Desalination and Water Treatment
www.deswater.com

51 (2013) 511–517
January

1944-3994/1944-3986
doi: 10.1080/19443994.2012.715421

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Bipolar membrane electrodialysis and ion exchange hybridizing for dilute organic acid solutions treatment

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Received 29 February 2012; Accepted 18 July 2012

ABSTRACT

In this work, treatment of very dilute effluents of organic acids by means of an electro-membrane hybrid process is studied. Dilute organic acids effluents are generated by numerous processes. Converting such effluents into pure more concentrated fluxes is a key step in the valorization process. An experimental study has been performed to recover acetic acid by bipolar membrane electrodialysis (BMED). The experiments performed when coupling BMED and ion exchange have clearly demonstrated that hybridization reduces energy consumption. This improvement is due to the decrease of the electrical resistance of the diluted compartment thanks to the ionic conductivity provided by the resins. The effect of back diffusion on the current efficiency was also studied. In the case of acetic acid effluent treatment, investigation of the influence of the resin initial form showed that hydroxyl and acetate initial forms result in very close performances. It is therefore useless regenerating the resin bed.

Keywords: Bipolar membrane electrodialysis; Ion exchange bipolar membranes; Very dilute solutions; Weak organic acid

1. Introduction

Dilute organic acids effluents are generated by numerous processes. Recovery of such effluents into pure more concentrated fluxes is a key step in the valorization process. Huang et al. [1] studied and discussed in detail the interest of electrodialysis (ED) process for the production of organic acids. Vertova et al. [2] carried out a qualitative analysis of the different organic acid recovery techniques. It appears that the best adapted technique depends on the salinity of water and on the pre-treatment requirements. When both water purification and carboxylic acid recovery are required, ED seems to be an appropriate technique. Vertova et al. studied the treatment of diluted (0.2–0.4 wt.% total concentration) solution of carboxylic acid. In order to overcome the difficulty generated by the increasing ohmic drop due to the lowering of the diluate conductivity, the authors chose to reduce the thickness of the diluate compartment. The present paper aims at studying another alternative technique which consists in introducing ion exchange (IEX) resins in the diluate compartment. It must be noted that an analogous approach was used with success by Zhang et al. [3] in the case of tartaric acid production, using a three-compartment configuration and strong

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Presented at the International Conference on Desalination for the Environment, Clean Water and Energy, European Desalination Society, 23–26 April 2012, Barcelona, Spain

acid resins. Wideasa et al. [4] used also this technique for continuous recovery of citric acid from fermentation broth. The current transport through the diluted compartment is almost entirely mediated by the mixed ion-exchange resins. The present study regards acetic acid recovery from diluted solutions, using a two-compartment configuration and strong anionic resins. In order to evaluate the influence of the presence of ion exchanger, experiments were first carried out in the absence of resins. The diluate compartment was then filled with an anion exchange resin.

2. Materials and methods

To investigate the benefits of adding IEX resins in recovering acetic acid from dilute solutions by ED using bipolar membrane, two sets of experiments were conducted using bipolar membrane electrodialysis (BMED) with and without IEX resins.

2.1. Bipolar membrane electrodialysis

In the first part of this work, the experimental set-up, illustrated in Fig. 1, is analogous to the one used by Yu et al. [5]. Thanks to the hydroxyl ions produced by the anodic face of bipolar membrane, acetic acid in the diluate compartment is in the form of anionic acetate. Acetate ions can therefore be transferred through an anion exchange membrane towards the concentrated compartment; then, thanks to the proton ions produced by the cathodic face of bipolar membrane, they are transformed into neutral acetic acid form.

The main difference with Yu et al. [5] set-up is the compartment with electrolytic solutions. For Yu et al. experimental set-up, the gap between the two adjacent membranes is 1.5 mm whereas, it is 15 mm in ours. Hence in the present work, the same experiment is used with and without IEX resins. Filling compartment with resin requires a larger gap.

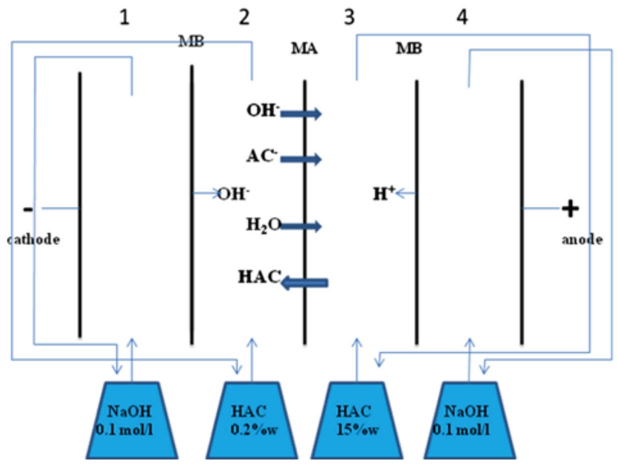

Fig. 1. Principle of BMED for the recovery of acetic acid from diluted solution.

The experimental cell has been realized in our laboratory. This cell is adjustable, and can include between 2 and 7 compartments. The cell used in the present work includes four 15-mm-thick compartments:

- Both anodic and cathodic compartments (Nos. 1 and 4, respectively) contain 60 cm^2 platinum-coated titanium grid electrodes. Both compartments are separated from the adjacent ones by a bipolar membrane.
- Compartments Nos. 2 and 3 are separated from each other by an anion exchange membrane.

The contact area of each membrane is 40 cm^2. Anionic membranes (AMs) were supplied by EURODIA. 0.25-mm-thick bipolar membranes were supplied by Tokuyama Soda. Experiments were conducted in batch mode, with recirculation of specific solutions for each compartment. Referring to Fig. 1.

- In compartment No. 2, circulates 500 mL of acetic acid solution initially at 0.2% wt.
- In compartment No. 3, circulates 500 mL of acetic acid solution initially at 15% wt.
- In each of the electrolytic compartments circulates 500 mL of sodium hydroxide 0.1 mol L^{-1} solution.

Acetic acid, sodium hydroxide and sodium acetate were of analytical grade. pH measurements were carried out by means of Symphony SC80PC VWR pH-meter and conductivity measurements by means of Radiometer analytical CDM 210 conductimeter.

2.2. BMED and IEX hybridizing

The configuration of the cell used in the second part of the work is illustrated on Fig. 2. No. 2 compartment is filled with anion exchanger resins bed. The capacity of the bed is about 0.063 eq.

2.3. Performance indicators

Concentration of acetic acid in No. 2 compartment was determined by titration with sodium hydroxide solution using BBT indicator. Determination of acetic acid concentration enables us calculate total acetate acid concentration, using the following equation:

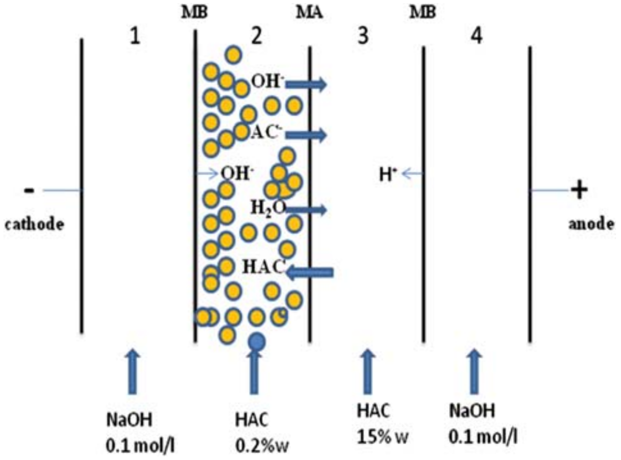

Fig. 2. Principle of BMED and IEX hybridizing.

$$C_{AC} = [CH_3COOH] + [CH_3COO^-] \tag{1}$$

where $[CH_3COO^-]$ is calculated from the acetic acid dissociation equilibrium relation:

$$[CH_3COO^-] = \frac{K_a[CH_3COOH]}{[H_3O^+]} \tag{2}$$

Concentration of acetic acid in compartment No. 3 can be considered as constant because only small amount of acetic acid is transferred, compared to the initial high concentration in this compartment.

Three parameters are estimated to evaluate process performances: purification rate of the diluted compartment, current efficiency and energy consumption. The purification rate can be defined by the following relation:

$$T_{AC}(t) = \left(\frac{C^0_{AC} - C^t_{AC}}{C^0_{AC}}\right) \cdot 100 \tag{3}$$

where, the exponents 0 and t refer to initial and instant acetate concentrations respectively. Current efficiency is given by:

$$\eta_F = \frac{\Delta n \cdot F}{\Delta t \cdot N \cdot I} \tag{4}$$

where Δn is the mole amount of acid transported during the time period Δt, F is the Faraday constant, I the current and N the number of AM ($N=1$). Knowing the applied current I and the measured ohmic drop U, the energy consumption can be calculated by integrating the product of U and I, i.e. the power, along the treatment period.

3. Results and discussion

3.1. ED with bipolar membrane

Experiments were carried out using a constant 36 mL/min flow rate. Current density was controlled while the potential between cathode and anode was measured as a function of time. Transfer of acetate ions from diluted towards concentrated compartments leads to a depletion of cell No. 2 lowering its conductivity, which can be clearly seen in Fig. 3. This requires an increase of the voltage drop between the electrodes, as illustrated in Fig. 4.

When voltage reaches around 150 V, experiments must be stopped, which limits purification rates, as presented in Table 1.

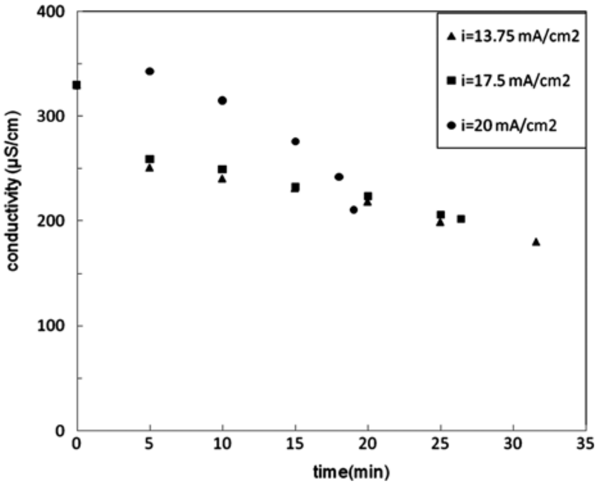

Fig. 3. Conductivity of the diluted compartment solution vs. time (BMED experiments).

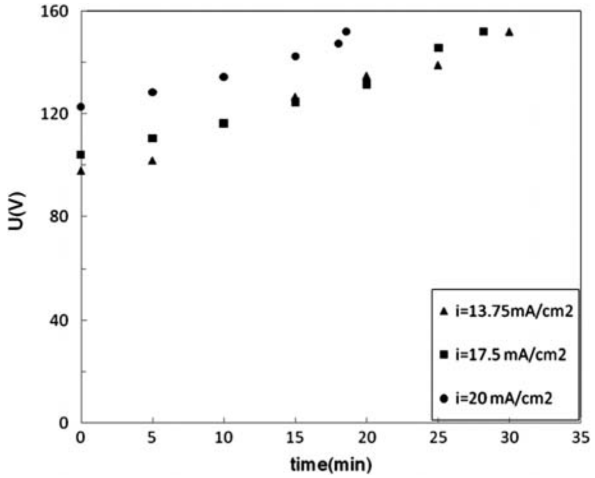

Fig. 4. Variation of voltage across the cell stack vs. time (BMED experiments).

Table 1
Final purification rates for different current densities (BMED experiment)

Current density (mA/cm^2)	Operation time(min)	Purification rate(%)
13.75	30.00	65.7
17.50	28.15	60.4
20.00	18.41	50.0

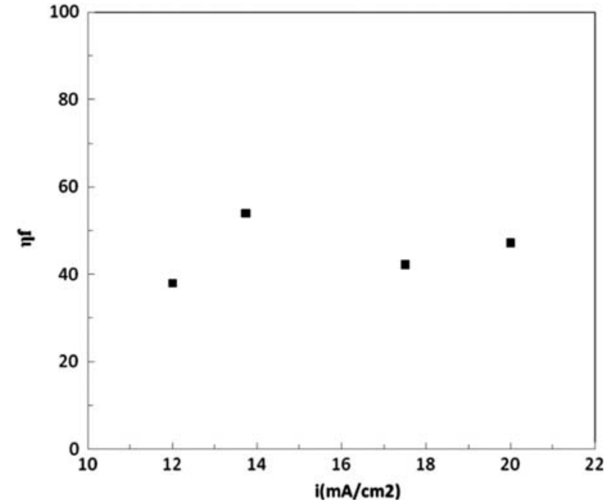

Fig. 5. Current efficiency vs. current density (BMED experiment).

Current efficiency as a function of the applied current density, estimated in all cases at 50% recovery rate, is given in Fig. 5. The current efficiency depends on the applied current density. It seems that, for the considered density range, the current efficiency presents a maximal value. The best current efficiency is for a current density somewhere located between 12.5 and 17.5 mA/cm^2. Such phenomenon was already observed by Yu et al. [5] who explained with detail the undesired transfers which occur through the AM. With low applied current density, back diffusion of acid from concentrated towards diluted compartment plays a predominant role compared to the desired transfer. Whereas, with high applied current densities, separation performances are altered by polarization concentration phenomenon.

3.2. Electrodeionisation

In order to overcome the difficulty generated by very high resistance of the diluted compartment, strong anionic exchanger resins were used to fill this compartment. Experiments were conducted in the case of two applied current densities: 17.5 and 20.0 mAcm^{-2}. Ion exchanger resins, initially under hydroxyl form, were first used. Fig. 6 presents the evolution of conductivity and of the voltage drop across the stack as a function of time.

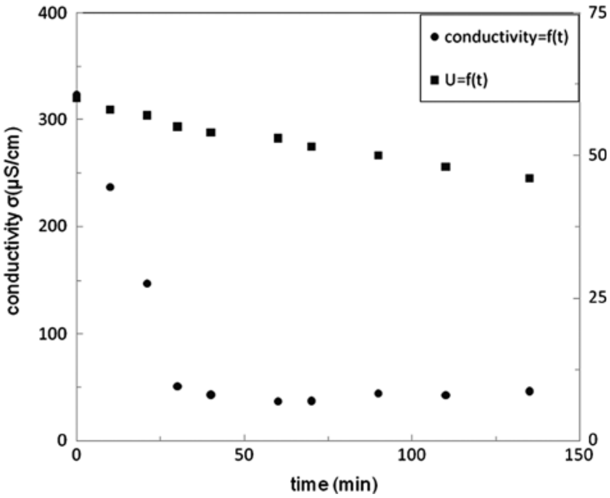

Fig. 6. Conductivity of the diluate compartment and cross-cell stack voltage variations vs. time (BMED witn IEX resins initially under OH$^-$ form; $i = 17.5\,\mathrm{mA\,cm^{-2}}$).

Solution conductivity decrease can be observed. However, contrary to the previous case, voltage is decreasing as well. This difference can be attributed to the role played by ion exchanger resins which enables both IEX and acido-basic reaction of ACH with the OH$^-$ initially fixed on the ion exchanger. Three equilibria can be considered:

- Acido-basic equilibrium in solution:

$$\mathrm{HAC} + \mathrm{OH^-} \rightleftharpoons \quad \mathrm{H_2O} + \mathrm{AC^-} \tag{5}$$

- IEX:

$$\mathrm{AC^-} + \mathrm{R{-}OH^-} \rightleftharpoons \mathrm{OH^-} + \mathrm{R{-}AC^-} \tag{6}$$

- “Reactive” IEX:

$$\mathrm{ACH} + \mathrm{R{-}OH^-} \rightleftharpoons \mathrm{H_2O} + \mathrm{R{-}AC^-} \tag{7}$$

where R–OH$^-$ and R–AC$^-$ correspond to the hydroxyl or acetate ions fixed in the resin. Solution conductivity is low, AC$^-$ migration in the diluted compartment occurs therefore mainly via IEX media. When AC$^-$ concentration in this compartment is very low, as hydroxyl ions are produced by bipolar membrane, IEX equilibrium (6) is displaced towards R–OH^- formation. The fact that OH^- mobility is higher than AC^- mobility leads to resistivity decrease.

The influence of OH^- production by BP membrane can also be observed in Fig. 7 which presents the solution pH evolution in the diluted compartment as a function of time. When acetic acid concentration reaches a very low value, a pH fast variation, analogous to that obtained during classical titrations, is observed.

When pH reached a plateau around 7.5–8, solution conductivity was very low (Fig. 6) and experiments had to be stopped because mainly OH^- migration occurs, which does not correspond to the desired transfer. It must be noted that this pH increase sometimes engenders coloration or even burning of the AM which then must be replaced.

In order to study the influence of the resin initial form, experiments were then carried out using resin under acetate form. The other operating parameters were the same as those used previously. The evolution with time of voltage across the cell stack and of the solution conductivity can be observed in Fig. 8.

It can be observed that, at the beginning of the experiment, voltage increases and then, similar to the previous case, decreases. This phenomenon can be explained as follows: first, as resin is saturated with AC^- ions, no IEX with AC^- in solution can occur. AC^- migrate both through resin and solution. Solution concentration depletion results in ohmic drop increasing. When solution concentration is low enough, OH^- produced by bipolar membrane are fixed on the resin, resulting in bed resistivity decrease because, as previously explained, OH^- mobility is higher than AC^- mobility. The corresponding pH evolution is shown in Fig. 9. It can be pointed out that this configuration leads also sometimes to membrane burning problems.

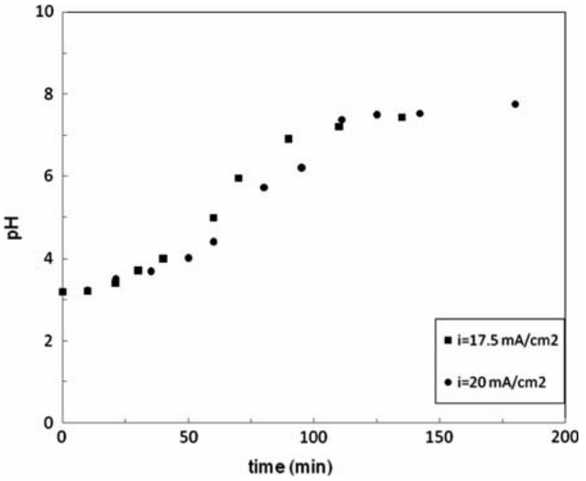

Fig. 7. pH of the dilute solution vs. time (BMED with IEX resins initially under OH^- form).

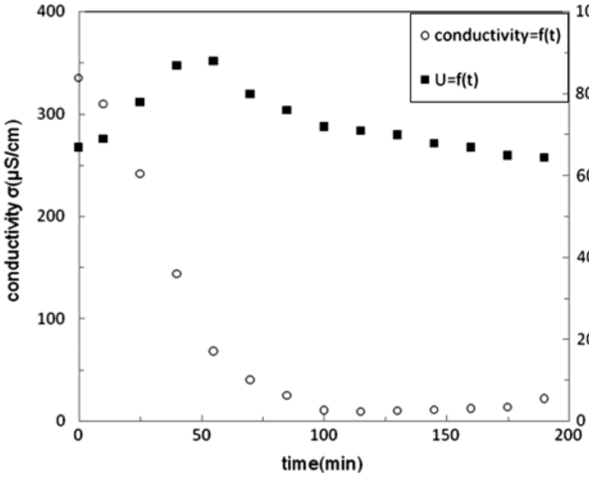

Fig. 8. Conductivity of the diluted compartment solution and cross-cell stack voltage variations vs. time (BMED with IEX resins initially under AC^- form; $i = 17.5\,mA\,cm^{-2}$).

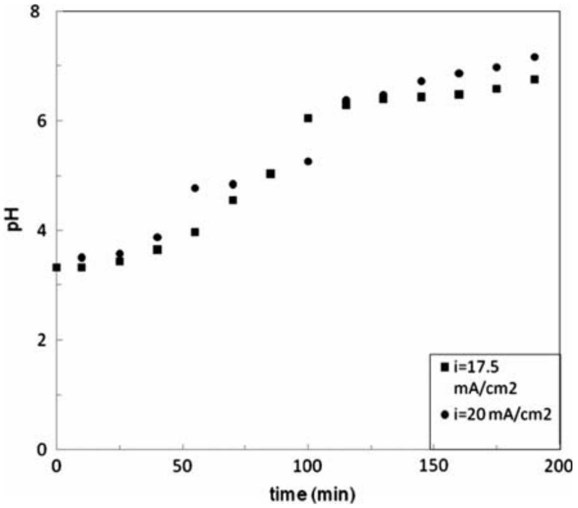

Fig. 9. pH of the diluted compartment solution vs. time (BMED-IEX experiments—resin initially under AC^- form).

3.3. Comparison of the three configurations

Fig. 10 presents the evolution of the concentration in the diluted compartment for the three previously described configurations, using the same current density $i = 17.5\,mA\,cm^{-2}$. The low purification rate obtained without resins is due to the fact that operation was rapidly stopped because of a too high ohmic drop. The corresponding purification rates are given in Table 2.

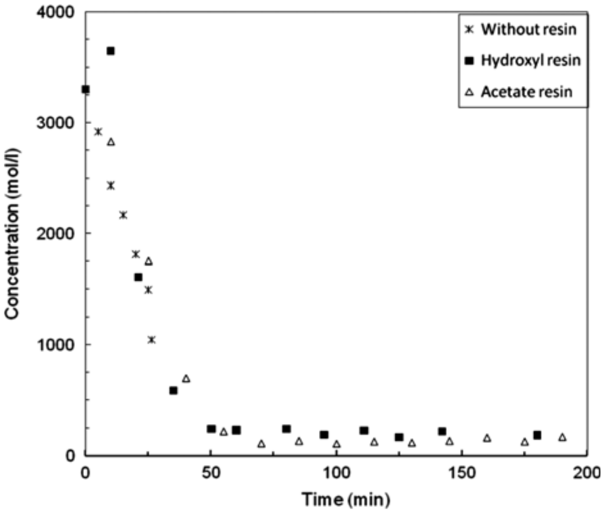

Fig. 10. Concentration of the diluted compartment solution vs. time ($i = 17.5\,\mathrm{mA\,cm^{-2}}$).

Table 2
Final purification rates comparison ($i = 17.5\,\mathrm{mA\,cm^{-2}}$)

Configuration	Resins initial form	Purification rate (%)
BMED	Without resins	60.4
BMED-IEX	AC^- form	96.1
BMED-IEX	OH^- form	94.5

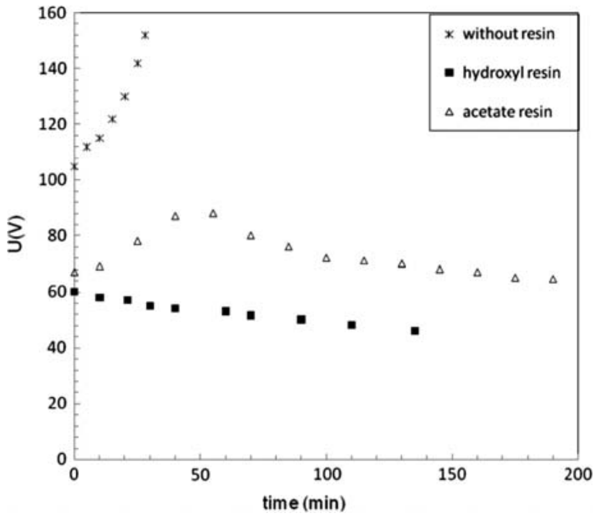

Fig. 11. Variation of voltage across the cell stack vs. time (comparison in the case of the three configurations).

Table 3
Energy consumption (comparison in the case of the three configurations)

Configuration	Resins initial form	Energy consumption (kJ)
BMED	Without resins	123
BMED-IEX	AC^- form	109
BMED-IEX	OH^- form	89

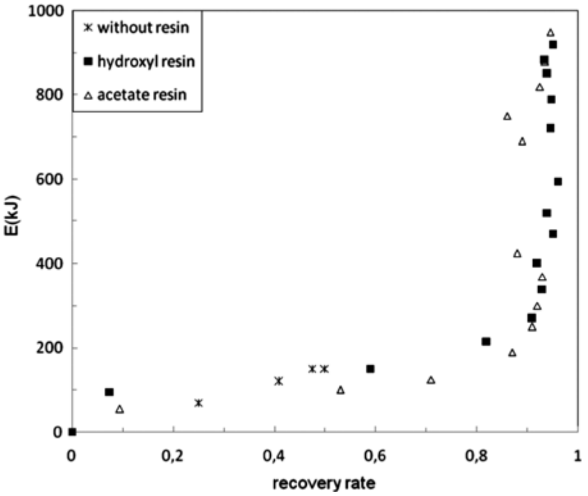

Fig. 12. Energy consumption vs. recovery rate (comparison in the case of the three configurations).

Fig. 11 enables us to compare the ohmic drop evolutions. As previously explained, ion exchanger resins insure high bed conductivity. However, it appeared that when acetic acid concentration is low, OH^- ions are mainly transported through the bed. Energy is then used for an undesired transfer. It is therefore worth comparing energy consumption for these various configurations for the same purification rate. Results for 50% recovery are presented in Table 3.

It can be observed that the use of IEX resin enables us to reduce energy consumption for a given purification rate. In fact energy consumption depends on final rate recovery because, as purification proceeds, a larger part of current is ensured by OH^- transport. The energy consumption was calculated for various rate recoveries. Results are illustrated in Fig. 12.

One can clearly observe, from a recovery rate around 90%, energy consumption suddenly increases: energy is then mainly consumed for undesired transfer and a slight increase of purification leads to a very significant increase of energy consumption. It therefore appears worth determining a compromise between recovery rate and energy consumption.

4. Conclusion

An experimental investigation has been conducted to recover acetic acid from a very diluted solution into a more concentrated solution. From the experimental results it may be concluded that coupling bipolar membrane ED and IEX enables us to reduce energy consumption. This improvement is due to the decrease of the electrical resistance of the diluted compartment thanks to the ionic conductivity provided by the resins. Recovery rates up to 90% can be obtained but, above this value, energy consumption increases very rapidly. A compromise between recovery rate and energy consumption is required. Investigation of the influence of the resin's initial form showed that hydroxyl and acetate initial forms result in very close performances. It is therefore useless regenerating the resin bed.

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