REWAGEN: Electrochemical water treatment system in the dairy industry with hydrogen recovery and electricity production

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Resumen

REWAGEN is an EU project for the development an eco-efficient process for dairy effluent treatment based on advanced electrochemical technologies enabling water reuse and valorisation of some by-products, including residual hydrogen.

The strategy includes an electro-coalescence pre-treatment, an electro-coagulation (EC), an electrooxidation step and a final conductivity reduction process. The energy needed for the treatment will be partially recovered from the valorisation of hydrogen produced during the electrochemical treatments. The project also aims the recovery of the metals from the electrocoagulation sludge so that the final separated organic sludge can be valorised for energetic or fertiliser purposes.

The main role of Leitat is the development of an innovative EC process that achieves the simultaneous reduction of turbidity, organic matter, nitrogen and phosphorous content of the dairy effluents, together with the recovery and valorisation of hydrogen. Moreover, the integration of electrocoagulation technology with other electrochemical technologies for a sustainable and costly efficient dairy effluent treatment is investigated.

Currently, a new electrocoagulation cell for simultaneous water treatment and hydrogen recovery has been built and properly tested. 99.6%, 33% and 24% of turbidity, COD and TOC removal efficiencies, respectively, have been obtained at 106mA/cm2 and 40L/h (retention time: 11.3s) at bicompartmental mode when dairy effluent has been treated without initial pH modification. The treatment implies an electrical cost of 4KWh/m3. It is worth to say that 100%, 90% and 60% of Mg, P and Ca content, respectively, have been also removed during electrocoagulation process. EC experiments with simultaneous hydrogen recovery are being carried out, showing promising results.

Palabras clave: tratamiento de efluentes industria láctea; tratamientos electroquímicos avanzados; electrocoagulación; recuperación de hidrógeno; energía

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ABSTRACT

REWAGEN is an European project for the development of an eco-efficient process for dairy effluent treatment based on advanced electrochemical technologies enabling water reuse and valorisation of some by-products, including residual hydrogen.

The strategy includes an electro-coalescence pre-treatment, an electrocoagulation (EC), an electrooxidation (EO) step and a final conductivity reduction process. The energy needed for the treatment will be partially recovered from the valorisation of hydrogen produced during the electrochemical treatments. The project also aims the study of the recovery of the metals from the electrocoagulation sludge so that the final separated organic sludge can be valorised for energetic or fertiliser purposes.

Leitat's role is the research and development of an innovative EC technology that achieves the simultaneous reduction of turbidity, organic matter and phosphorous content of the dairy effluents, together with the recovery of hydrogen. Moreover, the integration of electrocoagulation technology with other electrochemical technologies for a sustainable and costly efficient dairy effluent treatment is investigated.

KEYWORDS

Electrocoagulation, dairy effluent, hydrogen recovery, advanced electrochemical technologies.

INTRODUCTION

1. Context

The Food and Beverage sector is the largest industrial sector in Europe in turnover terms. Environmental issues in the food processing industry are diverse. One of the main issues is wastewater prevention and treatment. Food and Beverages has traditionally consumed large quantities of water as an ingredient, as cleaning aid and as means of conveyance.

Wastewater generated from food operations has distinctive characteristics that set it apart from common municipal wastewater managed by public or private wastewater treatment plants throughout the world: it is biodegradable and non-toxic, but has high concentrations of biochemical oxygen demand (BOD), chemicals and suspended solids. The compounds of food and agriculture wastewater are often too complex to predict due

46 to the differences in BOD and pH in effluents from vegetable, fruit, and meat products and
47 due to the seasonal nature of food processing and post-harvesting.
48   Wastewater in the sector varies a great deal due to the material and processing
49 degree. Raw material food processing requires large volumes of high grade water.
50 Vegetable washing generates waters with high loads of particulate matter and some
51 dissolved organics. It may also contain surfactants.
52   Animal slaughter and processing produces very strong organic waste from body fluids,
53 such as blood, and gut contents. This wastewater is frequently contaminated by significant
54 levels of antibiotics and growth hormones from the animals and by a variety of pesticides
55 used to control external parasites. Insecticide residues in fleeces are a particular problem
56 when treating waters generated in wool processing.
57   Processing food for sale produces wastes generated from cooking which are often rich
58 in plant organic material and may also contain salt, flavorings, colouring material and
59 acids or alkali. Very significant quantities of oil or fats may also be present. Water costs
60 and sewer charges are on the rise. The European legislation on industrial wastewater
61 treatment (IPPC Directive) and the protection of aquatic environments (Water Framework
62 Directive) demand more and more stringent discharge compliance levels - and therefore
63 treatment levels. A corporation's image can be tarnished and its sales hurt if its plants are
64 perceived as harming the environment or not respecting the national and European
65 legislations in terms of environmental protection and wastes treatment. Finally,
66 enforcement actions and fines are becoming more severe for those whom do not respect
67 water conservation rules. In this context, an increasing number of Food and Beverage
68 sites need to improve their wastewater management and to set up their own wastewater
69 treatment plants.
70   The dairy industry produces a large amount of wastewaters (from 2 to 5 times the
71 produced milk volume). This water is originated during cleaning operations including also
72 raw materials rests. Whey is a key problem in this industry since it has a high organic load
73 and can have high conductivity values. Although wastewaters can be very variable from
74 site to site they all share some common aspects: high chemical oxygen demand (COD)
75 and BOD, fats and oils content and high quantities of nutrients (phosphorous), presence
76 of suspended solids (especially in those sites with cheese production). Dairy effluent
77 variability from site to site is impaired by different water management protocols. While
78 some locations mix all effluents in a final tank, others separate fluxes for a more specific
79 water treatments/valorisation. However, it has to be considered that the dairy industry is
80 composed by a high number of small sites where wastewaters are usually mixed and
81 processed in a single treatment strategy or even externalised for treatment *ex-situ*. Even
82 when all this variety is considered, some processes are common and addressed in the
83 present project: initial homogenization of incoming fluxes to homogenize the inlet and
84 organic charges, initial separation of fats and oils, treatment for the separation of
85 suspended solids, COD/BOD abatement and a final conductivity reduction step to allow
86 the reutilization of water.
87   Traditionally the high biodegradability of dairy industries wastewaters has promoted
88 the use of biologic treatments. However whey constitutes a relevant problem in this
89 industry due to high conductivity and organic matter levels. Many projects and studies
90 have been addressed to organics recovery from whey prior to the water treatment.
91 However, many dairy producers are medium or small companies that do not have the
92 possibility to separate whey from dairy wastewater and to valorize some compounds from
93 whey. Therefore the project addresses a solution that allows for the treatment of
94 wastewaters together with the whey.

2. General concept and objectives of the REWAGEN project

The aim of the REWAGEN project is the development of an eco-efficient wastewater and whey treatment system in the dairy industry for the total abatement of contaminants. It is based on electrochemical technologies, enabling water reuse and separated waste valorisation. The energy needed for the treatment is foreseen that will be partially recovered from the hydrogen produced during the electrochemical treatments, thus improving process sustainability. The whole process includes an electro-coalescence pre-treatment, an electrocoagulation (EC) and electrooxidation (EO) step and a final conductivity reduction process. Moreover it considers the study of the separation of metals from the electrocoagulation sludge so final separated organic sludge can be valorised for energetic or fertiliser purposes. The key novelty of the process includes a hydrogen recovery and valorisation process where the gas produced during the electrochemical steps is purified and burned into a fuel cell enabling energy recovery for the sustainment of the water treatment process. Therefore a final global process will be designed for the dairy industry focused on 1) minimizing the use of water 2) valorisation of residues 3) sustainable in energy terms. The concept addresses the wastewater management as a whole, understood as an industrial process directly linked with the production performance. The concept of the project includes the design of a prototype of wastewater treatment system aiming at closing the water cycle, by integrating energy and water management.

The project develops a treatment system with technologies that have still not been jointly developed together with hydrogen recovery. The hydrogen generation from EC and EO systems for electricity production to be used to feed the wastewater treatment system has not yet been developed. Still a lot of research is needed for the recovery of hydrogen from these two water treatment technologies

Therefore, the purpose of the project is to develop an environmental sounding technological solution which will require research, development and testing phases covered by the project in order to reach the development of a perfectly functioning technological prototype.

The project aims to implement the system in a Spanish SME belonging to the dairy sector, in order to proceed to a more efficient treatment of its wastewater effluents and whey. The food and drink sector has been identified as relevant stakeholder that may find beneficial the application of a new water management solution that can offer advantages in terms of energy efficiency, environmental and economic impact.
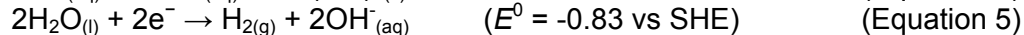
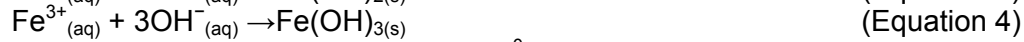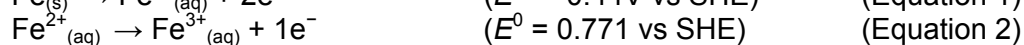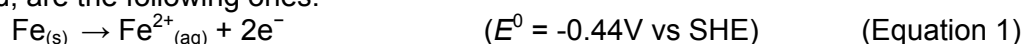## 3. Specific objectives of Leitat in REWAGEN project

The main role of Leitat Technological Center in the REWAGEN project is the research on a smart electrocoagulation system able to treat dairy effluent (turbidity, organic matter and phosphorous content reduction) and, at the same time, to recover as pure as possible hydrogen (produced as by-product). The integration of the output gases system from the electrocoagulation cell with a fuel cell stack is also researched at laboratory scale in order to valorise hydrogen produced.

In the project, EC process is applied after electro-coalescence system. However, preliminary research was carried out applying the innovative EC system directly to dairy effluent treatment. The most appropriated operational conditions found in this case are later applied for the treatment of the electro-coalescence effluent.

4. State of the art in EC

Electrocoagulation is an electrochemical process used as alternative to conventional coagulation/flotation processes. In this advanced technology, coagulum agents are *in situ* generated through electrochemical oxidation of sacrificial metallic anodes (*e.g.* iron or aluminium) (Equation 1). Obtained Fe(II)/Fe(III) (Equation 2) or Al(III) precipitate with hydroxide ions (Equations 3 and 4) generating coagulum particles which destabilize and adsorb water pollutants by surface complexation or electrostatic attraction[1]. Pollutants are removed by sedimentation or electroflotation owing to bubbles of hydrogen gas generated at cathode surface (Equation 5).

Between others, some of the main involved reactions during EC process, when iron anode is used, are the following ones:

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \qquad (E^0 = \text{-0.44V vs SHE}) \qquad \text{(Equation 1)}$$
$$Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + 1e^- \qquad (E^0 = \text{0.771 vs SHE}) \qquad \text{(Equation 2)}$$
$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)} \qquad \text{(Equation 3)}$$
$$Fe^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Fe(OH)_{3(s)} \qquad \text{(Equation 4)}$$
$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \qquad (E^0 = \text{-0.83 vs SHE}) \qquad \text{(Equation 5)}$$

Comparatively with conventional wastewater treatment processes, EC mainly offers low investment and operational costs, efficient removal of contaminants (organic compounds, suspended solids or turbidity, fats and oils, metals, nutrients, salts), no chemicals addition and a minimum level of residual and dense sludge.

The first EC patent dates from 1906[2], however significant improvements should be made in EC system to increase its market implantation since still do not exist a systematic efficient approach regarding its design and operational mode.

5. Progress beyond the state of the art in EC

EC was applied for suspended solids, turbidity, colour and TOC abatement in several sectors. However hydrogen recovery was not selected as a target in those applications. In REWAGEN project there is an important progress beyond the state of the art based on the EC unit design to allow the recovery of as pure as possible hydrogen. Also other important factors, such as reducing electrode fouling was considered and improved from actual equipment.

It can be stated as a strength that such kind of electrochemical and hydrogen valorisation technologies were not still jointly considered. As far as reviewed there is no previous work focused on the recovery of generated hydrogen from EC or EO systems for electricity production, neither in bench-scale nor in real-life. The scientific literature does only show some very recent studies [3,4] dealing on electrochemically generated hydrogen from electrocoagulation or electrooxidation studies but they are considering neither an integral solution for the wastewater of an industry such as the dairy one nor the recovery or utilisation of such hydrogen in a fuel cell. Therefore the project itself represents a progress beyond the state of the art in this field since the wastewater treatment will be linked to energy production and the waste reutilisation. Additionally, it has to be noted that other published works researching the electrochemical production of hydrogen are not additionally involved in water treatment issues [5,6,7].

The most important scientific articles related with hydrogen recovery from electrochemical systems are specified in Table 1. Low numbers of papers are found in the literature related with this issue, being the new EC unit design proposed by REWAGEN one of the most innovative ones.

190　**Table 1.** Summary of articles related to hydrogen recovery from electrochemical systems and progress to be
191　achieved within REWAGEN project.

Article reference	Content of the article and some considerations related with REWAGEN project	REWAGEN differences
C. Phalakornkule, P. Sukkasem, C. Mutchimsattha. "Hydrogen recovery from electrocoagulation treatment of dye-containing wastewater", *International Journal of Hydrogen Energy*, 2010, 35,10934-10943 [8].	In this paper, a technique of hydrogen recovery from an electrocoagulation process treating dye-containing wastewater is presented. They carry out an electrocoagulation process using a set of twenty-five pair of iron electrodes, in a single electrochemical reactor where hydrogen is recovered directly from the top of the reactor. The fact of working in a single electrochemical cell implies that hydrogen and oxygen (and other impurities) could be mixed, reducing purity of the hydrogen flow, and consequently, its valorisation options.	Bench scale electrocoagulation system of the REWAGEN project included a bi-compartment electrochemical cell where cathode and anode compartments were separated by an anionic exchange membrane.
M. Ansori Nasution, et al. "Electrocoagulation of Palm Oil Mill Effluent as Wastewater Treatment and Hydrogen Production Using Electrode Aluminium", *J. Environ. Qual.*, 2011, 40, 1332-1339 [9].	In this paper an electrocoagulation setup composed by twelve aluminium plates were used for palm oil mill effluent treatment and hydrogen recovery. They work in a mono-compartment cell where hydrogen is recovered from the top of the tank and treated wastewater was obtained from the middle of the tank.	A catholyte solution of NaOH was re-circulated from a sealed tank through the cathode compartment. Hydrogen produced on cathode was recovered inside of catholyte tank, reducing therefore the impurities associated to oxygen and carbon dioxide generated mainly in anodic compartment. Dairy effluent was treated in anode compartment, where coagulation nuclides were electrogenerated from an iron or aluminium anode.
S. Eker, F. Kargi. "Hydrogen gas production from electrohydrolysis of industrial wastewater organics by using photovoltaic cells (PVC)", *International Journal of Hydrogen Energy*, 2010, 35,12761-12766 [10].	Electrooxidation system based on the use of stainless steel electrodes for wastewater treatment and hydrogen generation, recovery and quantification. Single electrochemical cell and solar PVC for electrical power supply. The fact of working in a single electrochemical cell implies that hydrogen and oxygen (and other impurities) could be mixed, reducing purity of the hydrogen flow, and consequently, its valorisation options.	
J. Jiang, M. Chang, and P. Pan. "Simultaneous Hydrogen Production and Electrochemical Oxidation of Organics Using Boron-Doped Diamonds Electrodes", *Envrion. Sci. Technol*, 2008, 42, 3059-3063 [11].	Electrooxidation system based on the use of a BDD anode for wastewater treatment and the use of stainless steel as a cathode for hydrogen production, in a single electrochemical cell. The fact of working in a single electrochemical cell implies that hydrogen and oxygen (and other impurities) could be mixed, reducing purity of the hydrogen flow, and consequently, its valorisation options.	Electrical power supply in bench scale electrocoagulation system was provided by an electrical source (and not from solar PVC).

192　　　　On the other hand, the most interesting patent related with hydrogen recovery from
193　an electrochemical system (electrodialysis) is specified in Table 2, where main
194　characteristics and differences with REWAGEN project are exposed.

195

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197

198 **Table 2.** Summary of patents related with hydrogen recovery from electrochemical systems and progress to
199 be achieved within REWAGEN project.

Patent information	Content of the patent	REWAGEN differences
System for recovering gas produced during electrodialysis. US 7,909,975 B2 Mar. 22, 2011 Inventor: Vitselle S.O. Martez [12]	System for recovering gas produced during electrodialysis of a saline solution from gas entrained in an electrolyte solution circulation through anode and cathode compartments of an electrodialysis unit. Separate catholyte and anolyte towers within a closed and a re-circulating loop between the cathode and anode compartment.	In the current patent, catholyte tower include (i) a complex system for achieving hydrogen release from the alkaline catholyte solution and (ii) a hydrogen purification system (mainly nitrogen and oxygen removal) inside the tower. It is composed by a different drain ports, a perforated frit, and a gas scrubber system (mixed bed of carbon molecular sieve and iron powder) for hydrogen purification. Bench scale electrocoagulation system of REWAGEN project included a sealed NaOH catholyte solution tank for hydrogen recovery that had a simple external and internal structure where hydrogen was recovered from the top of this tank and catholyte was re-circulated. The outlet of hydrogen was directly coupled externally to a HORIZON FUEL CELLS (EDUSTACK PRO), at laboratory scale.

200

MATERIALS AND METHODS

1. Chemicals

203 Analytical grade sulphuric acid 95-97% and NaOH 50% solution was purchased from
204 Scharlau and were used to pH adjustment and for preparing catholyte solution. 70% HNO_3
205 for trace analysis was purchased from Sigma Aldrich.
206 Hydrogen, oxygen and nitrogen patrons for the calibration of MicroGC They were supplied
207 and certified by Carburos Metálicos S.A.

2. Instruments and analytical procedures

209 Galvanostatic experiments were carried out with a KEPCO power supply KLP 75V-
210 33A-1200W potentiostat–galvanostat. The pH was measured with a CRISON pH meter
211 GLP 21 and the electric conductivity (CE) by a CRISON CE-meter Basic 30+ meter.
212 Before analysis, all samples withdrawn from treated solutions were filtered with
213 0.45μm PVdF filters in order to measure the dissolved total organic carbon (TOC). The
214 mineralization of organic compounds was monitored by the quantification of the TOC,
215 determined on a Shimadzu V-C DCH TOC analyzer, following the UNE-EN 1484:1998.
216 Reproducible TOC values, with ±2% accuracy, were obtained by injecting 50 mL aliquots
217 into the TOC analyzer.
218 Chemical oxygen demand (COD, mg O_2/L) was determined after the effluent filtration
219 using a Digestor Hach Large DR 3000 and a spectrophotometer Hach Large HT 2005.
220 Turbidity measurements were performed following the UNE-EN ISO 7027:2001.
221 Anion analysis was carried out by ion chromatography with conductimetric detection
222 (IC-CD,Dionex ICS3000) fitted with an IonPac Anion Exchange Column AS19 and a
223 Precolumn AG19. This analysis was carried out by injecting 25 μL samples into the
224 chromatograph using a flow rate of 1mL/min of 10mM NaOH (0-10min) and applying a
225 concentration gradient from 10 to 50mM NaOH (10-35min) as mobile phase (prepared
226 from NaOH 50-52% in water, eluent for IC, Sigma Aldrich).
227 The procedure used for the microwave acid digestion and ICPMS analysis of the
228 sludge samples is detailed as follows:

229 *a) Microwave acid digestion*. Samples were directly weighed (0.5g sample) into the
230 microwave vessels using an AG245 Balance (Mettler Toledo), readability 0.0001g.
231 Samples are digested with an acid solution (10 ml of 70% HNO_3 for trace analysis, Sigma
232 Aldrich) in an analytical microwave digestion system (MARS, CEM, 1600W). Specifically,
233 the microwave digestion program consists on heating from room temperature to 200ºC in
234 10 min, then maintain this temperature 15 min and, finally, cold down to room temperature
235 to manipulate the samples safely. After having carried out the described digestion
236 program, all samples were filled with MilliQ water to 50 ml. Then, further dilutions were
237 made with 2% HNO_3 aqueous solution to obtain the desired concentrations for ICP-MS
238 characterization.

239 *b) Multielemental ICP-MS characterization*. Elements of interest (such as Fe, Al, P...)
240 analyses were performed by ICP-MS (Agilent 7500, Agilent Technologies). The
241 quantification is done by interpolation in a standard curve obtained from commercial
242 1000ppm standards of the elements under study (Sigma Aldrich).

243 For Elemental Analysis (CHN), samples were weighed in a tin capsule to perform the
244 analysis of carbon (C), hydrogen (H) and nitrogen (N) by combustion (Elemental Analyser
245 EuroEA3000, Eurovector).

246 Hydrogen and analysis of its impurities was carried out by gases micro-
247 chromatography (MicroGC). The gas produced was sampled using a Tedlar® 1.263-01
248 FlexFoil gas sampling Bag of 1L of capacity. Gas was analyzed by Agilent 490 Micro-GC
249 with dual channel cabinet and thermal conductivity detector:

250 ▪ Channel 1 (equipped with a 10-meter CP-Molsieve 5A column) separates and
251 analyses the permanent gases: H_2, O_2, N_2, CH_4 and CO with back flush. Argon is
252 used as carrier gas, providing excellent sensitivity and linearity for hydrogen.

253 ▪ Channel 2 (with a CP-PoraPolt U column) separates and analyses the C2 gases,
254 hydrogen sulphide, and CO_2.

255 The columns were equipped with blackflush to vent functionality. For the Molsieve column,
256 this backflush to vent is required to maintain the separation. Moisture and carbon dioxide
257 tend to adsorb quickly to the Molsieve stationary phase and change its chromatographic
258 properties.

259 Instrument calibration was performed by using gas standards of H_2, O_2 and N_2. The
260 calibration curve for each gas was generated according to the concentrations shown in
261 the following table.

262

Table 3. Concentration of patrons used.

Compound	Concentration (% mole)
H_2	5, 50, 99.9
O_2	0.1, 1, 10
N_2	0.1, 1 20

263

264 In the following table, a typical equation for the curve is given for each compound. The
265 MicroGC software automatically calculated the concentrations of all samples using the
266 calibration equation. The detection limits for all gases were found to be 0.01 % mole.
267
268
269
270
271

Table 4. Equations used for interpolation.

Compound	Equation
H_2	346.58 X - 5442.4
O_2	25,81 X -0,449
N_2	21,157 X +0,2432

274

275 The chromatographic conditions are summarized in the Table 5.

276

Table 5. Chromatographic conditions.

Parameter	Channel 1	Channel 2
	Molsieve	CP-PoraPLOT U
Injector Temp (ºC)	90	110
Column Temp (ºC)	80	100
Carrier Gas	Argon	Argon
Column Head Pressure (kPa)	150	205
Injection Time (ms)	40 ms	40 ms
Backflush (s)	11,0	7,1
Detector Sensitivity	Auto Range	Auto Range
Sampling time	30 s	30 s

277 **3. Electrochemical system**

278 EC system was designed in Leitat Technological Centre and it was composed by three
279 main modules:

280 ▪ An **electrochemical bi-compartment cell (or divided EC cell)**, where anode and
281 cathode compartment were separated by an anionic exchange membrane. Hydrogen
282 was recovered from cathode compartment and dairy effluent was treated in anode
283 compartment.

284 ▪ **A sealed tank for hydrogen recovery** and catholyte (NaOH solution) recirculation.

285 ▪ **A settle tank where electro-generated coagulants are removed** from the treated
286 effluent coming from anode compartment.

287 Figure 1 shows a section view of the continuous EC system at bench scale used for dairy
288 effluent treatment and simultaneous recovery of hydrogen. The electrochemical cell is a
289 one-compartment filter-press cell used as electrolytic reactor, composed of several
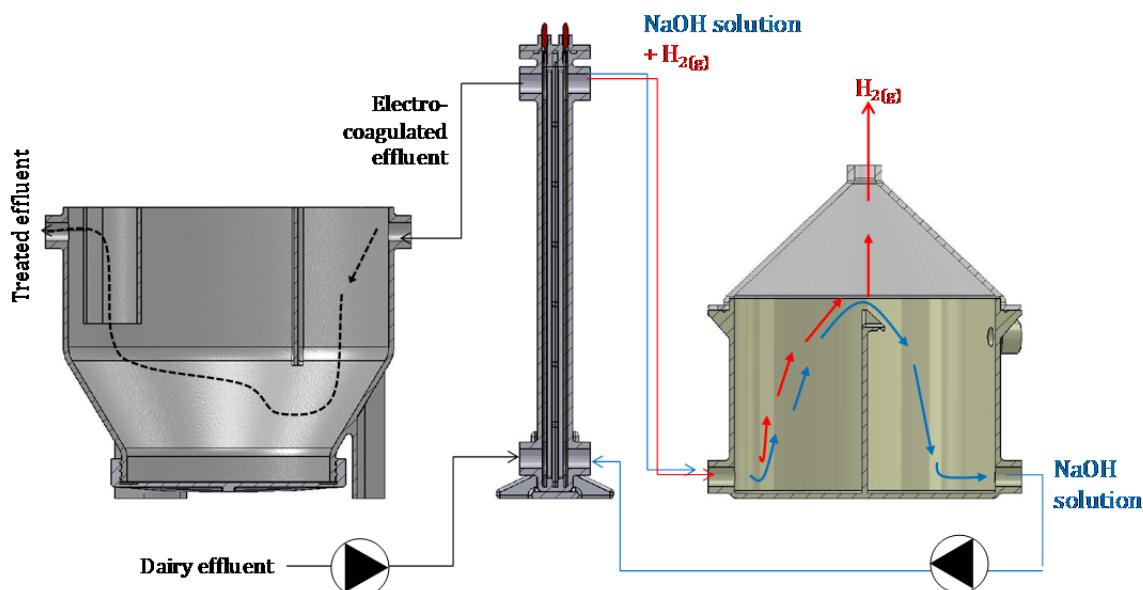290 components in order to allow water treatment and simultaneous hydrogen recovery.

Figure 1. Section view of bench scale EC unit.

In the bi-compartment electrochemical cell, anode and cathode compartment were separated by an anionic membrane (AHA membrane from EURODIA INDUSTRIE SA), with high chemical and physical resistance. In this case, catholyte is composed by 2L of NaOH 1M solution, working in continuous recirculation from/to the hydrogen recovery tank. Hydrogen generated on cathode was collected by NaOH solution and recovered from the top of the sealed tank by a gas collection setup.

Anode solution was composed by dairy effluent. In each trial the dairy effluent was introduced in a reservoir and continuously recirculated through the anode compartment of the electrochemical cell by a peristaltic pump. After finalizing its treatment, it was sent to a settle tank where coagulum/floccules were removed by filtration with a 15-20µm filter.

Several electrocoagulated samples were collected through the time in order to determine the main analytical parameters after their previous coagulum removal.

Under the best operational parameters, the electrocoagulation sludge was filtered, quantified, dried and its composition determined.

Output gases from cathode compartment were collected under the most appropriated operational conditions during around 3min (from 2.00Ah/L to 2.65Ah/L) using Tedlar® sample bags. The samples were characterized by the MicroCG.

The operational conditions used during electrocoagulation trials are listed below:

- Type of electrochemical cell:
  a) Mono-compartment (non-divided EC cell)
  b) Bi-compartment (divided EC cell)
- Continuous mode
- Anode:
  a) Aluminium
  b) Iron
- Cathode: Pt/Ti
- Anionic exchange membrane
- Type of effluent: dairy effluent
- Current density (amperostatic conditions):
  a) $j = 50mA/cm^2$

324   b) j = 56mA/cm^2
325   c) j = 64mA/cm^2
326   d) j = 106mA/cm^2
327 ▪ Temperature: ~ 25ºC (without temperature control during the process).
328 ▪ pH:
329   a) Without pH modification
330   b) Acid conditions
331   c) Basic conditions
332 ▪ Flow rate:
333   a) 6L/h
334   b) 12L/h
335   c) 19L/h
336   d) 25L/h
337   e) 31L/h
338   f) 40L/h

339 RESULTS AND DISCUSSION

340 1. Wastewater source and characteristics

341 Dairy effluent coming from a Spanish SME company was composed by 12.97% of
342 whey from mató cheese, 13.61% of whey from soft cheese, 1.97% of whey from hard
343 cheese, 1.97% of whey from semi-hard, semi-soft, pepper semi-soft cheese, 69.45% of
344 domestic/company wastewater and 0.03% of brine.
345 The values obtained for the main analytical parameters from the dairy effluent
346 characterisation are specified in Table 6.

347

Table 6. Main dairy effluent parameters.

Parameter	Dairy effluent (n = 7)
Turbidity (NTU)	$3.0 \cdot 10^3 \pm 0.6 \cdot 10^3$
COD (mg O_2/L)	$24.8 \cdot 10^3 \pm 2.2 \cdot 10^3$
TOC (mg C/L)	$7.4 \cdot 10^3 \pm 0.8 \cdot 10^3$
pH	6.2 ± 0.4
CE (mS/cm)	10 ± 1
Total P (mg/L)	132 ± 13

348 Table 6 shows high organic matter content and relatively high conductivity and turbidity
349 values.
350 Relatively high standard deviation of some parameters are due to high variability specially
351 in wastewater from one week to other, and also from day to day.

352 2. Non-divided electrocoagulation system.

353 Several current densities (from 50mA/cm^2 to 106mA/cm^2) and flow rates (from 6L/h to
354 40L/h) were tested for treating the dairy effluent, working with aluminium as anode
355 material and under the mono-compartment mode (without anion exchange membrane).
356 Operational conditions, consumed power and obtained results for the treatment of
357 dairy effluent by the use of aluminium anodes are summarized in Table 7 and Table 8.

358 **Table 7.** Operational conditions and electrical costs for the treatment of dairy effluent by EC process at
359 continuous mode using aluminium as anode material, without pH modification.

Anode material	I (A)	j (mA/cm^2)	Flow rate (L/h)	Retention time (s)	Q (A h/L)	V (V)	Power (W)	Consumption (kWh/m^3)
Al	12.5	50	6	145.6	2.02	13.0	163	26
Al	12.5	50	12	72.8	1.01	12.7	159	13
Al	12.5	50	19	48.4	0.67	12.8	160	9
Al	12.5	50	25	36.3	0.50	12.0	150	6
Al	12.5	50	31	28.8	0.40	12.5	156	5
Al	12.5	50	40	22.7	0.32	12.5	156	4
Al	14.0	56	40	22.7	0.35	13.3	186	5
Al	16.0	64	40	22.7	0.40	14.4	230	6
Al	26.5	106	40	22.7	0.67	23.3	617	16

Table 8. Removal efficiencies for the treatment of dairy effluent, theoretical Al(OH)$_3$ generation and theoretical anode consumption by EC process at continuous mode using aluminium as anode material, without pH modification.

| CE (mS/cm)	pH	Dissolved Al (mg/L)	Theoretical anode consumption (Kg/m^3)	Theoretical [Al(OH)$_3$] (Kg/m^3)	TOC removal (%)	COD removal (%)	Turbidity removal (%)
7.6	8.1	5.0	0.68	1.96	10%	20%	99%
7.3	10.0	93.0	0.34	0.98	17%	24%	97%
8.7	7.4	8.3	0.23	0.65	9%	18%	99%
7.5	7.5	9.6	0.17	0.49	9%	17%	99%
10.5	7.4	13.3	0.13	0.39	9%	16%	98%
8.4	7.2	15.3	0.11	0.31	6%	13%	97%
9.0	7.4	11.6	0.12	0.34	8%	14%	99%
8.0	7.7	10.8	0.14	0.39	10%	19%	98%
4.4	8.1	9.7	0.22	0.64	20%	34%	99%

Influence of flowrate

The influence of dairy effluent flowrate on the efficiency of the EC process was studied applying a current density of 50mA/cm^2.

The removal efficiency for turbidity, TOC and COD removal as well as the theoretical Al(OH)$_3$ production are shown in Table 8 and Figure 2.

369
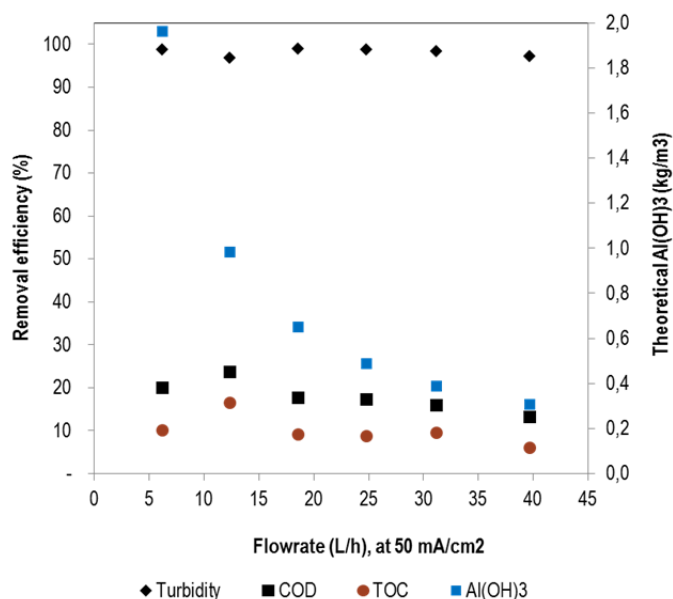
Figure 2. Removal efficiency for dairy effluent treatment and theoretical $Al(OH)_3$ generation by EC system at continuous mode, under several flowrates, using aluminium as anode material and $50mA/cm^2$ without pH modification.

373
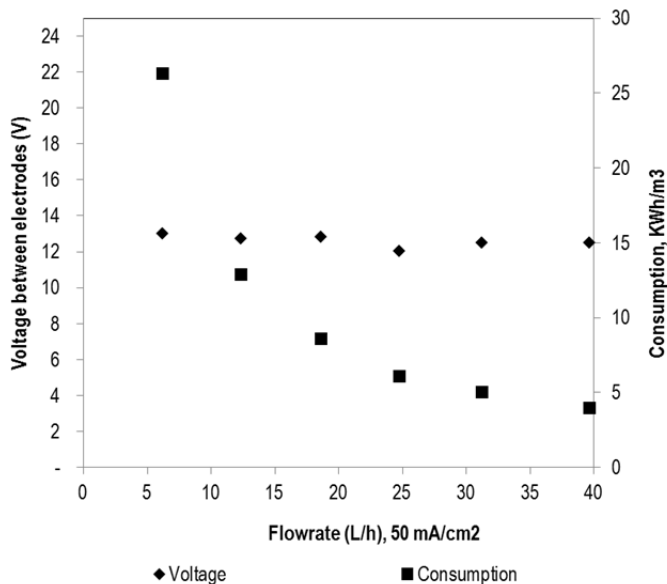
Figure 3. Cell voltage and electrical consumption for dairy effluent treatment with EC system at continuous mode, under several flowrates, using aluminium as anode material and $50mA/cm^2$, without pH modification.

Figure 2 shows no significant improvement on turbidity removal when flowrate was increased from 6L/h to 40L/h for a same applied current density ($50mA/cm^2$), achieving values higher than 97%.

TOC and COD removal (around 10% and 20%, respectively) slightly decreased at higher flowrate, except for 12L/h where higher removals were obtained.

381   However, the theoretical quantity of generated $Al(OH)_3$ significantly decreased when
382   flowrate increased, being around 0.3 kg $Al(OH)_3/m^3$ when the system worked at 40L/h.
383   Moreover, Figure 3 shows that cell voltage was kept around 13V under the several
384   flowrates tested, being then the electrical consumption reduced when flowrate was
385   increased (from 26KWh/m^3 at 6L/h to 4KWh/m^3 at 40L/h, implying a decrease of 84% in
386   electrical consumption).
387   Therefore, taking into account the efficiencies for turbidity, TOC and COD removal as
388   well as the minimization of the generated $Al(OH)_3$ quantity (thus minimization of metal
389   content in produced sludge) and the electrical consumption, the most appropriated tested
390   flowrate was 40L/h.
391

392   **Influence of applied current density**
393   The influence of applied current density on process efficiency was evaluated using
394   the most appropriated flowrate obtained in the above study (40L/h). Results are shown in
395   Figure 4 and Figure 5.
396   As higher was the current density (from 50 to 106mA/cm^2) higher the TOC and COD
397   removal obtained. At 50mA/cm^2, TOC and COD eliminations were around 9% and 20%,
398   respectively, being these values increased to 20% and 34%, respectively, at 106mA/cm^2.
399   However, turbidity removal was similar in all cases (higher than 97%).
400   It is worth mentioning that theoretical quantity of generated $Al(OH)_3$ also increased
401   proportionally to higher current densities.
402   Voltage and electrical consumption rose proportionally and lineally with applied current
403   density, as could be seen in Figure 5.
404   Therefore, focusing only on turbidity removal, electrical consumption and $Al(OH)_3$
405   generation, the best current density would be 50mA/cm^2 (an applied charge of 0.32 Ah/L).
406   However, if higher COD and TOC removals were needed, then the most appropriated
407   current density was 106mA/cm^2 (an applied charge of 0.67Ah/L).
408
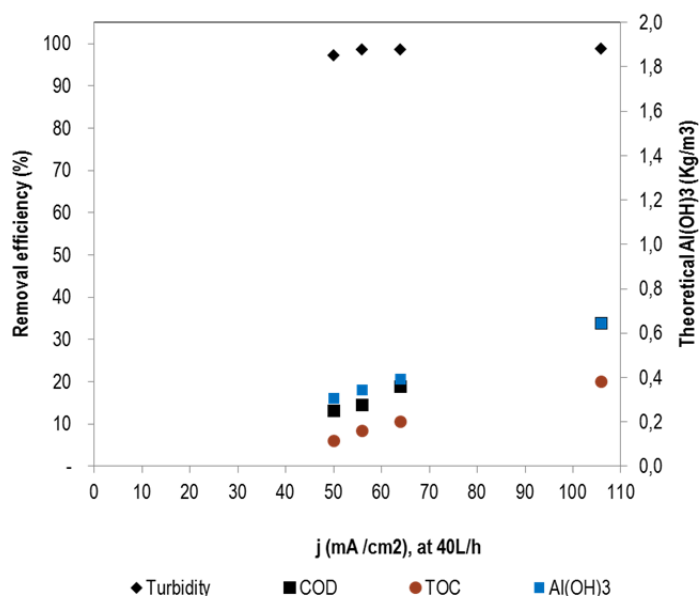
409
410   **Figure 4.** Removal efficiency for dairy effluent treatment and theoretical $Al(OH)_3$ generation by EC system at
411   continuous mode, under several current densities, using aluminium as anode material and 40L/h.
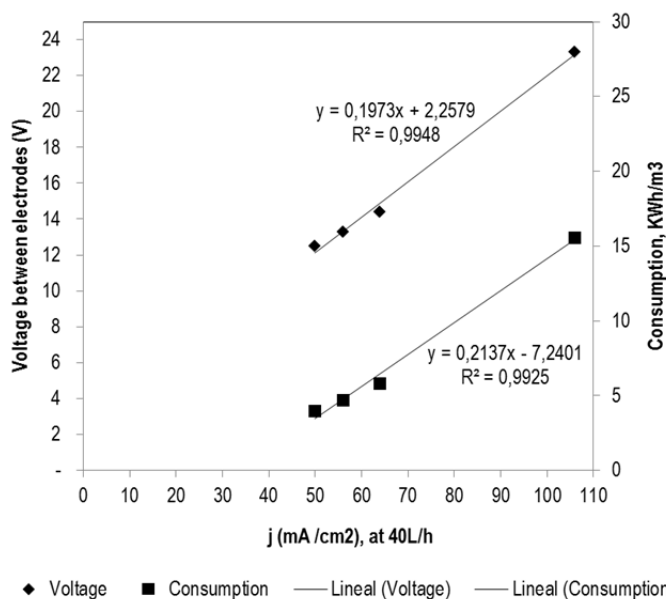
Figure 5. Cell voltage and electrical consumption for dairy effluent treatment with EC system at continuous mode, under several current densities, using aluminium as anode material and 40L/h.

Briefly, the non-divided electrocoagulation system designed by Leitat (where the output gases were not separated either recovered) was an efficient technology for reducing the turbidity of the dairy effluents, reaching a removal of 97% when applying 50mA/cm^2 and 0.32Ah/L. Under these conditions, 13% and 6% of COD and TOC, respectively, were simultaneously removed. The electrical consumption of the process was 4kWh/m^3, being this value minor than in other studies were the EC process were carried out at batch mode or under recirculation [13].

When higher COD and TOC removals are wanted, an applied current density of 106mA/cm^2 (applied charge of 0.67 AL/h) brought to 99%, 34% and 20% on turbidity, COD and TOC removal, respectively, being the theoretical quantity of generated Al(OH)$_3$ around 0.6kg/m^3. However, in this case, the electrical consumption increased four times (16KWh/m^3).

3. Divided electrocoagulation system.

Influence of anode material, initial pH and applied charge (Ah/L) were studied in this section. EC system was used in bi-compartment mode, *i.e.*, using the divided EC cell where cathode and anode compartment were separated with an anion exchange membrane.

In these experiments, 106mA/cm^2 was selected in order to obtain relatively high organic matter removals and simultaneous high hydrogen production in cathode compartment.

Results with aluminium sludge were first of all presented. Afterwards, EC results with iron anode were shown.
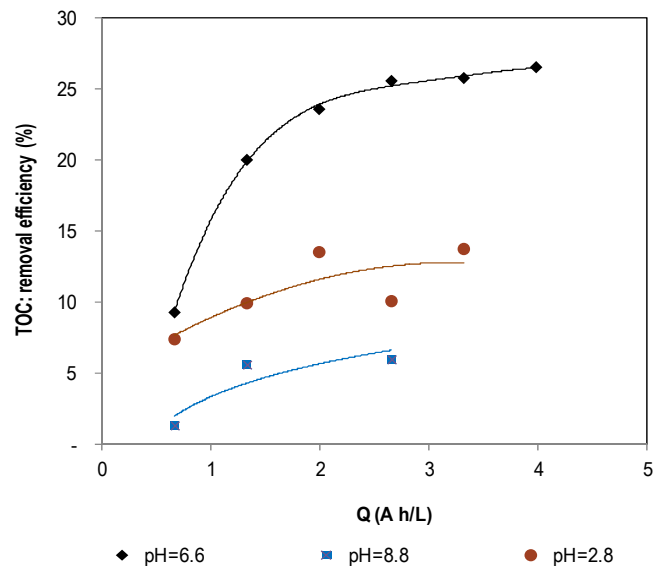
Aluminium anode

Influence of initial pH of dairy effluent on the EC process efficiency was studied when aluminium was used as anode. Turbidity, TOC and COD removals throughout the applied charge (Ah/L) are depicted in Figure 6, Figure 7 and Figure 8, respectively.
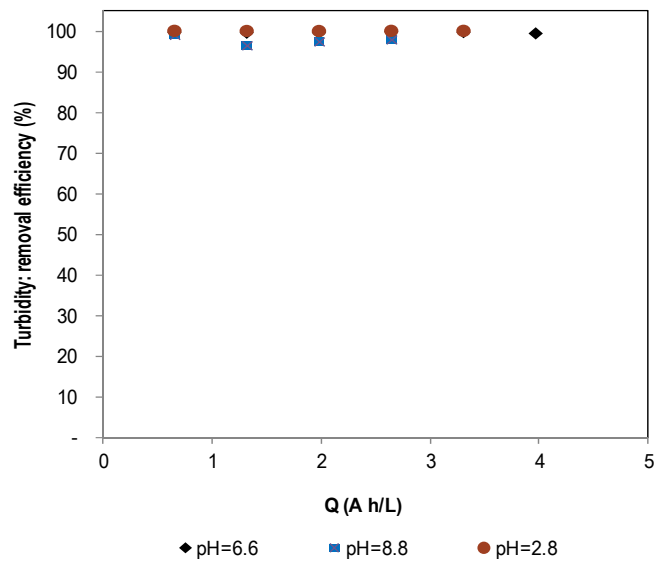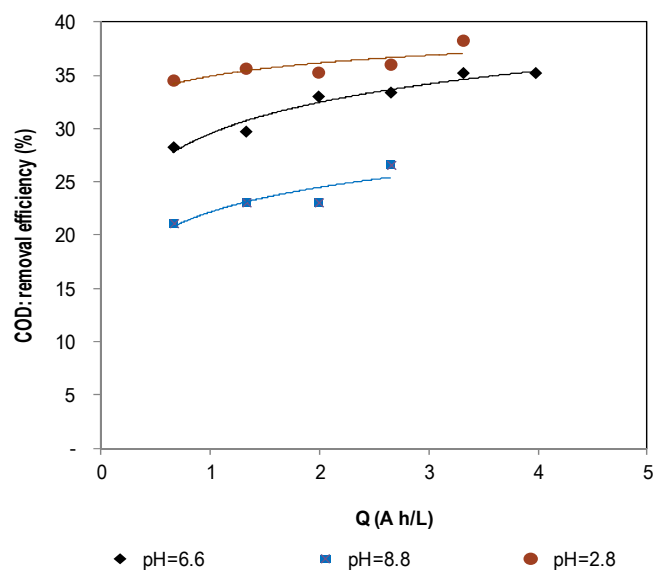
441

442   **Figure 6.** Turbidity removal percentage as function of applied charge for the direct treatment of the dairy

443   effluent by EC technology under several initial pH, using aluminium anode, at $106mA/cm^2$ and 40L/h.

444

445   **Figure 7.** TOC removal percentage as function of applied charge for the direct treatment of the dairy effluent

446   by EC technology under several initial pH, using aluminium anode, at $106mA/cm^2$ and 40L/h.

Figure 8. COD removal percentage as function of applied charge for the direct treatment of the dairy effluent by EC technology under several initial pH, using aluminium anode, at 106mA/cm^2 and 40L/h.

The results of the above figures show that low applied charge (0.66Ah/L) was necessary for removing 99% of turbidity, when initial pH of the dairy effluent was not modified. This applied charge implied an electrical consumption of 7.9kWh/m^3. This value was similar to that obtained in other studies at laboratory scale where EC process with aluminium anodes was used [13]. Under these conditions, 9% of dissolved organic matter was mineralized or adsorbed on the sludge, whereas COD removing efficiency increased up to 28%. The quantity of aluminium dissolved in the treated effluent was 0.5 mg/L.

Divided EC cell brought a 100% reduction on electrical consumption (7.9kWh/m^3), compared with non-divided cell (16kWh/m^3), especially due to the increase on electric conductivity between electrodes provided by NaOH 1M catholyte. This means that the designed electrochemical system was smart not only in terms of as pure as possible hydrogen recovery, but also in terms of reducing electrical consumption. However, the lower potential between electrodes in divided EC cell implied a reduction on TOC removal from 20% (non-divided cell) to 9% (divided cell).

Therefore, in order to achieve similar TOC and COD reductions by means of divided cell, the double of applied charge would be needed. At 1.33Ah/L, 20% and 30% of TOC and COD removals were obtained, implying the same electrical cost than in non-divided cell (16.2kWh/m^3).

An applied charge of 2.65Ah/L implied the increase of TOC and COD removal up to 26% and 33%, respectively, being the electrical consumption associated of 28.5KWh/m^3. In this case, the quantity of aluminium dissolved in the treated effluent was 2.6 mg/L.

Initial pH modification at acidic conditions (pH ~ 3) or basic conditions (pH ~ 9) did not imply an increase on TOC removal. However, under an initial pH~3 the removal of COD was slightly higher than when the pH was not modified. This fact could be associated to proteins denaturation at acidic pH that provoked the faster precipitation of some of the proteins contained in the dairy effluent.

478 **Iron anode**

479 Influence of initial pH and applied charge (Ah/L) during divided EC system using iron
480 as anode material was presented in this section.

481 Turbidity, TOC and COD percentages evolution throughout the applied charge under
482 several pH was depicted in Figure 9, Figure 10 and Figure 11, respectively.
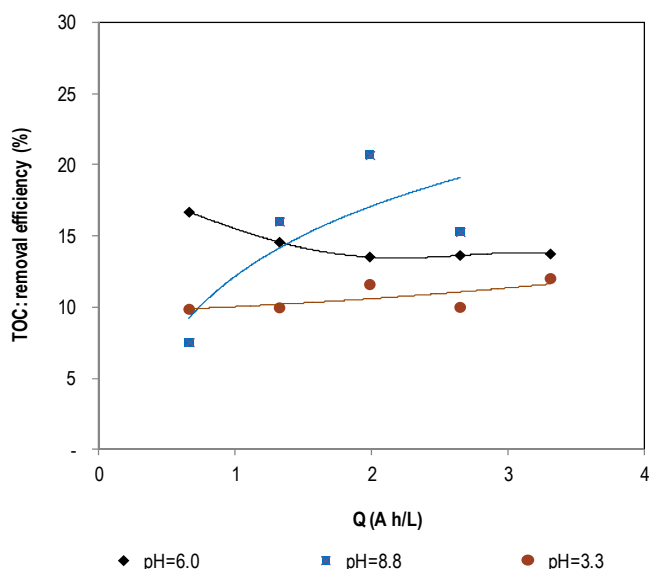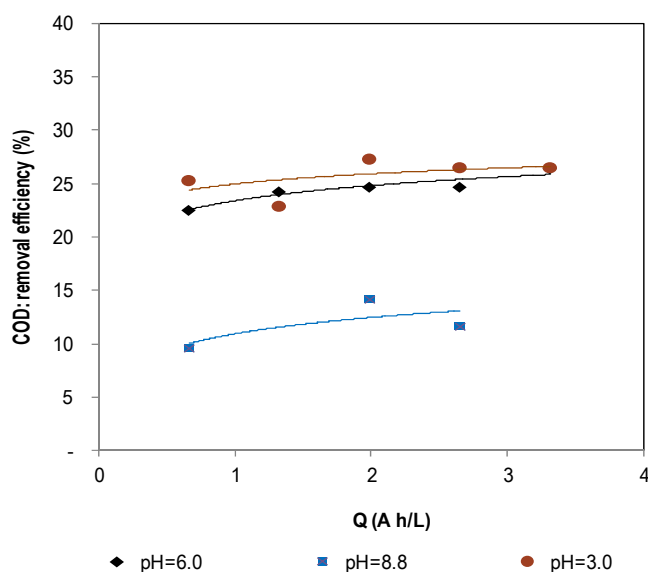
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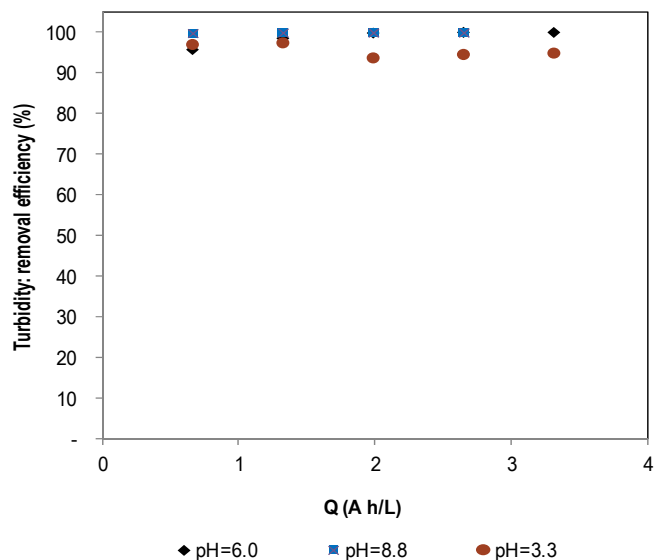
484

485 **Figure 9.** Turbidity removal percentage as function of applied charge for the direct treatment of the dairy
486 effluent by EC technology under several initial pH, using iron anode, at 106mA/cm^2 and 40L/h.

487

488 **Figure 10.** TOC removal percentage as function of applied charge for the direct treatment of the dairy effluent
489 by EC technology under several initial pH, using iron anode, at 106mA/cm^2 and 40L/h.

Figure 11. COD removal percentage as function of applied charge for the direct treatment of the dairy effluent by EC technology under several initial pH, using iron anode, at 106mA/cm^2 and 40L/h.

Turbidity and COD removals achieved at 0.66Ah/L were slightly lower (96% and 22%, respectively) with iron anode than when aluminium was used as anode (98% and 28%, respectively), when initial pH of diary effluent was not modified. However, higher TOC removal was obtained (17%) in front of 9% when aluminium is used. This meant that absorption process produced during EC technology when iron was used as electrode was slower than when anode is aluminium, but that dissolved organic matter was faster removed probably due to Fe-complexes interaction. In this case, the electrical consumption was similar to the above section (7.9KWh/m^3).

Turbidity removal was completed when 2.65Ah/L was applied; however, no significant differences in TOC and COD removals were observed when applied charge increases during EC process. 0.35mg/L of iron was dissolved in the final effluent. In this case, electrical consumption increased up to 35KWh/m^3. In terms of COD removal, 1.5kWh/Kg COD removed was needed using iron anode whereas 0.8KWh/Kg COD removed was obtained when aluminium is used as electrode.

The difference on electrical consumption seems to indicate that aluminium is a better material than iron for EC process. However, in terms of investment costs, iron is cheaper than aluminium.

Finally, it is also worth to say that 98% and 92% of total phosphorous removals were achieved after applying 2.65Ah/L during EC process when aluminium and iron were used, respectively. This fact indicated that EC process was a really suitable technology not only for turbidity elimination, but also for phosphorus removing from wastewaters.

4. Electrocoagulation sludge composition

Sludge obtained during EC process under the most appropriated operational conditions found in terms of turbidity, COD and TOC removal (106mA/cm^2, 2.65Ah/L, 40L/h, and without modification of pH) was collected and filtered. It was weighed before and after drying and later on, it was quantified and characterised.

519 After applying 2.65Ah/L, both wet sludges had around 80% of water. The quantity of dry
520 sludge was around 7.3Kg/m^3 and 8.9Kg/m^3 when aluminium and iron were used as
521 anode, respectively. The relatively high quantity of sludge produced during EC was due to
522 high applied current densities. High current densities implied higher hydrogen generation
523 and higher oxidation power; however, this augmented the quantity of produced sludge. If
524 no suitable valorisation ways are found for the EC sludge, then it would be necessary to
525 reduce the applied intensity in order to minimize this waste.

526 The theoretical quantity Al^{3+} and Fe^{3+} in the dried samples would be around 12% and
527 20%, respectively. The theoretical quantity of iron in the dry sludge is similar to that
528 obtained in the experimental analysis, whereas the quantity of aluminium found in the
529 experimental part is slightly higher, fact that probably indicates aluminium dissolution non-
530 associated to direct applied current.

531 The composition of both type of dry EC sludge was collected in the following tables.
532 Oxygen was not quantified during elemental analysis since its quantification implied the
533 modification of the whole setup for the elemental analysis performance.

534
535 **Table 9.** Sludge composition when aluminium was used as anode material during the EC process of the
536 Spanish dairy effluent under the following conditions: 106mA/cm^2, 2.65Ah/L, 40L/h, and without modification of
537 pH).

Na (% w/w)	Mg (% w/w)	Al (% w/w)	P (% w/w)	Ca (% w/w)	Fe (% w/w)	N (% w/w)	C (% w/w)	H (% w/w)	S (% w/w)
1.0	0.6	16.6	1.2	2.6	<0.1	1.7	28.2	5.8	<0.5

538
539 **Table 10.** Sludge composition when iron was used as anode material during the EC process of the Spanish
540 dairy effluent under the following conditions: 106mA/cm^2, 2.65Ah/L, 40L/h, and without modification of pH).

Na (% w/w)	Mg (% w/w)	Al (% w/w)	P (% w/w)	Ca (% w/w)	Fe (% w/w)	N (% w/w)	C (% w/w)	H (% w/w)	S (% w/w)
1.0	0.1	<0.1	1.3	0.6	21.0	1.7	28.6	5.1	<0.5

541
542 As above tables show, around 30%(w/w) of the dry sludge content corresponded to
543 carbon (C) and around 5-6% (w/w) to hydrogen (H). Aluminium represents around 17%
544 (w/w) of the composition of the EC sludge when this material was used as anode whereas
545 iron was 21% (w/w) when EC was performed by this anode material. The rest of metal
546 content was no-significant. Theoretically, the rest of the sludge content (~45-50% (w/w))
547 could correspond to oxygen (O).

548 Considering the above data, a study of potential valorisation ways of the sludge is
549 being performed by another partner of the project. It is also considered the extraction of
550 the main metals (such as aluminium or iron) and the valorisation of the rest of the sludge.

551 **5. Hydrogen production and composition**

552 In this section, the composition of output gases from cathode compartment of EC
553 system is presented. The results include these ones where hydrogen was recovered from
554 the EC process when 0.66Ah/L was applied and the other ones where 2.65Ah/L was
555 applied.

556 Theoretically, around 12L/h and 48L/h of hydrogen (in standard conditions and
557 considering hydrogen as ideal gas) as a maximum flowrate should be produced in
558 cathode compartment under the above mentioned conditions (106 mA/cm^2, 40L/h, and
559 without pH modification of dairy effluent) at 0.66Ah/L and 2.65Ah/L, respectively. The
560 superior limit of the used flowmeter in Leitat facilities was around 22L/h. However, the

output gases quantification was higher than 22L/h due to the presence of other gases in the final composition.

The main output gases composition using aluminium or iron as anode is indicated in the following tables.

Table 11. Output gases composition average (n= 3) obtained from cathode compartment during the treatment of the dairy effluent under the following operational conditions: $106 mA/cm^2$, 0.66Ah/L, 40 L/h and without modification of pH.

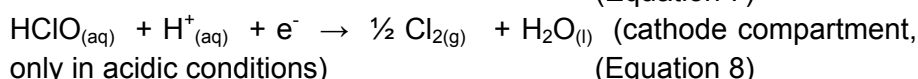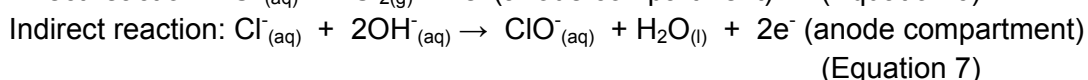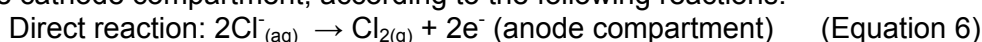| ALUMINIUM ANODE			IRON ANODE		
H_2 (% mole)	O_2 (% mole)	N_2(% mole)	H_2 (% mole)	O_2 (%)	N_2(%)
61.4	1.3	43.1	63.9	1.4	38.6

Table 12. Output gases composition average (n= 2) obtained from cathode compartment during the treatment of the dairy effluent under the following operational conditions: $106 mA/cm^2$, 2.65Ah/L, 40 L/h and without modification of pH.

ALUMINIUM ANODE			IRON ANODE		
H_2 (% mole)	O_2 (% mole)	N_2(% mole)	H_2 (% mole)	O_2 (%)	N_2(%)
82.1	1.8	20.5	67.9	1.3	32.0

Some potential impurities such as CO, CO_2 and H_2S were not detected (< 0.01% mole), whereas some other potential ones such as NH_3 or Cl_2 were not possible to detect with MicroGC. Nevertheless, it was not expected the generation of Cl_2 in basic conditions in the cathode compartment, according to the following reactions:

Direct reaction: $2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$ (anode compartment)   (Equation 6)

Indirect reaction: $Cl^-_{(aq)} + 2OH^-_{(aq)} \rightarrow ClO^-_{(aq)} + H_2O_{(l)} + 2e^-$ (anode compartment)
(Equation 7)

$HClO_{(aq)} + H^+_{(aq)} + e^- \rightarrow \frac{1}{2} Cl_{2(g)} + H_2O_{(l)}$ (cathode compartment, only in acidic conditions)   (Equation 8)

Ammonia could be obtained in the applied conditions. Thus the most suitable ways to determine this compound are being studied.

In general terms, no significant differences should be observed as a function of anode material since the most important influence for hydrogen generation is the cathode material (Pt/Ti) and to have relatively high current densities ($106 mA/cm^2$). Using both anode materials, the proportion of hydrogen generated and collected (by the conditions mentioned in the experimental part) was around 60%, at 0.66Ah/L. Around 40% of nitrogen was present in the output gases since it was used as carrier gas for removing the air from the pipes of the collecting gas setup. Oxygen, one of the potential impurities that could affect the yield of the fuel cell, represents around 1.5%.

When applied charge was higher (2.65Ah/L), purer hydrogen was achieved, especially when aluminium was used as anode. Probably this differences between anodes were due to differences in the procedures to collecting gas, thus purity of hydrogen collected using iron anode could be increased.

The injection of the output gases directly to a HORIZON FUEL CELLS (EDUSTACK PRO), without any previous purification system, is currently being studied in Leitat.

CONCLUSIONS

A smart electrocoagulation cell for dairy effluent treatment and simultaneous hydrogen recovery was designed, built and properly tested by Leitat Technological Centre.

Non-divided electrocoagulation system (where the output gases were not separated either recovered) was an efficient technology for turbidity reducing, reaching more than 97% removal when applying $50mA/cm^2$ and 0.32Ah/L (at 40L/h, without pH modification and using an aluminium anode). Under these conditions, 13% and 6% of COD and TOC, respectively, were removed. The electrical consumption was $4kWh/m^3$.

Divided electrocoagulation cell allowed the simultaneous dairy effluent treatment (anode compartment) and relatively pure hydrogen recovery (cathode compartment). In this case, 99% of turbidity was removed by the application of 0.66Ah/L and $106mA/cm^2$, working with an aluminium anode at 40 L/h and without pH modification. In this case, 28% and 9% of COD and TOC of the dairy effluent, respectively, were reduced. Electrical consumption was around $8kWh/m^3$.

An applied charge of 2.65Ah/L implied the increase of TOC and COD removal up to 26% and 33 %, respectively. 98% of total phosphorous content was also eliminated in this conditions Electrical consumption associated was $28.5kWh/m^3$.

In general terms, aluminium anode brought higher removal efficiencies and lower electrical consumption than iron anode. However, aluminium is more expensive and also it use to be passivated by an isolating layer (Al_2O_3) that must be removed before to start the electrocoagulation process.

The EC treatment of dairy effluent without pH modification implied higher efficiencies than when pH was acidified or basified.

Around $7.3Kg/m^3$ of dry Al-EC sludge were produced, being the total quantity of aluminium in the sludge of around 17%. Potential ways for valorising this type of waste are being studied within the REWAGEN project.

Hydrogen generated at cathode compartment was efficiently recovered. Around 60% of the output gases corresponded to hydrogen, whereas around 40% was associated to nitrogen used as carrier gas. Oxygen impurity represents 1.4%. CO, CO_2 neither H_2S were detected.

AKNOWLEDGMENT

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