000 ppm/100 ppm/1,000 ppm, Fig. 4b; show positive values. pH in the cation compartment is comprised between 9 and 10 for these experiments. As NH_4^+/NH_3 pKa is 9.25 at 25°C [20], some of the ammonium ions become deprotonated. Then, concentration ratio is no longer applicable and movement of ammonium ions is due to the applied electric field.

These results clearly indicate that sulphate and ammonium recovery would best be achieved in a counter-current arrangement where diffusion and electrodialysis are working together. In all runs involving lignocellulosic effluent, insignificant amounts of colour and COD pass through either membrane, raising the possibility of developing a cost-effective means of separating organic and inorganic compounds.

4.6. Anion experiments with different concentration ratios

In Microbiogen's process to produce ethanol from lignocellulose, dilute sulphuric acid is used for pretreatment, resulting in the solubilisation of hemicellulose [2]. This stream is then pressed, giving wet solids and a liquid stream with a significant xylose concentration. This separation allows for a more concentrated solids stream to be subjected to subsequent enzymatic hydrolysis and hence higher glucose and ethanol concentrations, whilst the xylose-rich stream is directed to the aerobic propagators where the yeast for the fermentation stage (and excess yeast for animal feed purposes) is produced. Both streams resulting from this separation are highly acidic, and ammonia is used to neutralise them before the addition of enzymes or yeast. The ammonia provides nitrogen, but is far in excess of the yeast's requirements for either fermentation or aerobic growth.

Instead of simply treating effluents at the end of the process, the approach being examined here is one inspired from Goldstein et al. [15], whereby much of the sulphuric acid is recovered immediately after pretreatment to enable it to be recycled. This would allow a reduction in the amount of ammonia needed to neutralize the effluents and should potentially decrease the cost of ethanol production from lignocellulose. The economics of such an approach are likely to be considerably more favourable now than they were in the 1990's (after the Goldstein et al. paper was published) as the concentration of sulphuric acid is 20 times lower.

Runs were thus conducted using the Neosepta anion-exchange membrane with an applied voltage of 5 V for 3 h. The anion chamber was filled with sulphuric acid at a 3,000 ppm sulphate concentration (approximately 0.03 M). The feed compartment was filled with a range of sucrose and sulphuric acid concentrations, as shown in Table 5.

As can be seen in Table 5 and Fig. 5a, current efficiency is greatest when the ratio of sulphuric acid in the feed and draw compartments is highest. As this ratio decreases, current efficiency decreases, in line with our previous results. Decreasing the amount of sulphuric acid in the feed compartment does, however, lead to a greater percentage recovery of the acid, as the same voltage, membrane area and run-time were used in all cases (Fig. 5b).

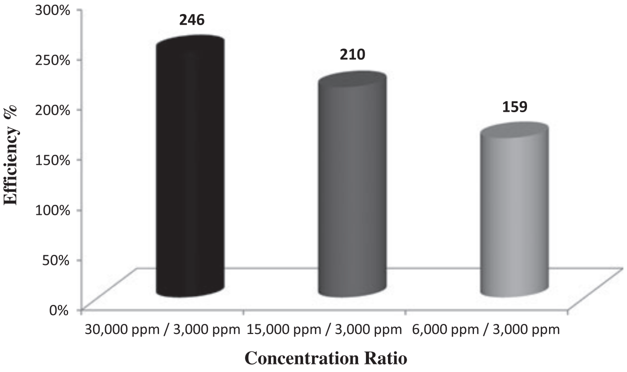

Fig. 5a. Variation of SO_4^{2-} efficiency with concentration ratio.

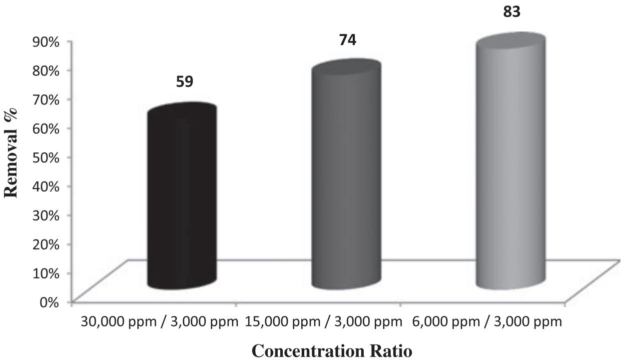

Fig. 5b. Variation of SO_4^{2-} removal with concentration ratio.

The efficiencies determined here were all greater than those found by Goldstein et al. [15], who reported a maximum experimental value of 26% (although these authors undertook feasibility calculations for efficiencies up to 40%). There are several factors that could account for this improvement. The first is due to the lower concentrations of sulphuric acid used in this present study due to our focus

Table 5
Conditions for sulphuric acid recovery at differing concentration ratios

	Feed compartment			
Anion compartment, H_2SO_4 (ppm)	H_2SO_4 (ppm)	Sucrose (ppm)	Current efficiency (%)	Recovery (%)
3,000	30,000	10,000	246	59
3,000	15,000	5,000	210	74
3,000	6,000	2,000	159	83

being on acid recovery after dilute acid pre-treatment, while the second possibility is the undoubted improvement in ion-exchange membranes during the last two decades.

COD measurements were used to determine the extent to which sucrose was passing through the membranes. This technique was used rather than either an HPLC or enzymatic technique in case the sucrose was degraded by the acid. Fig. 6a shows that the COD is essentially unchanged in the feed compartment over the course of the run, whilst Fig. 6b shows very low COD levels in the final compartment. It would thus seem that at most no more than 1% of the sucrose had moved through the membrane. These results are encouraging enough to warrant follow-up studies using effluent from actual cellulosic biorefineries.

4.7. Economic implications

The development of a membrane system to allow the recycling and/or reduction of sulphuric acid and ammonia has the potential for large capital savings and hence a reduction in the MESP. The capital savings, arising from the incorporation of such technology into the wastewater treatment plant of the current 61 million gallons per annum (231 million litres per annum) NREL cellulosic ethanol design, would be significant, eliminating the need for the anaerobic and aerobic basins, the membrane bioreactor and blowers. However, the evaporator capacity would need to be increased fourfold to enable direct evaporation. Based on Steinwinder et al.'s [3] estimates for these items, the savings in equipment costs would be $35.5 million, which equates to around $50 million when the 45% additional costs for installation assumed by Humbird et al. [1] are used. This is a reduction of approximately 50% in the total capital investment for the wastewater plant, or an 11% reduction for the entire plant. The move to direct evaporation would also result in a significant operational saving by not needing to supply aeration energy, polymer addition or the "iron sponge" which together amount to around $10 million annually. Assuming a plant lifespan of 30 years, and straight-line depreciation, these savings collectively represent a decrease in the MESP of $0.24 per gallon ($0.06 per litre).

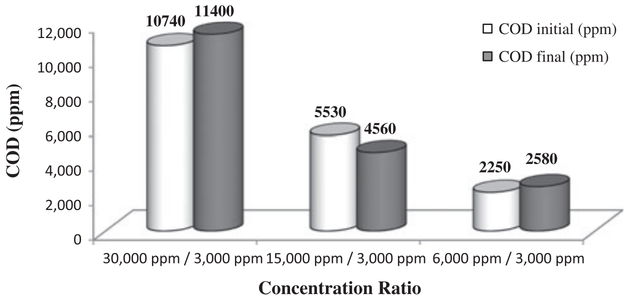

Fig. 6a. Variation of COD in feed compartment with concentration ratio.

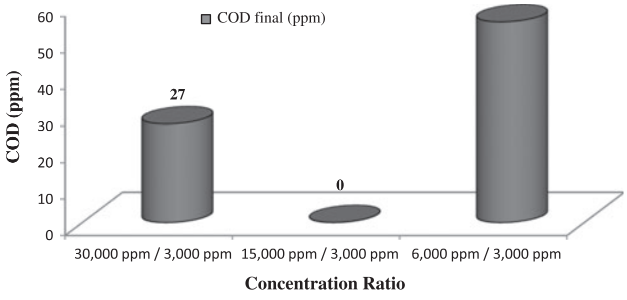

Fig. 6b. Variation of the final COD in the anion compartment with concentration ratio.

However, the use of electrodialysis would require both capital investment for the membranes plus the operational cost of the electricity. To compare these additional costs to the potential savings, two scenarios were examined. The first involved using electrodialysis only as an end-of-pipe treatment for the 2011 NREL design, with both sulphuric acid and ammonium hydroxide being recovered from the effluent for plant reuse. The second scenario was where sulphuric acid was recovered from the pressate stream of the "Food and Fuel" process [2], as well as for end-of-pipe treatment. Both designs require 17,000 tpa of sulphuric acid and 2,500 tpa of ammonia, however, the 2011 NREL design is for 61 million gallons (231 million litres) per year of ethanol against the 41 million gallons (155 million litres) per year for the Microbiogen design. The cost per gallon of ethanol is used here as the basis for comparison.

In all cases, it was assumed that 90% of the sulphuric acid and ammonium hydroxide were recovered with the savings from recycling these materials set as equal to their purchase price of $81 and $407 per ton, respectively. Current efficiency for both the end-of-pipe recovery and internal recycle was assumed to be 80% based on the current efficiency determined using real cellulosic effluent without a concentration gradient shown in Fig. 4b. The voltage difference across the membranes was assumed to be 5 V for the base case, the current density 500 A/m^2, and the price of electricity $120/MWh for the base case. Membranes were assumed to cost $100/m^2 [21] and have a lifespan of 3 years. The cost of membrane cleaning has not been included.

Table 6
Sensitivity analysis of electrodialysis costs to power price and the applied potential difference

		Cost per gallon of ethanol	
Cost of power ($/MWh)	Potential difference (V)	End of pipe (NREL)	Integrated (MBG)
50	5	$0.01	$0.02
120	5	$0.07	$0.11
150	5	$0.10	$0.17
50	3.75	$0.00	$0.00
120	3.75	$0.05	$0.07
150	3.75	$0.07	$0.14
50	2.5	$0.01	-$0.01
120	2.5	$0.02	$0.03
150	2.5	$0.03	$0.11

The use of electrodialysis for both the NREL and Microbiogen design requires 6.6 MW of electric power, the annual electricity cost is $6.6 M for the base case power price, and the required membrane area is 2,642 m^2, which translates into an annualized membrane cost of $22,000. This is considerably less than the calculated electricity cost and stands in contrast to the findings of Goldstein et al. [15] that membranes were the major cost. However, in the 20 years since this study, the price of membranes has dropped by at least 75% in absolute terms, whilst the electricity price has risen by some 140%.

These additional electricity and membrane costs equate to $0.07 per gallon ($0.018 per litre) for the NREL process and $0.11 per gallon ($0.029 per litre) for the Microbiogen process. It is interesting to note that while the fixed costs for both the Microbiogen and NREL processes are similar the savings per volume of product are greater for the NREL process due to the higher amount of ethanol produced.

Hence, it would seem that the overall saving from introducing electrodialysis into the production of cellulosic ethanol by treating the resultant wastewater has the potential to lower the MESP by ~$0.13–0.17 per gallon ($0.034-$0.045 per litre), which would be a considerable step towards eventual commercialisation of this technology.

To further investigate the feasibility of electrodialysis, a sensitivity analysis was carried out for the likely range of power prices in the US Mid-West ($50–150/MWh, based on the mid-2012 wholesale price range given by the US Energy Information Administration [22]) and the potential to reduce the operating voltage from 5 to 2.5 V, just above that needed to hydrolyse water, and hence the minimum possible voltage. The results of this sensitivity analysis are shown in Table 6.

As expected, the cost per gallon of ethanol using electrodialysis is sensitive to the power price but this drops as the applied voltage is reduced. Hence, there exists an opportunity to further reduce the cost of electrodialysis (and hence cellulosic ethanol production) through optimisation of the process (e.g. parallel membranes to use the power more efficiently) and its operating conditions. Undoubtedly, further research is needed to determine how best to improve the current efficiency and reduce the operating voltage in large-scale electrodialysis units. However, these preliminary experiments and the potential for significantly reducing the MESP for cellulosic ethanol would seem to warrant such targeted research.

5. Conclusions

UF membranes can provide good colour and COD removal from lignocellulosic wastewater. However, the rejection of ionic species was also high, and hence there was no preferential separation.

By comparison, ion-exchange membranes proved capable of preferentially recovering both ammonium hydroxide and sulphuric acid from an effluent stream. The electrical efficiency of the system is strongly dependent on the internal concentration gradients; hence a counter-current system would be needed industrially. The potential also exists to recycle a significant portion of the sulphuric acid within some proposed processes, reducing the likely ammonia requirements. Economic analysis of such electrodialysis systems reveals the central importance of using the current as efficiently as possible.

Research is on-going on how best to apply electrodialysis for the industrial-scale recovery of diverse salts from biorefinery wastewaters.

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