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ORIGINAL PAPER

Electrodialytic recovery of light carboxylic acids from industrial aqueous wastes

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Abstract A study has been carried out on the possibility of recovery light carboxylic acids (C1–C6) from an acidic waste stream by means of electrodialysis (ED) technique. The starting solution has very low concentration in organic acids and low specific conductivity. The main object of the study is the identification of the critical aspects for a complete electrodeionization of the water in a scheme of water reuse as process water or boiler feed-water. Concentration and recovery of carboxylic acids from wastewater streams can be a sustainable "green" alternative to biological degradation and turn into a valuable alternative, the more the higher the possibility of reusing the concentrated organic acid stream. In this work an ED cell was assembled and experiments were performed with acetic acid solution as model trace chemical in water. A real wastewater stream was also treated and results are discussed in term of current efficiency and energy consumption.

Keywords Light carboxylic acids · Recovery · Separation · Electrodialysis · Water treatment · Membrane

1 Introduction

Water is a very valuable commodity and reuse and recycling of treated water is of high priority. Low water price for years accustomed us to waste it in an unsustainable way. The present and near future priority is industrial reuse of wastewater in order to preserve high quality water for more precious uses, i.e. civil uses, with contemporary recovery of valuable contaminants.

Light carboxylic acids are formed as by-products in many industrial processes. In food, textile, paper mills, pharmaceutical, fine chemical and petrochemical industries there are oxidation reactions, generating large water fluxes with organic acid contamination [1–4]. In some cases these fluxes, if suitably intercepted during the production process, do not contain other contaminants than these carboxylic acids, thus simplifying the necessary purification treatment. The optimal process should lead to a water stream that fulfils the conditions to be either discharged in surface waters or reused as process water or boiler feed water (BFW), and to the recovery and reuse of the valued carboxylic acids.

By now in Europe, the environment emissions have been regulated through standard parameters. The implementation of the Water Framework Directive (WFD—2000/60/EC) is challenging the industry as it aims to protect surface waters through the definition of environmental objectives and as a consequence it defines the quality of the industrial discharge water, based on local environmental targets. It focuses heavily on water quality and represents a reasonable compromise which takes into account the needs of all water users. In Italy the actual law (DDL 152/2006) contains concentration limit criteria in order to discharge in surface water (i.e. pH 6–9.5, COD 160 mg dm^{-3}).

Supranational guidelines or directive on water reuse is missing in Europe. Most European countries practicing wastewater reuse have issued national standard to guide reuse schemes. Italy has published technical norms (for industrial reuse i.e. pH 6–9.5, COD 100 mg dm^{-3}) fixed as

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ministerial decree (Decree of Environmental Ministry 185/2003), but local authorities can change or implement the parameters.

About reuse or recycling of wastewater contaminated with light carboxylic acids as process water or BFW attention has to be paid, not only at the total COD target, but also at the residual concentration of formic acid, because of its corrosiveness impact.

Pure carboxylic acid has several uses in the industry. The recovery of blend acids can offer other possibilities. Trials to use them as oxygenate compounds in fuels [5] have already be done on blend acids coming from biomass fermentation.

As a valid alternative, an effective separation technique could be applied to the extraction from their aqueous reaction medium, as final step of their chemical or fermentation synthetic route [6].

Conventional applied techniques are ion-exchange, solvent extraction, distillation or reactive distillation, precipitation and membrane separations [7–13]. However, to meet the requirements of green and sustainable chemistry the mentioned techniques have to overcome several drawbacks as: sludge production, use of solvents, high energy consumption. Purification of water from carboxylic acids can be achieved by biological processes, but the biological digestion, either aerobic or anaerobic, leads to the exhaustive degradation of the substrates to CO_2 and CH_4, thus preventing any possibility of recovery.

On the other hand, the screening between different physico-chemical techniques, to select the most suited treatment for organic acid wastes, has to reckon on the water complex composition and the physico-chemical properties of the compounds to be recovered.

In Table 1 the most relevant information for the selection of the separation techniques are summarized in terms of molar mass, M (g mol^{-1}), molar volume, V_m (dm^3 mol^{-1}), acid dissociation constant, $pK_a = -\lg(K_a)$, chemical oxygen demand (COD) for 1,000 mg dm^{-3} of acid, boiling point, T_{bp} (°C), boiling point of the methylester derivative (useful for reactive distillation), $RCOOCH_3$ T_{bp} (°C), activity coefficient at infinite dilution at 100 °C, $\gamma°_{100}$, vapour pressure at 100 °C, $p°_{100}$ (kPa), relative volatility, α, and melting point, T_{mp} (°C).

On the basis of these parameters a brief discussion of the various treatment methods can be proposed.

Membrane separations, as reverse osmosis (RO) and nanofiltration, are mainly affected by molar mass and volume of organic acids, which affect the values of the rejection coefficients [12]. The application of RO is limited by the low rejection of organic acids at the natural pH of their solution ($pH < 4$).

Thermal treatments, as evaporation or distillation, are affected by the relative volatility, α, of each organic substances with respect to water. In the case of distillation applied to light carboxylic acids dissolved in water at very low concentration, $\gamma°_{100}$ values show (Table 1) that the non ideality of the solution increases with the molar mass of the acid. α values are proportional to $\gamma°_{100}$ and $p°$; formic and acetic acids, which exhibit α's close to but less than 1, remain mainly as tail products, while the other acids, with $\alpha > 1$, constitute the head products. Reactive distillation, by means of the esterification of the organic acids [14], can be successfully applied as separation process, but this technique is mainly devoted to remove high concentrations of organic acids and implies the addition of one chemical step in the process, the esterification reaction, with the ensuing chemical and energy consumption.

Adsorption or ion-exchange processes, for which a charge interaction is requested, strongly depends on pK_a's of the different compounds and can be easily accomplished only for formic acid, as the other carboxylic acids present very similar values of the acid dissociation constant.

In order to preliminary define a reference frame in which locating the present study results, Table 2 qualitatively compares the removal/recovery techniques discussed so far, in terms of chemical requirements (NaOH for neutralization and other chemicals), secondary waste formation, energy consumption, grade of treated water quality and possibility of acid recovery. None of the methods fulfils the target of contemporary water purification (COD of treated water <100 mg dm^{-3}), carboxylic acid recovery, low energy consumption and no chemicals addition, thus

Table 1 Key physico-chemical properties of different light carboxylic acids

Carboxylic acid	M (g mol^{-1})	V_m (dm^3 mol^{-1})	pK_a	COD (mg dm^{-3})	T_{bp} (°C)	T_{bp}, $RCOOCH_3$ (°C)	$\gamma°_{100}$	$p°_{100}$ (kPa)	α	T_{mp} (°C)
Formic $C_1H_2O_2$	46.0	38	3.75	347	100.6	31.5	0.78	99.30	0.8	8.4
Acetic $C_2H_4O_2$	60.1	58	4.75	1,070	117.9	129.8	1.23	56.74	0.7	16.7
Propionic $C_3H_6O_2$	74.1	75	4.87	1,510	141.2	79.8	5.60	24.32	1.3	−20.7
Butyric $C_4H_8O_2$	88.1	93	4.81	1,820	163.3	102.3	24.0	9.12	2.3	−5.2
Valeric $C_5H_{10}O_2$	102.2	109	4.82	2,040	185.8	126.5	70.3	2.63	2.5	−34.0
Caproic $C_6H_{12}O_2$	116.2	126	4.88	2,200	205.7	151.0	204	1.42	2.9	−3.0

Table 2 Qualitative analysis of the different organic acid recovery techniques

Technique	NaOH for pH modification stoichio[a] (cost[b])	Other chemical addition (cost[b])	Secondary waste formation (kg m^{-3} [c] conc.[d])	Energy consumption EE[e] (cost[b])	Treated water quality COD[f]	Acid recovery (conc.)
Biological (aerobic)	80% (0.3 € m^{-3})	Nutrient: P, N microelements O_2 (0.2 € m^{-3})	3–5 kg m^{-3} conc. 10–20%	2 kWh m^{-3} (0.2 € m^{-3})	Ok	No
Biological (anaerobic)	80% (0.3 € m^{-3})	Nutrient: P, N microelements (0.2 € m^{-3})	3–5 kg m^{-3} conc. 10–20%	1 kWh m^{-3} (0.1 € m^{-3})	Ok	No
Ion exchange	120% (0.5 € m^{-3})	Resine biocide (0.1 € m^{-3})	50–70 kg m^{-3} conc. 5–7%	0.2 kWh m^{-3} (0.02 € m^{-3})	Ok	No
Adsorption		Activated carbon (>2 € m^{-3})	5–10 kg m^{-3} solid waste	0.2 kWh m^{-3} (0.02 € m^{-3})	No (COD >1,000 mg dm^{-3})	No
Reverse osmosis		Biocide antiscale (0.1 € m^{-3})		5 kWh m^{-3} (0.6 € m^{-3})	No (COD >500 mg dm^{-3})	Yes (conc. 5–6%)
Reverse osmosis	105% (0.4 € m^{-3})	Biocide antiscale (0.1 € m^{-3})	30–50 kg m^{-3} conc. 7–10%	2.5 kWh m^{-3} (0.3 € m^{-3})	Ok	No
Evaporation	105% (0.4 € m^{-3})		20–25 kg m^{-3} conc. 15–20%	(1 € m^{-3})	Ok	No
Distillation		Antifoaming		(1 € m^{-3})	No	Yes (conc. 2–6%)
Azeotropic distillation		Antifoaming solvent (0.2 € m^{-3})		10 kWh m^{-3} (>1 € m^{-3})	No	Yes
Reactive distillation		Antifoaming resine solvent (0.2 € m^{-3})		(1 € m^{-3})	No	No

[a] NaOH consumption calculated as % of the amount necessary to reach pH = 7

[b] Estimated cost in € for each m^3 of water to be treated

[c] Ratio between flow rate, in kg h^{-1}, of secondary waste stream and flow rate of water to be treated, in m^3 h^{-1}

[d] Concentration of the secondary stream as wt% of salts or acid in aqueous solution

[e] Energy request for pumping in term of kWh for each m^3 of water to be treated

[f] Ok = COD < 100 mg dm^{-3}

highlighting the need of further investigation on advanced systems.

To provide a qualitative rating of the applicable techniques, in Table 2 an estimate of the order of magnitude of the main direct costs is introduced, based on the following selected case: wastewater flow rate = 300 m^3 h^{-1}, carboxylic acid concentration in the water to be treated = 2,300 mg dm^{-3}, NaOH = 0.3 € kg^{-1}, Urea = 0.4 € kg^{-1}, steam = 0.01 € kg^{-1}, energy = 0.05 € kWh^{-1}.

In order to effectively apply evaporation, reverse osmosis (membrane techniques), anionic exchange or biological processes it is necessary to neutralize the acidic water with additional chemicals consumption and contemporary production of a secondary wastewater stream. Without neutralization RO (or nanofiltration) cannot reach treated water quality target. The cost associated with NaOH neutralization (to reach pH = 7) can be estimated as 0.4 € m^{-3} of water to be treated, for the selected case. Adsorption technique has a high impact in term of solid consumption. As environmental impact there are two main issues: secondary waste stream discharge and the atmospheric emissions related to mechanical or thermal energy input, but also any chemicals added to the water has an environmental impact.

Ion exchange and RO can employ biocides which are discharged, RO can also require anti-scaling additives to enhance membrane performance. For RO, the main energy costs come from the electric power needed to run the process pumps, it can be estimate in the order of 0.3 € m^{-3} for the selected case. On the other hand, the distillation processes use anti-foaming agents. Moreover distillation techniques cannot reach the treated water quality target because formic and acetic acids remain in the water. Reactive and azeotropic distillation use solvents, which impact the COD of the treated water, and present high energy (steam) consumption. Evaporation of water can take a reduced amount of steam if multieffect evaporation or multistage flash are applied. The minimum cost is estimate in 1 € m^{-3} for the selected case [15].

Therefore, none of the aforementioned methods are clear cut winners when it comes to impact on the environment.

Acid recovery can be obtained with RO, without pH modification, or with distillation but both do not reach the treated water quality target.

In the reference frame, biological techniques can achieve treated water quality target at sustainable cost, but the degradation of the acids to CO_2 and CH_4, prevents any possibility of recovery, viceversa in the hypothesis of 90% carboxylic acids recovery, with a market value of 0.2 € kg^{-1} (fuel compound), it can be estimated an income of 0.4 € m^{-3} of treated water, for the selected case.

Even the intense efforts [16–19] devoted to advanced oxidation processes (AOPs), which adopt powerful oxidants like ozone or $^{\bullet}OH$ radicals, imply also the effective degradation of the organic substrates, thus preventing the recovery of valuable compounds. The same happens to the combination of TiO_2 photocatalysis and sonochemical promotion of mass transfer by means of ultrasound irradiation of the treated solution, which significantly accelerates the degradation of pollutants [20–22], leading to the production of purified water thanks to the partial or total degradation of the organic acids.

When the combined water purification and substrate recovery are preferential goals, ED [6] can be a sound candidate process thanks to its flexibility and to the concentration range (800–2,000 mg dm^{-3}) of its applicability [23]. By a more general point of view distillative techniques are considered primary candidates when the salinity of water is over 35,000 mg dm^{-3}. RO and ED are generally the most economical processes for desalinating water with salinities less than 10,000 mg dm^{-3}. ED tends to be more economical than RO at salinities less than 3,000 mg dm^{-3}. Overall costs depend to a large extent on pre- and post-treatment requirements [24].

State of the art presents a large variety of papers dealing with ED technique to treat water streams and concentrate/separate organic acids, but the majority of them adopt a two-stage approach: the first one for producing a concentrate stream of carboxylic salts, via NaOH neutralization of the corresponding acids, and the second one, based on a bipolar membrane electrodialysis (BMED) for the recovery of the carboxylic acid and the recycling of NaOH to the first stage, with large energy consumption and demanding working conditions for the bipolar membranes. For example, Ferrer et al. [4] studied the ED/BMED scheme for the recovery of formic acid from diluted sodium formate aqueous solutions. Formic acid solution up to 32% was obtained with current efficiency of 80% under a current density of 0.5 A dm^{-2}. The electrochemical energy consumption was about 2.6 kWh kg^{-1} of formic acid.

Fidaleo and Moresi report the recovery of sodium acetate [25] and sodium propionate [26] by ED. In the latter case they estimate an acid recovery of about 95% at 0.2–0.4 A dm^{-2} current density, with a specific energy consumption of about 0.22–0.35 kWh kg^{-1}.

Wang et al. [3] studied the recovery of butyric, valeric, adipic, caproic and oxalic acids from a waste salt solution derived from the manufacturing of cyclohexanone using a 2-compartment electro-electrodialysis (EED) cell divided by an anionic membrane. They obtained current efficiencies ranging from 40% to 20% and specific energy consumptions ranging from 4 to 23 kWh kg^{-1} with the increase of the cell potentials from 5 to 15 V.

The use of BMED technology for the conversion of sodium carboxylate solutions into the corresponding aqueous streams of carboxylic acid(s) and sodium hydroxide (to be recycled for the acid neutralization) has attracted the interest of several authors [27–31], due to the simplified stack design and the promising performances provided that the transport of ions and solutes across the membranes can be adequately limited.

In this context, the present work is aimed at elucidating the key conditions for the treatment of a diluted (0.2–0.4 wt% total concentration) wastewater solution of carboxylic acids, from formic to *n*-caproic (C1–C6), as obtained from the production of hydrocarbons, in a simple ED scheme, with no chemical pre-treatment. The goal is the contemporary recovery of purified water to be recycled either into the production plants or to be discharged into natural waters (COD < 100 mg dm^{-3} [32]) and of concentrated carboxylic acid solution (>10 wt%). The energy consumptions for both recovery processes and water treatments are evaluated.

In an ED cell set-up, preliminary electrolyses were performed using acetic acid model solutions to verify the possibility of obtaining very low acid concentration in the diluate while maintaining high acid concentration in the concentrate. The process was then applied to the treatment of a real wastewater effluent, coproduced in the production of hydrocarbons, to check the separation performances with respect to the weaker acids an evaluate the energy consumption. Results demonstrate the possibility to perform electrodialysis on a real wastewater carboxylic acid stream to recover the organic compounds and to purify water with competitive energy costs and in the presence of large concentration gradient between diluate and concentrate.

2 Experimental

The in-house designed and made ED cell is shown in Fig. 1. It consists of a plate-and frame cell with four compartments, separated by alternating two cationic (CM) and one anionic (AM) membranes. They identify, from left to right, the anodic (An), concentrate (C), diluate (D) and cathodic (Cat) compartments. Two recirculating pumps are connected to the concentrate and diluate compartments and to their recirculating tanks, respectively. A third pump is used to recirculate an aqueous solution of H_2SO_4 0.5 M through both anolyte and catholyte compartments.

The reduced thickness of the diluate compartment (overall size: 20 cm × 5 cm × 0.2 cm = length × width × thickness = 20 cm^3), with respect to the concentrate one (20 cm × 5 cm × 1 cm = 100 cm^3) was adopted to reduce the ohmic drop bound to the progressive lowering of the diluate conductivity. Electrolyses were run intensiostatically and in batch mode.

The cationic membranes was Nafion® 117; the anionic membrane was IONAC® MA3475. Each membrane was 30 cm × 10 cm, with an exposed area of 20 cm × 5 cm = 100 cm^2. The working electrodes were a ruthenium oxide activated Ti mesh as anode and an AISI 316 stainless steal mesh as cathode, both of total geometric area of 75 cm^2.

Figure 2 shows a flow scheme of the entire equipment, with the relevant physico-chemical and electrochemical controlled parameters, recorded by National Instruments box SCIX 2000 driven by LabView software®.

The flow rates were: 250 $cm^3\ min^{-1}$ for anolyte and catholyte (total solution volume 450 cm^3), 120 $cm^3\ min^{-1}$ for concentrate and 60 $cm^3\ min^{-1}$ for diluate. Diluate and concentrate volumes are reported in Table 3 together with the relevant current densities.

Before starting each electrolysis, diluate and concentrate circuits were filled up with pure water, in order to verify possible leakage from sulphuric acid circuit. After this control, the right amount of acetic acid was added in pure water in order to obtain the sought organic acid concentration in both circuits. When a real wastewater effluent was used, after the leakage control procedure, pure water was spilled out and replaced by the real wastewater solutions in both diluate and concentrate circuits.

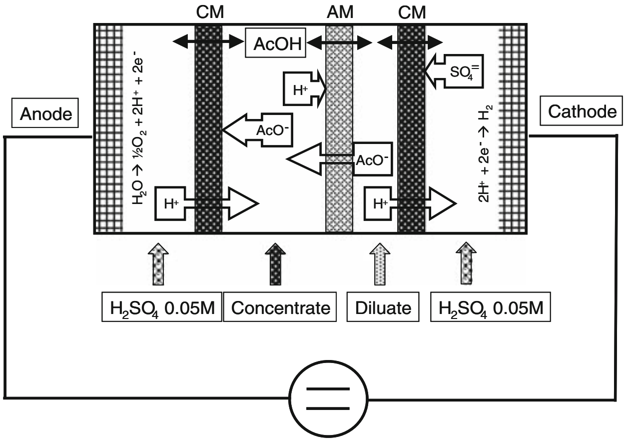

Fig. 1 ED cell with the relevant fluxes

All electrolyses were performed in galvanostatic mode using a Philips power supply model PE1649. To follow the recovery process, concentrate and diluate conductivities were recorded with an AMEL Conductimeter model 160. Occasionally, pH measurements on diluate and concentrate streams were performed to check for sulphuric acid leakage. Preliminary calibration of the two stream conductivities allowed the continuous monitoring of diluate and concentrate acid concentrations. Periodically, concentrate and diluate aliquots were sampled during the electrolysis for COD determinations, performed with an Merck Photometer SQ300. The independent COD measurements were used to confirm the on-line recorded conductivity data.

In the case of the organic acid mixture, in addition to COD and conductivity measurements, which are proportional to the cumulative content of carboxylic acids, ionic liquid chromatography analysis, carried out with a DIONEX BIOLC 4000 instrument with a conductivity pulsed electrochemical detector and a Ice-AS1 column (diameter: 9 mm, length: 250 mm), was added to determine the speciation and concentration of each carboxylic acid in the diluate and concentrate.

All chemicals were of analytical grade and the aqueous solutions were prepared using highly deionized water (MilliQ® Millipore System).

3 Results and discussion

Upon application of the electric field anions (here labelled as acetate, AcO^-) and protons move as depicted in Fig. 1, evidenced by the empty arrows. Black double arrows denote the free diffusion of the uncharged species (e.g. water and undissociated acids, here labelled as acetic acid, AcOH, for the sake of simplicity). Table 3 lists the main characteristics of the diluate and concentrate fluxes for three key electrodialyses performed using acetic acid as model molecule.

The results obtained using synthetic acetic acid stream can helpfully provide information on the rate of the removal process in the presence of weakly dissociated electrolytes and on the lowest concentration limit that can be reached in this electrodialytic process due to the presence of undissociated organic acids, which can cause a large back diffusion process that can reduce the efficiency of the treatment.

Fig. 2 Process flow chart with legend

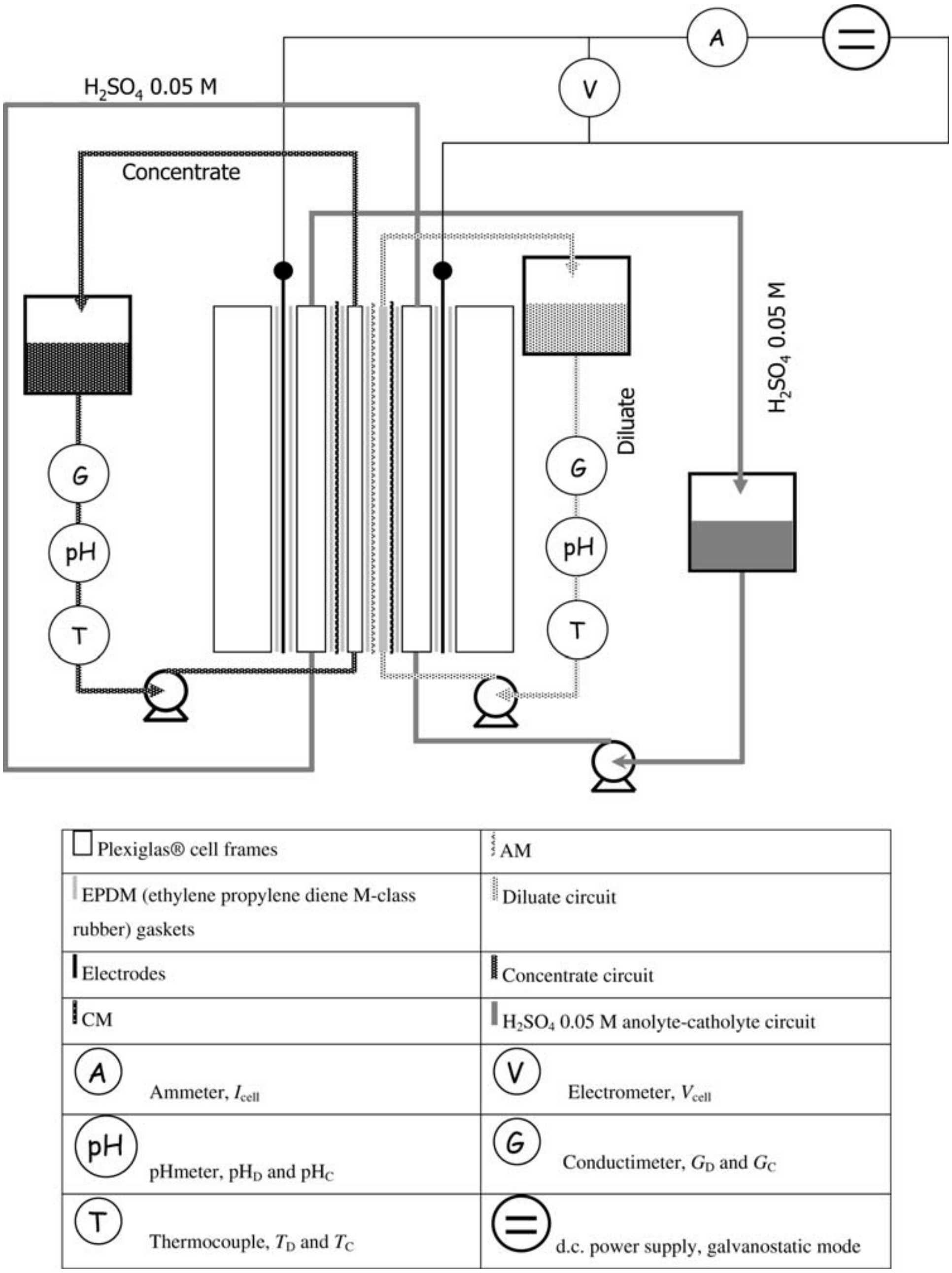

Table 3 Summary of the experimental conditions for electrodialysis of acetic acid solutions

Run	Diluate$_{\mathrm{initial}}$ (ppm)	Diluate$_{\mathrm{final}}$ (ppm)	Concentrate$_{\mathrm{initial}}$ (ppm)	j_{cell} (A dm^{-2})	Diluate (volume/cm^3)	Concentrate (volume/cm^3)
1	3,300	<30	3,300	0.3 and 1.0	230	280
2	3,800	<30	82,000	1.0	220	280
3	4,300	<30	120,000	1.0	230	320

A general framework must be underlined: while the starting concentration of the diluate was maintained approximately constant for the three runs, at around 3,500–4,000 ppm, the concentrate was progressively increased from about the same diluate concentration up to 40 times higher, in order to evidentiate the effect of the concentration gradient across the anionic membrane and detect the conditions at which back diffusion of undissociated acid started to prevail.

Figures 3, 4 and 5 show the trend of diluate acid concentration during run 1, 2 and 3, with the relevant removal rates and current efficiencies. It is worthwhile to note that the final current density value of 1.0 A dm^{-2} was reached, for run 2 and 3, by applying a stair-case current of 3 min duration and 0.2 A dm^{-2} amplitude. For the sake of clarity the other acquired quantities: concentrate stream concentration, H_2SO_4 concentration, current densities, cell potentials, temperatures, pH's, are omitted; mass balance analyses, involving diluate and concentrate chambers, was performed using both conductivity data and COD measurements, at the end of run 3, in order to verify the efficiency of the removal process and to discard the possibility that acetic acid has entered the H_2SO_4 chamber, as discussed later. In any case no particular effects are recorded other than the increase of cell potential, in connection with diluate concentration decrease at the higher current density values, and the increase of T_D, by less than 5 °C during the entire runs.

In the first run two different current densities were applied: 0.3 and 1.0 A dm^{-2}, to which correspond two different trends of the diluate concentration. It is evident that even at the starting value of 0.3 A dm^{-2} the concentration immediately decreased for the contemporary removal of acetate anions and of protons. At 1.0 A dm^{-2} the removal rate increased until the upper voltage limit of the supply was reached and the current was accordingly reduced, thus reducing the removal rate. Shutting down the cell, we observed the back diffusion of acetic acid, witnessed by the increase of diluate conductivity.

Removal rate and current efficiency were calculated for the two linear regions, corresponding to the two applied current densities, of Fig. 3 and for the linear regions of Figs. 4 and 5 (see boxes inside graph).

By comparing the current efficiencies of the three runs it is evident that the increase of the concentration gradient across the anionic membrane caused a small but progressive increase of the undissociated acid back diffusion. This, in turn, governs the lower end of the concentration versus time characteristics, which departs from linearity at progressively higher concentration values (250–500–1,600 ppm from run 1 to 2 to 3, as indicated in the relevant figures by the boxes with the arrows).

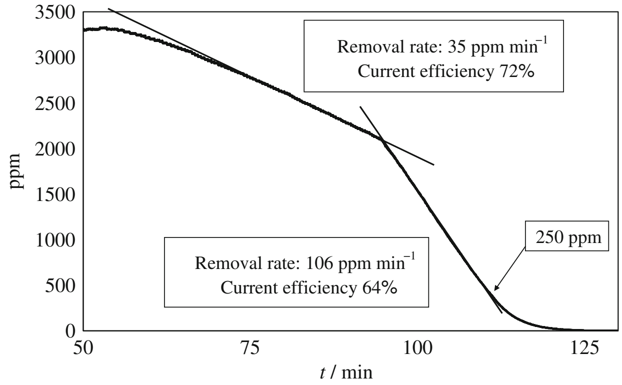

Fig. 3 Acid concentration in diluate during run 1 with the relevant removal rates and current efficiencies calculated at 0.3 and 1.0 A dm^{-2}. ppm at which concentration departs from linearity (low limit) is also indicated

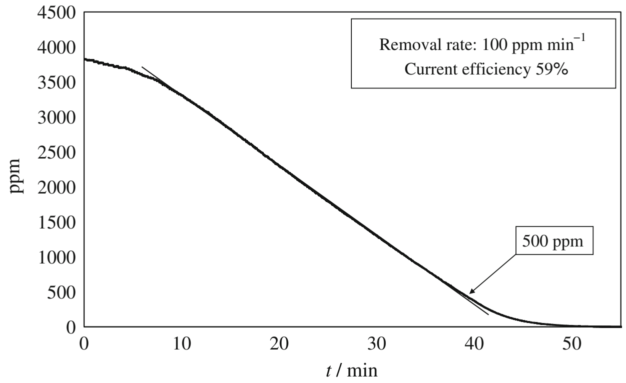

Fig. 4 Acid concentration in diluate during electrodialysis 2 with the relevant removal rate and current efficiency; current density = 1.0 A dm^{-2}. ppm at which concentration departs from linearity (low limit) is also indicated

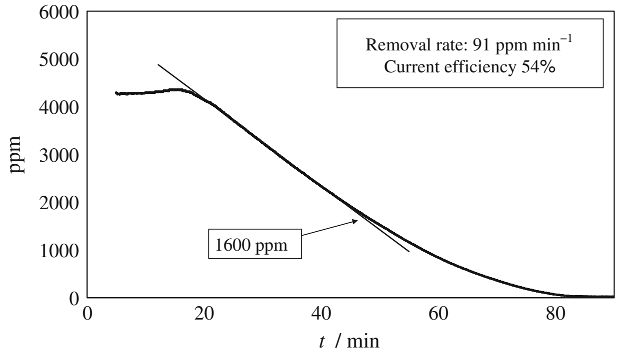

Fig. 5 Acid concentration in diluate during electrodialysis 3 with the relevant removal rate and current efficiency; current density = 1.0 A dm^{-2}. ppm at which concentration departs from linearity (low limit) is also indicated

Nonetheless, the electrolysis can be prolonged to meet the diluate target composition of less than 100 ppm, with overall current efficiencies of 60%, 54% and 41% for run 1, 2 and 3 respectively.

On the basis of COD measurements, in all of the three cases, the final water stream resulted to contain less than 30 ppm of organic compounds. In run 3, taking into account the different concentrate and diluate volumes, the mass balance between diluate and concentrate demonstrates that the removed acid entered completely the concentrate stream, whose concentration increased from 120,000 ppm to about 123,000 ppm.

It has to be stressed that the large increase of cell potential, at this stage, is mainly due to the mass transfer issues. All experiments were carried out in a laminar flow regime; Reynolds numbers less than 100 can be easily calculated and this provokes a large concentration gradient between the diluate and concentrate chambers. The future scaling up of the process must include the presence, in both the chambers, of turbulence promoters in order to reduce the concentration gradient by increasing Reynolds number.

The treatment of real carboxylic acid mixture, coming from hydrocarbons production, was also carried out. Table 4 summarizes composition and concentration of diluate and concentrate, with their volumes, before (initial) and after (final) electrodialysis; for concentrate intermediate information at 146 min was added. At the end of the electrodialysis catholyte and anolyte were also analysed, to exclude any leakage between compartments, and the carboxylic concentrations of electrode chambers are listed in Table 4. The wastewater stream contained also 0.03–0.2 ppm Fe^{3+}, 0.6–1.0 ppm Ca^{2+} and less than 5% methanol. The electrolysis was performed at two different current densities, 1.0 and 1.7 A dm^{-2}, with corresponding cell voltages of 25 and 55 V, respectively. The entire process lasted about 250 min, for a total charge consumption of 20,000 C. The final content of diluate and concentrate were about 100 and 12,000 ppm, respectively, with an overall current efficiency of 18%. By considering only the first 146 min, at 1 A dm^{-2}, the efficiency increased to about 30%.

This excellent result evidences that: (i) all the acids are transferred from diluate to concentrate, without any appreciable selectivity between the various components; (ii) appreciable concentrate concentrations ($\geq$10,000 ppm) can be reached even in the batch mode and (iii) no fouling problems, both for membranes or electrodes, were encountered after more than 30 h of electrodialysis.

As far as current efficiency is concerned, it can be noted that the back diffusion of undissociated acids usually prevails at longer times, when large concentration gradients are present between diluate and concentrate.

It has to be stressed that the cell is not optimized; in fact, by appropriately reducing the thickness of the diluate and concentrate chambers to 1 mm, a cell voltage of 6 V can be reasonably expected at 1.0 A dm^{-2}. This leads, for the same 30% current efficiency, to an energy consumption of 29.0 kWh kg^{-1} of recovered carboxylic acids, about 2.4 € m^{-3} of the treated stream. It is evident that further increase of current efficiency, e.g. to 60%, would imply an energy consumption of 14.5 kWh kg^{-1}, and 1.2 € m^{-3} of water to be treated as energy costs. Also investment costs can be estimated, starting from similar size electrodialysis plant [33]. To treat 300 m^3 h^{-1} of waste stream containing around 2,000 mg dm^{-3} of organic acids at 0.5 A dm^{-2} (current density must be reduced when concentration decrease) with a current yield of 60%, in order to obtain a 100 mg dm^{-3} COD diluate stream, it is necessary to use about 10,000 m^2 of membrane surface in 30 stacks with a total investment cost of 13,000,000 € and operative costs of 0.15 € kg^{-1} of acid for membranes replacement and 0.02 € kg^{-1} for electrodes replacement. However, when the electrodialysis process produces a concentrate stream containing acids and their value may be comparable to the market price of fuel, 0.2 € kg^{-1}, it is possible also to estimate an income in the order of 0.4 € m^{-3} of waste effluent treated. In this latter case it is possible not only to dispose effluents in surface water, without any other costs, but also ED choice has sustainable and competitive cost with respect to other techniques, with advantage in term of environmental impact because ED does not form any secondary waste stream.

4 Conclusions

Electrodialysis was successfully applied to treat real wastewater stream for recovering light (C1–C6) carboxylic acids in a single electrochemical step and without any chemical pre- or post-treatment.

In the case of model solutions of acetic acid it was possible to reduce the diluate concentration down to 30 ppm while obtaining a concentrate stream of 12 wt% of acid, with 50% current efficiency.

Table 4 Initial and final concentration and speciation of diluate and concentrate circuits for electrodialysis of real wastewater

Acids	Diluate (2.0 dm^3) (ppm)		Concentrate (0.2 dm^3) (ppm)			Catholyte and anolyte (ppm)
	Initial	Final	Initial	$t = 146$	Final	Final
Formic	201	2	401	2,008	2,030	26
Acetic	720	66	2,628	6,506	7,684	70
Propionic	145	18	336	1,082	1,323	1
Iso-Butyric	19	3	31	136	150	<1
n-Butyric	83	9	170	595	716	<1
Iso-Valeric	<1.0	<1	<1	<1	<1	<1
n-Valeric	43	5	55	193	264	<2
n-Caproic	4	<2	<2	20	26	<2

In the case of a real wastewater stream, the acid mixture was concentrated up to 10,000 ppm, without any appreciable selectivity between the various acidic components, while reducing the diluate stream down to 120 ppm, at 30% current efficiency, with a projected energy consumption of 14.5 kWh kg^{-1}.

Long life tests to design bench scale ED stacks has to be performed, however the lack of membrane fouling during the treatment of a real wastewater stream can be considered encouraging.

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