

Jackson Ricardo Rodriguez Silva

**Electrocoagulation Removal
of Heavy Metals from
Industrial Wastewater in
Continuous Flow**

Electrocoagulation Removal of Heavy Metals from Industrial Wastewater in Continuous Flow

Von der Fakultät für Georessourcen und Materialtechnik
der Rheinisch-Westfälischen Technischen Hochschule Aachen

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Jackson Ricardo Rodriguez Silva

aus Bucaramanga, Kolumbien

Berichter: Univ.-Prof. Dr.-Ing. Dr.h.c. (UA) Karl Bernhard Friedrich
Universitätsprofessor Dr. rer. nat. Wolfgang Dott

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“Logic will get you from A to B. Imagination will take you everywhere.”

Albert Einstein

*To my mother Carmenza,
my love and soul mate Lika,
and my dear son Mathias;
my past, present and future.*

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List of Abbreviations

AD	Anodic Dosage
BAT	Best Available Techniques
BREF	Reference Documents on Best Available Techniques
COD	Chemical Oxygen Demand
CP	Chemical Precipitation
CWW	Common Waste Water and Waste Gas Treatment
DIR	Direct Iron Reduction
EC	Electrocoagulation
EDTA	Ethylenediaminetetraacetic Acid
EOR	Enhanced Oil Recovery
FGT	Flue-Gas Treatment
ICP	Inductively Coupled Plasma Atomic Emission Spectrometry
IED	Industrial Emissions Directive
IHU	Institut für Hygiene und Umweltmedizin, RWTH
IME	Institut für Metallurgische Prozesstechnik und Metallrecycling, RWTH
IPPC	Directive for Integrated Pollution Prevention Control
NFM	Non-Ferrous Metallurgy
NTU	Nephelometric Turbidity Unit
pH	Hydrogen Potential
PID	Proportional-Integrative-Derivative
PLC	Programmable Logic Controller
ppm	Parts Per Million
R&D	Research and Development
REDOX	Reduction-Oxidation Reaction
RWTH	Rheinisch-Westfälische Technische Hochschule Aachen
SA:V	Surface Area to Volume Ratio
TMT	Trimercaptotriazine, chemical reagent
TSS	Total Suspended Solids
UNESCO	United Nations Educational, Scientific and Cultural Organization
UPB	Universidad Pontificia Bolivariana, Colombia
WHT	World Heritage Technology
WI	Waste Incineration
WIPO	World Intellectual Property Organization
XRF	X-Ray Fluorescence Spectrometry

Summary

Electrocoagulation (EC) treatment of industrial and municipal wastewaters has existed for over a century without getting much attention, partly because of lack of know-how from specialists who have tried to implement this technology, often chemical and civil engineers, but also because of the misunderstood simplicity of its electrolytic reactions. This research work is intended to provide clarity from the perspective of a process metallurgist, while paying special attention to the design issues of related engineering fields playing a decisive role in the successful implementation of this key technology.

In doing so, aim of this work was to provide *techno-economical evidence* about the sustainability of EC technology for the efficient removal of heavy metals from industrial wastewater, with main focus on its online process control in continuous flow. Like this, five major issues were found to be fundamental to achieve the expected requirements:

1. selection of iron as sacrificial anode material, because of its simplified recycling path and agglomeration properties, allowing gas encapsulation and floc flotation;
2. conditioning of pH value in the neutral range for effluents to be cleaned, otherwise there is no chance for colloidal particles to build up and to agglomerate;
3. design of a concentric geometry for inline electrocoagulation reactor, due to the electromagnetic and hydrodynamic factors, avoiding mechanical energy losses;
4. use of a closed-loop process control based on online measurement of conductivity, enabling an adequate dosage of electrolytic iron from anode in real-time;
5. utilization of the synergic flotation effect produced by the simultaneous release of hydrogen gas, which still contains 50% of energy consumed by EC reactions.

Like this, experimental trials were conducted using real wastewaters from four different companies, a copper and a lead smelting plant, and two from waste incineration facilities handling *toxic waste cocktails* including antimony, arsenic, cadmium, chromium, copper, lead, mercury, nickel, thallium and zinc. Additional to these trials, evidence of successful results handling petrochemical and municipal effluents is as well provided.

Thanks to the implementation of the *online process control*, it was possible to unleash the hidden capabilities of electrocoagulation, to achieve unparalleled performance in heavy metals removal, with minimum consumption of sacrificial anodes and electricity. Even though prices of steel are twice or more those of lime, electrolytic dosages of 15 times less allow to achieve competitive prices for cubic meter of wastewater treated with unsurpassed safety against fluctuations in the quality of effluents to be cleaned. Evidence of lower costs to the ones reported in the literature is presented in detail.

Last but not least, sustainability issues regarding heavy metals removal, recycling and reuse of sludge recovered, and the potential for renewable power, have been integrated on a *zero-waste concept* towards the circular economy of water, waste and energy. Based on the successful results achieved with online EC treatment of wastewater, and the final remarks from the interdisciplinary research on the World Heritage Technology initiative, it is now expected that these scientific findings can help promote the proliferation of water technologies for the benefit of the environment and public health.

Zusammenfassung

Die Elektrokoagulation (EK) von industriellen und kommunalen Abwässern gibt es seit über einem Jahrhundert, ohne viel Aufmerksamkeit zu erlangen, zum Teil wegen des Mangels an Know-how der Spezialisten, oft Chemie- und Bauingenieuren, die versucht haben, diese Technologie zu implementieren, aber auch wegen der missverstandenen Einfachheit ihrer elektrolytischen Reaktionen. Ziel dieser Arbeit ist es, aus der Perspektive eines Prozessmetallurgen, Klarheit zu schaffen, wobei den Designfragen der verwandten Technikfelder eine entscheidende Rolle bei der erfolgreichen Umsetzung dieser Schlüsseltechnologie zukommt.

Die Absicht dieser Arbeit war es, *technisch-ökonomische Nachweise* über die Nachhaltigkeit der EK für die effiziente Schwermetallentfernung aus industriellem Abwasser mit Schwerpunkt auf Online-Prozesskontrolle im kontinuierlichen Durchfluss zu liefern. So wurden fünf wesentliche Themen als grundlegend erachtet, um die erwarteten Anforderungen zu erfüllen:

1. Auswahl von Eisen als Opferanodenmaterial aufgrund seines vereinfachten Recyclingweges und der Agglomerationseigenschaften, die eine Gaseinkapselung und die Flotation von Flocken ermöglichen;
2. Konditionierung des pH-Wertes im neutralen Bereich für zu reinigende Abwässer, sonst gibt es keine Möglichkeit, um kolloidale Partikel aufzubauen und zu agglomerieren;
3. Design einer konzentrischen Geometrie für den Inline-Elektrokoagulationsreaktor aufgrund elektromagnetischer und hydrodynamischer Faktoren, die mechanische Energieverluste vermeiden;
4. Einsatz einer Prozessregelung auf Basis von Online-Messung der Leitfähigkeit, die eine adäquate Dosierung von elektrolytischem Eisen aus der Anode in Echtzeit ermöglicht;
5. Nutzung des durch die gleichzeitige Freisetzung von Wasserstoffgas erzeugten synergistischen Flotationseffekts, der noch 50% der von EK-Reaktionen verbrauchten Energie enthält.

So wurden experimentelle Versuche mit echten Abwässern aus vier verschiedenen Unternehmen, einer Kupfer- und einer Bleischmelzerei, sowie zwei Abfallverbrennungsanlagen durchgeführt, die giftige Abfallcocktails mit Antimon, Arsen, Blei, Cadmium, Chrom, Kupfer, Quecksilber, Nickel, Thallium und Zink, erzeugen. Zusätzlich zu diesen Versuchen sind auch erfolgreiche Ergebnisse mit petrochemischen und kommunalen Abwässern erzielt worden.

Durch die Implementierung der Online-Prozesskontrolle konnten die verborgenen Möglichkeiten der Elektrokoagulation entfaltet werden, um eine unvergleichliche Höhe Leistung bei der Entfernung von Schwermetallen bei minimalem Verbrauch an Opferanoden und Strom zu erlangen. Obwohl Stahlpreise zwei- bis dreifach so hoch sind wie die des Kalks, erlauben die 15 mal weniger elektrolytische Dosierungen, wettbewerbsfähige Preise für Kubikmeter an behandelte Abwässer mit einer unübertroffenen Sicherheit gegen Schwankungen in der Qualität der zu reinigenden Abwässer zu gewinnen. Der Nachweis der geringeren Kosten im Vergleich zu den in der Literatur berichteten, wird detailliert dargestellt.

Nicht zuletzt sind Nachhaltigkeitsaspekte im Bezug auf die Entfernung von Schwermetallen, das Recycling und die Wiederverwendung von erzeugtem Schlamm und das Potenzial für erneuerbare Energien, in ein Null-Abfall-Konzept Richtung Kreislaufwirtschaft von Wasser, Abfall und Energie integriert worden. Auf der Grundlage dieser erfolgreichen Ergebnisse der Abwasserbehandlung durch EK-Online und der abschließenden Bemerkungen aus der interdisziplinären Forschung zur Initiative des Technologischen Welterbes, wird nun erwartet, dass diese wissenschaftlichen Erkenntnisse die Verbreitung von Wassertechnologien für Umwelt und öffentliche Gesundheit fördern werden.

Resumen

A pesar de conocerse desde hace más de un siglo, el tratamiento de aguas residuales industriales y municipales por electrocoagulación (EC) no ha tenido gran acogida, en parte por falta de conocimiento de quienes han implementado esta tecnología, usualmente ingenieros químicos y civiles, pero también debido a una mala interpretación de sus procesos electrolíticos. Este trabajo de investigación pretende brindar claridad desde una perspectiva metalúrgica, sin descuidar los conceptos de diseño de las ingenierías relacionadas que impactan el desarrollo exitoso de esta tecnología clave.

De esta forma, el objetivo de este trabajo fue proveer evidencia técnica y económica de la sostenibilidad de la tecnología EC para la remoción eficiente de metales pesados en aguas industriales, con énfasis en el control en línea bajo flujo continuo. Con esto, 5 aspectos fundamentales fueron identificados para lograr los resultados esperados:

1. uso del hierro como ánodo sacrificial, por la simplicidad de su reciclaje y sus propiedades de aglomeración, que facilitan la flotación por encapsulación de gas;
2. acondicionamiento previo de los efluentes al pH neutro, de lo contrario no hay forma de promover la formación y aglomeración de las partículas coloidales;
3. diseño del reactor EC con geometría concéntrica, que optimiza las condiciones de flujo electromagnético e hidrodinámico, reduciendo las pérdidas mecánicas;
4. implementación de un control en lazo-cerrado basado en la conductividad en línea, el cual permite la dosificación exacta del hierro electrolítico en tiempo real;
5. uso del efecto de flotación ejercido por la producción simultánea de gas hidrógeno, el cual aún contiene el 50% de la energía consumida por las reacciones EC.

Asimismo, las pruebas experimentales se llevaron a cabo con aguas residuales de cuatro compañías, dos fundidoras de cobre y plomo, y dos incineradoras de basuras que generan *cócteles tóxicos* con contenidos de antimonio, arsénico, cadmio, cromo, cobre, mercurio, níquel, plomo, talio y zinc. Adicional a estas pruebas, se presenta evidencia de resultados exitosos con aguas residuales municipales y petroquímicas.

Gracias a la implementación del *control en línea*, fue posible revelar las capacidades ocultas de la electrocoagulación, para alcanzar resultados sin precedentes en la remoción de metales pesados, con mínimo consumo de ánodo sacrificial y de energía. Aunque el precio del acero con respecto a la cal es del doble o más, dosificaciones 15 veces inferiores permiten lograr precios competitivos por metro cúbico tratado, con seguridad insuperable contra fluctuaciones en la calidad del efluente residual a tratar. Se presenta evidencia detallada de costos más bajos a los reportados en la literatura.

Por último pero no menos importante, los temas de sostenibilidad en relación a la remoción de metales pesados, el reciclaje y reutilización de lodos recuperados, y el potencial de energía renovable, han sido integrados en un concepto de *residuo-cero* hacia una economía circular en torno al agua, los residuos y la energía. Con base en los resultados exitosos del tratamiento del agua por EC en línea y las conclusiones de la investigación interdisciplinaria sobre la iniciativa del Patrimonio Tecnológico de la Humanidad, se espera que estos hallazgos científicos ayuden a promover la masificación de tecnologías del agua para el beneficio del medio ambiente y la salud pública.

Extended Abstract

Electrocoagulation (EC) treatment of industrial and municipal wastewaters has existed for over a century without getting much attention, partly because of lack of know-how from specialists who have tried to implement this technology, often chemical and civil engineers, but also because of the misunderstood simplicity of its electrolytic reactions. This research work is intended to provide clarity from the perspective of a process metallurgist, while paying special attention to the design issues of related engineering fields playing a decisive role in the successful implementation of this key technology.

Background and Motivation

According to international efforts coordinated by the United Nations through its World Water Assessment Programme, it has been concluded that the planet Earth is running out of freshwater resources that many living species, including humans, depend upon. Figure I shows official figures on total water resources that the United Nations have estimated through its World Water Development Report [1]. Based on stress and pollution figures of water resources on Figure II, it is likely to realize why water-related diseases are responsible for 80% of all illnesses and deaths in the developing world [3].

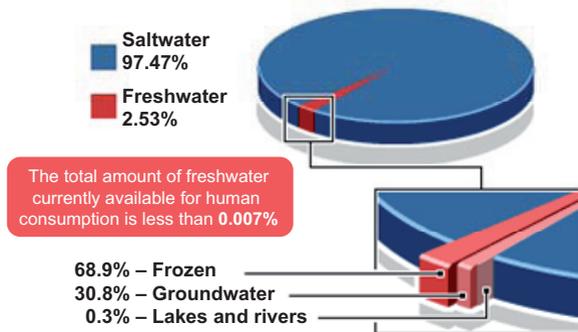


Figure I: Estimated total water resources according to the United Nations [1]

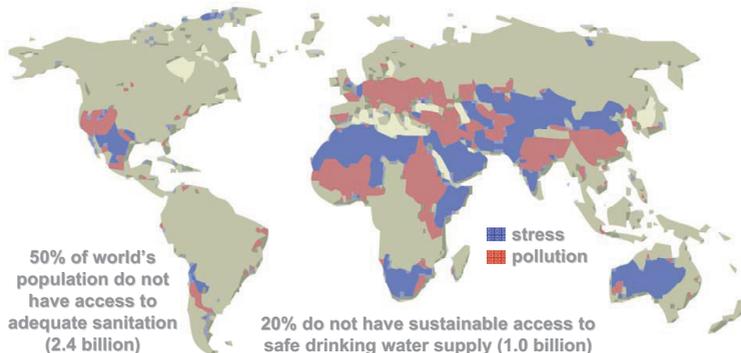


Figure II: Stress and pollution of freshwater resources around the world [1]

Environmental regulations on heavy metal removal for industrial wastewater

Socioeconomic development always required a degree of industrialisation, for which the processing of raw materials (e.g. heavy metals) brought blessings to modern life, but also curse and degradation to both public health and the environment. For the purpose of this research work and based on the range and scope of trials performed with EC technology at IME, Figure III introduces the related environmental regulations, here defined as BREF, on heavy metal removal for industrial wastewater that have been taken into account to define and to assess all competing practices for this study.

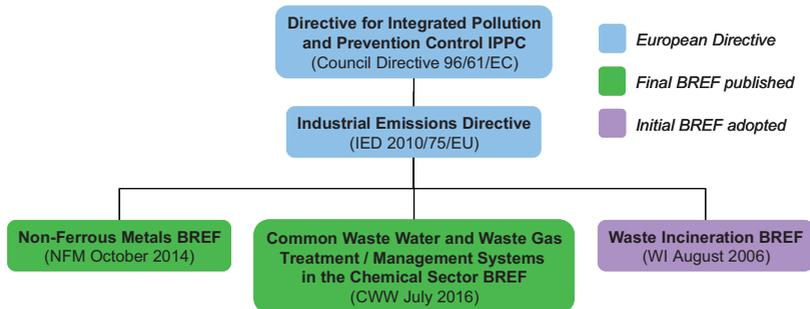


Figure III: Related environmental regulation on heavy metal removal for wastewater

Since all other BREF are based on the CWW practices as the underlying and most comprehensive document to be referred to when dealing with wastewater emissions, including Non-Ferrous Metals (NFM) and Waste Incineration (WI), Figure IV describes the range of wastewater treatment techniques in relation to type of contaminants, in the way that it has been defined and established as optimum in current BAT models.

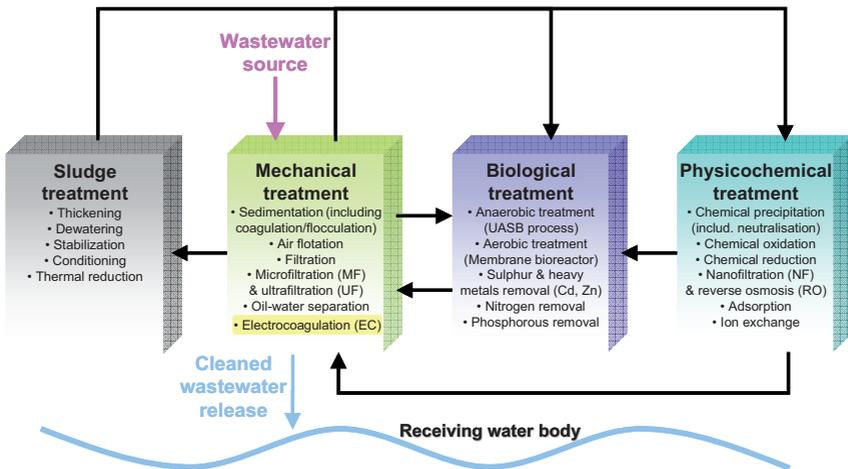


Figure IV: Wastewater treatment techniques in relation to type of contaminants [9]

In this regard, it was remarkable the lack of information about the electrocoagulation technology at the very beginning of this research. It was only until 2008 that the European Commission became aware of this technique and then required the experts to “*indicate whether electrocoagulation (not mentioned in the CWW BREF) is used or could be used in the chemical industry sector and include information if relevant.*” [10]

Nowadays electrocoagulation technology is now listed in the current version of CWW BREF from July 2016, under the end-of-pipe techniques section, as an effective solution able to separate suspended solids and insoluble liquids. Unfortunately, based on the two-page superficial explanation of its functional principle, this still indicates a major lack of understanding about its process dynamics in terms of transport phenomena and the physicochemical properties governing the reactor design for electrochemical processes. In order to provide clearness about the range and scope in the application of BAT covered by the CWW BREF, Table I introduces the major wastewater contaminants as well as their respective treatment techniques.

Table I: Wastewater contaminants and their respective treatment techniques [9]

Technique	Heavy metals	PO ₄ -P	BOD COD TOC	NH ₄ -N	TSS	Oil	Phenol
Sedimentation			○		●		
Coagulation/flocculation	●		○		●	○	
Flotation			○		●	●	
Filtration			○		●		
Microfiltration (MF) / Ultrafiltration (UF)			○		○	●	
Oil-water separation			●		●	●	
Electrocoagulation (EC)	●	●	●	○	●	●	●
Anaerobic treatment			●				
Aerobic treatment		●	●	●			●
Sulphur & heavy metals removal (Cd, Zn)	○						
Nitrogen removal				●			
Phosphorous removal		●					
Chemical precipitation (includ. neutralization)	●	●			○		
Chemical oxidation			●				●
Chemical reduction	●						
Nanofiltration (NF) / Reverse osmosis (RO)	○	●	●	●			●
Adsorption	●		●	●		●	●
Ion exchange	●		○				

● primary application

○ secondary application

Based on this information it is safe to conclude that EC describes the broadest spectrum of pollutants removal. It ranges from suspended solids (TSS) and insoluble liquids such as oils traces and undissolved organic compounds, up to dissolved heavy metals and organic content such as ammonia, phosphate and phenolic compounds. Reason for EC success is based on its robustness and suitability to deliver unparallel results using REDOX reactions, and main goal of this research work was to avoid or where it was not practicable, to reduce current dependency on chemical reagents.

Drawbacks of BAT for heavy metals removal in wastewater treatment

According to Table I, the existing European regulations acknowledged mainly six BAT as effective for the removal of heavy metals in industrial wastewater, listed as follows:

- coagulation / flocculation
- electrocoagulation (EC)
- chemical precipitation (including neutralization)
- chemical reduction
- adsorption
- ion exchange

Since the experimental benchmarking of this research work took place between electrocoagulation versus conventional chemical precipitation, this section shall shortly discuss each one of the aforementioned technologies, in order to mainly focus on the functionalities and drawbacks behind coagulation, flocculation and precipitation as the most widespread solutions for heavy metal removal in industrial wastewater treatment.

Adsorption refers to the transfer of soluble substances (solutes) from the wastewater phase to the surface of a solid, highly porous particle (the adsorbent) [9]. Since the adsorbent has a limited capacity to reach saturation, when this capacity is exhausted, spent materials must be either regenerated or incinerated, and replaced by fresh ones [9]. Since the adsorbent-active surface is very susceptible to clogging and fouling, an upstream filtration step is often required to retain any insoluble content. Main adsorbents for wastewater treatment are activated carbon, lignite, resins and zeolites [9].

By means of ion exchangers, undesired and/or hazardous ionic constituents can be removed from the wastewater while being replaced by more acceptable ions from an ion exchange resin, in order to be temporarily retained and then released afterwards into a regeneration or backwashing liquid [9]. According to CWW BREF, ion exchange is feasible as an end-of-the-pipe technique, but its greatest value lies in its recovery potential, as integrated operation to recover process chemicals and rinse waters, which can be reused in waste gas scrubbers [9]. Besides the need for process automation, further limitations are its sensitiveness to corrosive agents; and to interfering compounds, which can cause irreversible adsorption to resins [9].

Chemical reduction is defined as the conversion of pollutants by chemical reducing agents into similar but less harmful compounds [9]. Bearing in mind the potentially hazardous nature of typical reducing agents such as sulfur dioxide SO_2 , sodium sulfide Na_2S or ferrous sulfate FeSO_4 , among others, storage facilities for these chemicals must be adequate and dosage to influents shall take place under proper pH and concentration conditions, in order to transform waste species into byproducts that can be treated more easily in downstream treatment facilities (e.g. chemical precipitation) [9].

According to the description provided in the CWW BREF, coagulation and flocculation occur in successive steps which are intended to overcome the forces stabilising the suspended particles, thus allowing particle collision and growth of the floc [9]. In a first step, coagulation aims at destabilizing the electrostatic charge of particles by neutralizing their electrical surface charge, performed by addition of coagulants with charges opposite to those of the suspended solids in the wastewater [9]. In a second step, flocculation aims at increasing the particle size, where collisions of microfloc particles cause them to bond in order to produce larger flocs [9].

On the other side, precipitation as defined in the CWW BREF is a chemical reaction intended to build particulates (i.e. stable precipitates) that can be separated from the water portion by subsequent processes (e.g. filtration, flotation, sedimentation, EC). Like this, heavy metals build into colloidal precipitates, which then must be removed as close as possible to the source in order to avoid dilution [9]. Among the most common chemical reagents used in chemical precipitation (CP) there is lime milk, prepared out of calcium oxide CaO or calcium hydroxide $\text{Ca}(\text{OH})_2$, sodium hydroxide NaOH , calcium carbonate CaCO_3 (useful to precipitate sulphate or fluoride), sodium carbonate Na_2CO_3 and sodium sulfide Na_2S . CP delivers high yields but the achievable final concentration highly depends on the compound's solubility product [9]. Therefore, it is difficult to determine the final concentration for a combination of pollutants, due to the interaction of substances with each other (competing reactions) [9].

Amphoteric species (which can react as an acid or base), such as metallic hydroxides being precipitated out of the wastewater, and even water itself as a self-ionizable compound, are extremely dependent on pH value, due to the isoelectric nature governing their stability as newly-formed compounds. In this case, performance of flocculation, coagulation and thus precipitation, may be maximized at the isoelectric point (or zero charge), since minimum solubility is frequently exhibited within that range [16].

Taking into account that industrial wastewater matrix often describes a "toxic cocktail" of several metal species (particularly true in effluents from incineration processes), adequate removal of all hazardous materials using conventional technologies for heavy metal removal is extremely challenging, as it will be seen in the experimental part of this research work. To make this point clear, Figure V shows the residual metal content as a function of pH for a precipitation test on the same wastewater using three different reagents, calcium (lime), sodium hydroxide (soda) and sodium carbonate.

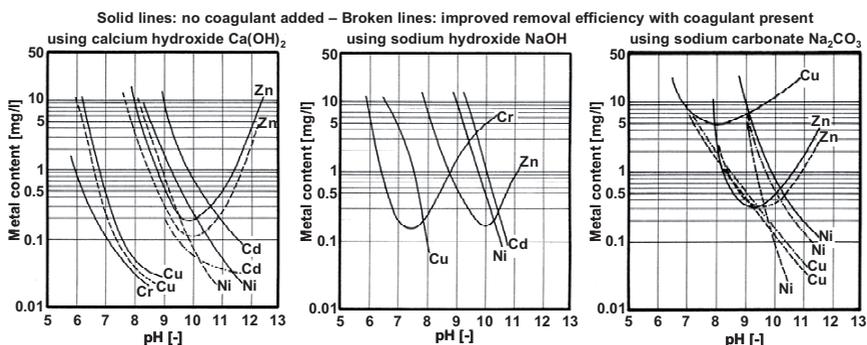


Figure V: Effect of pH on precipitation of metals for three different reagents [16]

As it can be seen from the curves, upon increasing the pH above a certain critical value using NaOH , chromium and zinc hydroxides tend to redissolve; likewise is the negative effect of carbonate ions very tangible when compared to Na_2CO_3 . In the case of lime, only zinc hydroxide describes the same behaviour, for which it is in most cases the superior reagent for achieving the highest removal yield. Therefore, following the conclusions from CWW BREF, in a mixture of heavy metals, the pH ideally suited for efficient removal of one metal may be unfavourable for efficient removal of the others [9]. This is the main strength of EC technology over CP, as it will be seen experimentally.

State of the art in electrocoagulation technology

At the very beginning of this research work in early 2006, it was remarkable to see how little information about electrocoagulation was available back then, and now 10 years later, there are thousands of scientific articles, and almost all of them pointing out the substantial benefits this technique would bring to the environment and public health. Yet, it is remarkable to find out that nothing has changed in regard to the lack of industrial applications, despite of hundreds of patent claims and a handful of small companies offering wastewater treatment facilities based on this emerging technology.

After one decade of experience on this field, the most likely conclusion that comes to mind for this outcome is that many enthusiastic scientists and engineers dealing with environmental related issues (civil and chemical engineers for the most part), have failed at understanding the thermodynamics of electrochemical reactions, and how they impact transport phenomena in colloidal systems, as well as the reactor design. Once these concepts become clear, it is then possible to design electrocoagulation reactors that perform efficiently with retention times of a couple of seconds instead of hours, as found in many research papers reviewed in this work [26]-[47].

First of all, electrocoagulation is not a modified electrolysis; they are related to some extent in sort of an electrochemical sense, as they both rely on electricity to perform, but from their purpose and operation, they are completely different technologies. It is appropriate to make a strong emphasis at this point; because there is no way oxygen gas can be produced when using sacrificial anodes, as in the case of the electrocoagulation, which is the completely opposite purpose of the electrolysis. An example of this misconception was found in the Best Available Technologies Reference Documents CWW BREF from the European Commission, when describing electroflotation effect as a result of using electrolysis to split H_2O into hydrogen H_2 and oxygen O_2 [9].

In addition, right there is the second misconception about the electrocoagulation and electroflotation being referred as two different technologies; they are the same one. In fact and this will be demonstrated in the experimental part, flotation effect occurs at a very specific pH value known as the *"isoelectric point"* or *"point of zero charge"*, which will be further explained in detail, enabling an outstanding coagulation effect using the metallic hydroxides released from the anode. These colloidal particles encapsulate the hydrogen gas evolving from the cathode, causing sludge to be pushed upwards, as H_2 reaches for its way out into the atmosphere. This flotation effect lasts only until the hydrogen gas permeates through the flotation cake; that is why particle separation must take place in a flotation column right after EC. Figure VI reflects these concepts properly, as the electrocoagulation process needs a pH-conditioning step in order to perform within the isoelectric conditions required to achieve the flotation effect, which care for the best particle separation with no additional filtration steps needed.

As already described in Figure V, pH values do not need to be raised up to very alkaline ranges ($pH > 10$) to effectively remove heavy metals such as cadmium, nickel or zinc. The electrocoagulation approach is a more sustainable one, since its only requirement towards the wastewater to be cleaned, is that it must be delivered in the neutral range ($6.5 > pH > 8.5$). Due to its electrolytic nature, effluent cleaned with this process never changed its neutral pH condition, it is not electrochemically possible because for each pair of OH^- ions brought into solution from the sacrificial anode, a stoichiometric amount of hydrogen gas H_2 would be released at the cathode surface.

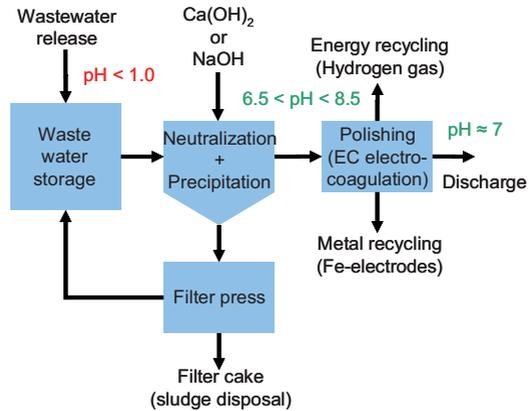


Figure VI: Simplified scheme for EC treatment of wastewater with pH-conditioning

As for the coagulation mechanism (chemically or electrochemically based), net surface charge of particles to be agglomerated plays a decisive role for the adsorption properties of the bulk to take place. Surface charge influences the distribution of nearby ions in the liquid, while counter-ions are attracted towards the surface of colloidal particles, leading to the formation of the so-called “*electrical double layer*” [52]. Figure VII describes this and how the portion of the electrical double layer that confers stability to charged particles, known as the “*zeta potential*”, hinders the agglomeration and coalescence behaviour on which coagulation of particles relies for their effective removal from the bulk solution.

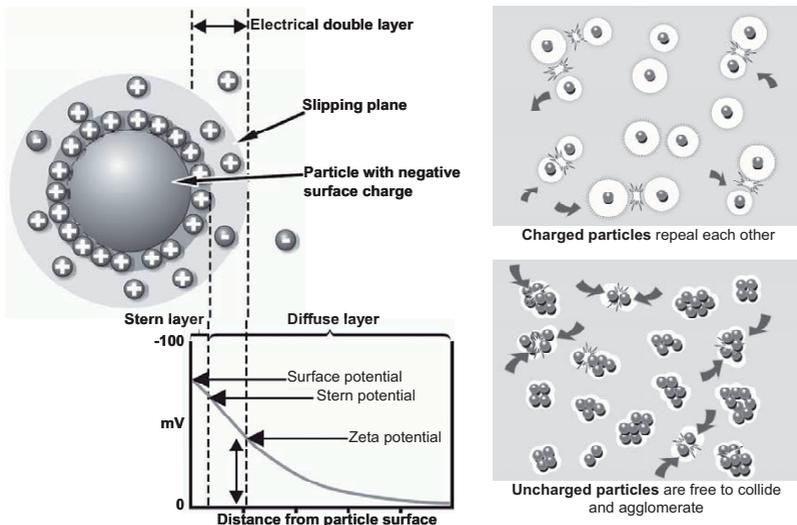


Figure VII: Zeta potential description and its effect on particle agglomeration [54][55]

Development of continuous electrocoagulation with online process control

This research work on the development of electrocoagulation technology has been the result of interdisciplinary efforts to provide a sustainable solution to current drawbacks of wastewater treatment. Figure VIII introduces the experimental methodology implemented for the development of EC treatment in continuous flow. Like this, three main aspects received special attention during this research: (1) the **isoelectric conditions** enabling heavy metals removal, (2) **reactor design**, and last but not least, (3) **online process control** required to unleash the full potential of this wastewater technology.

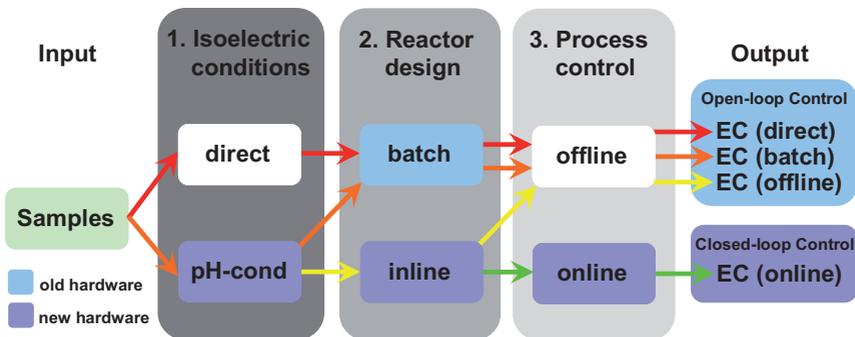


Figure VIII: Experimental methodology for the development of EC in continuous flow

Each aspect involved the design, construction and integration of new hardware, which led to several different configurations that need some introduction, for the purpose of facilitating the navigation through the experimental part of this research work. Figure IX summarizes all investigated cases during the development of the electrocoagulation treatment for the heavy metals removal in industrial wastewater, using a lab scale set-up with batch and inline reactors. Industrial wastewaters were delivered by four different companies, two of them from the non-ferrous metals industry, from a copper and a lead smelting plant; and two of them by service providers operating waste incineration facilities at two different chemical parks, all located in Germany.

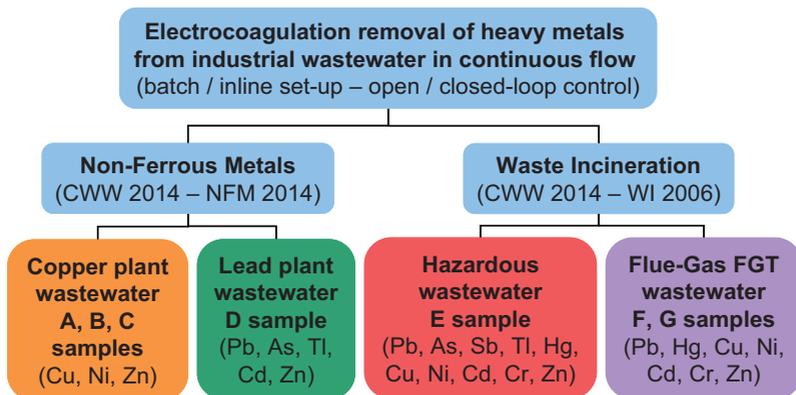


Figure IX: Investigated samples during the development of EC in continuous flow

For the first part based on open-loop process control, experiments were carried out using prototype shown in Figure X, without any automation equipment, on a Plexiglas reactor with a total capacity of 10 liters, and powered by a 640W power supply (16V/40A) from Elektro-Automatik. Data loggers from Protek were connected via serial port to a laptop computer, to acquire all energy data about the power consumption of the electrocoagulation process, as well as electrical conductivity and pH value.

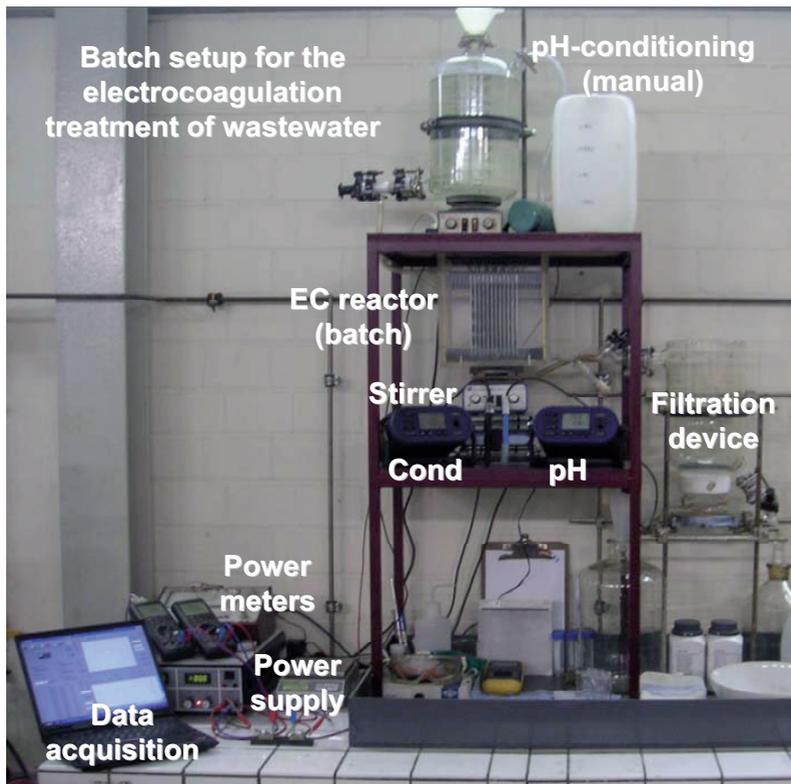


Figure X: Old batch set-up for the electrocoagulation treatment of wastewater [58]

Since coagulation effect is only possible at pH neutral range, experiments performed without previous neutralization proved to be inadequate. Taking this technical constraint into account, there was a need for the automation of pH-conditioning step in the process requirements of EC treatment in continuous flow. In doing so, Figure XI introduces new inline setup developed for the EC treatment of wastewater used for all experiments in continuous flow, based on the closed-loop process control approach. Process starts in the stirred tank reactor T3, where addition of lime milk is controlled by a pH sensor connected to a programmable logic controller PLC (Siemens® S7). Then, neutralized effluents settle in the sedimentation tank T4, and from there enter the inline EC reactor, where the rest of heavy metal removal takes place, controlled by an inductive conductivity sensor, connected as well to PLC.

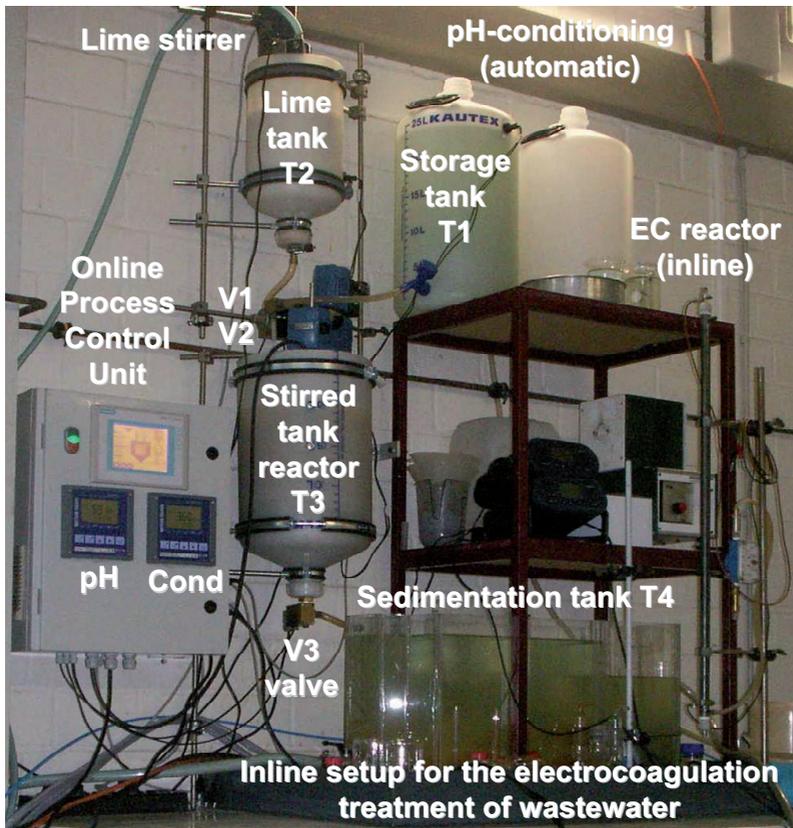


Figure XI: New inline set-up for continuous electrocoagulation with pH-conditioning

Next on the list of improvements to the hardware for EC treatment of wastewater in continuous flow, was the development of a new inline reactor. Figure XII shows the old EC batch reactor made of Plexiglas with capacity for 10 liters for a current density of 29 A/m^2 , using as electrode materials 12 square plates of 2 millimeter thickness and dimensions $20 \times 20 \text{ cm}$, made of regular steel; and 12 ones made of aluminium.

In the end, the best configuration developed for the new inline reactor is presented in Figure XIII, by means of a concentric arrange of electrodes using regular steel pipes in the shown dimensions. This allowed to operate under the same conditions from old batch reactor but in continuous flow with 20 L/h , using the same current density of 29 A/m^2 , but reducing the power consumption drastically, for instance in EC of sample F from 46.7 Wh (batch) to 3.2 Wh (offline), while improving overall metal removal yields.

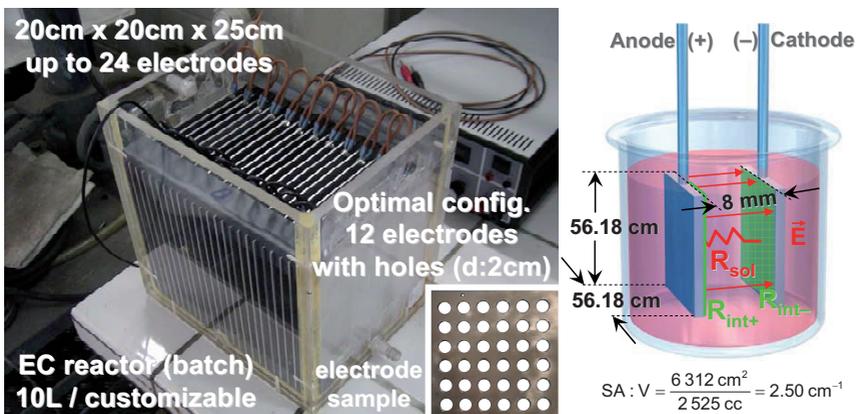


Figure XII: Old EC reactor (batch) and equivalent EC cell with SA:V ratio

The scientific reason behind such a significant improvement in the power consumption of the inline reactor is related to several facts, among of which it is worth mentioning: (1) higher SA:V ratio, (2) better circulation and mixing properties with iron hydroxides produced electrolytically (in situ) by a sacrificial anode, (3) no mechanical losses from stirring of the solution, and last but not least, (4) the concentric geometry of electrodes enables the best distribution of electromagnetic field, effecting kind of additional electrodynamic pressure on the surface of central bar, to promote its efficient dissolution.

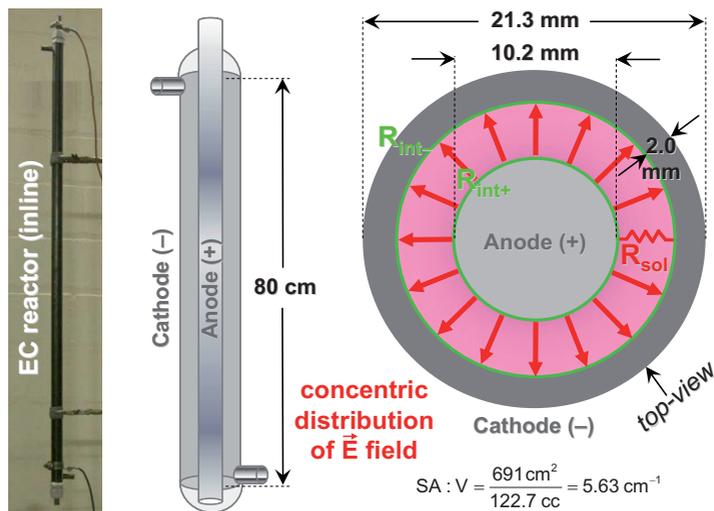


Figure XIII: New EC reactor (inline) and equivalent EC cell with SA:V ratio

In order to operate the electrocoagulation process within the isoelectric range, it was required to implement a closed-loop process control with online monitoring of the two main variables, pH of the solution before entering the EC reactor, and the electrical conductivity of the solution leaving the reactor after treatment. Figure XIV and XV describes the schematic and real integration of the developed Online Process Control Unit with the two EC process variables, pH value and electric conductivity, based on Siemens® S7 PLC, which was successfully implemented during research work at IME.

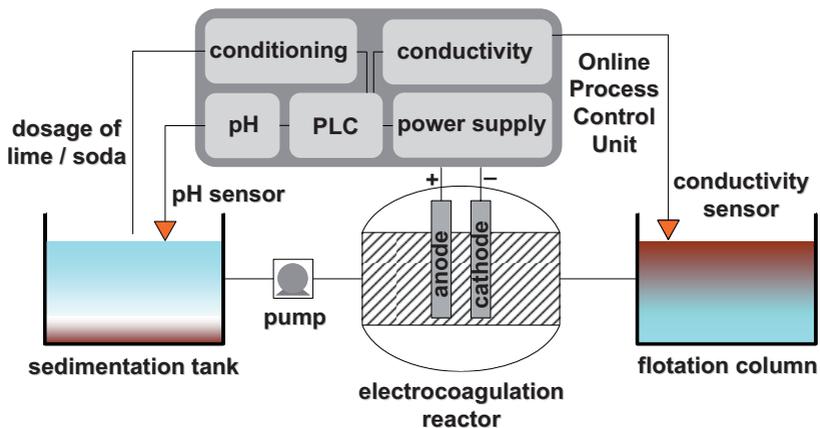


Figure XIV: Integration of Online Process Control Unit with EC process variables

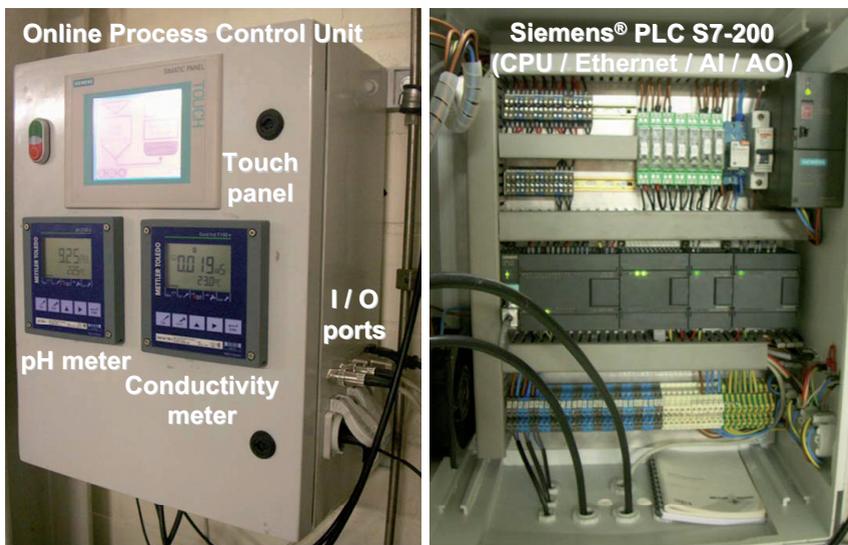


Figure XV: Online Process Control Unit developed for EC treatment in continuous flow

Besides regular automation tasks like checking over tank levels and turning pumps or valves on and off, successful operation of a continuous electrocoagulation was in fact a bit more complex and required the expertise from the control theory field. In chemical reactions, process equipment is considerably overdamped, and despite the low inertia given its electrochemical nature, EC reactions are not the exception to this rule.

Like this, using established control techniques like the conventional PID (Proportional-Integrative-Derivative) controller, it was possible to optimize the system response in a way that inertia of the electrochemical and colloidal reactions were taken into account, enabling lower power consumptions, while saving energy and electrode materials. To achieve this, heuristic estimations like the Ziegler–Nichols tuning method, helped find the optimum coefficients k_p (proportional gain), τ_i (integrative time), τ_d (derivative time), to adapt the system response to the transfer function of the EC inline reactor.

To describe the implementation of Ziegler-Nichols method, it was required to perform an open-loop run of EC treatment using G sample (offline). This allowed to generate the process reaction curve of inline reactor (0.0691 m²), to estimate the transfer function of EC system. Figure XVI shows the typical conductivity response that is obtained for an uncontrolled EC treatment (open-loop), with current step input (ΔCO) of 50%, equals to 2 Amperes (29 A/m²) from the maximum current available of 4 A (58 A/m²).

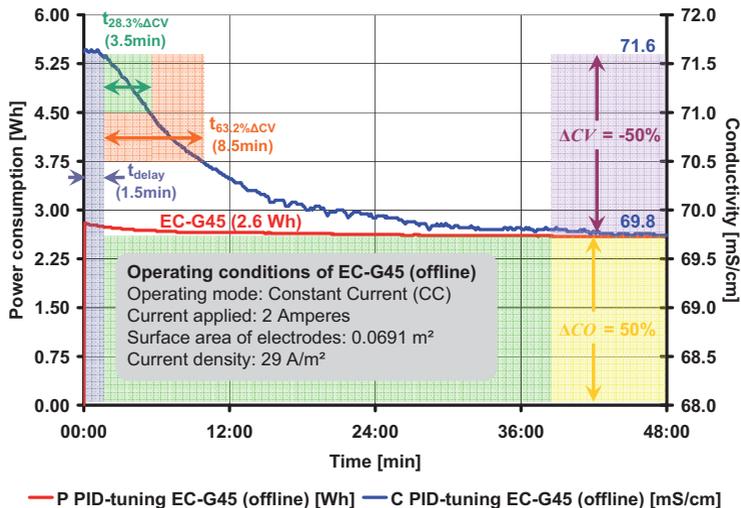


Figure XVI: Process reaction curve used for PID-tuning with Ziegler-Nichols method based on EC-G45 treatment of sample G with the inline reactor (offline)

To calculate time constant τ , and dead time t_0 , two time values must be extracted from the process reaction curve, for which conductivity dropped 28.3% (71 mS/cm after 5 min) and 63.2% (70.5 mS/cm after 10 min) of minimum value reached for this open-loop run. Due to the inertia, delay time or time of the first change of conductivity was 1.5 min, then $t_{28.3\% \Delta CV}$ was equal to 3.5 min and $t_{63.2\% \Delta CV}$ was equal to 8.5 minutes.

Like this, time constant τ is equal to:

$$\tau = 1.5(t_{63.2\% \Delta CV} - t_{28.3\% \Delta CV}) = 1.5(8.5 - 3.5) = 7.5 \tag{a}$$

and dead time t_0 is equal to:

$$t_0 = t_{63.2\% \Delta CV} - \tau = 8.5 - 7.5 = 1 \tag{b}$$

As for the process gain K :

$$K = \frac{\Delta CV}{\Delta CO} = \frac{69.8 - 71.6}{71.6 - 68.0} \times 100\% = \frac{-50\%}{50\%} = -1 \tag{c}$$

The transfer function of the EC system can be expressed as:

$$\frac{O(s)}{I(s)} = \frac{Ke^{-t_0s}}{\tau s + 1} = \frac{-e^{-s}}{7.5s + 1} \tag{d}$$

Finally, the coefficients to be programmed in the PID controller, proportional gain k_p , integrative time τ_i , and derivative time τ_d , can be estimated using these formulas:

$$k_p = \frac{1.2}{K} \left(\frac{t_0}{\tau} \right)^{-1} = \frac{1.2}{-1} \left(\frac{1}{7.5} \right)^{-1} = -9 \tag{e}$$

$$\tau_i = 2t_0 = 2 \tag{f}$$

$$\tau_d = \frac{t_0}{2} = 0.5 \tag{g}$$

These approximations are based on the response of G sample to EC treatment with inline reactor. With a new sample these coefficients might need to be adjusted again. Figure XVII shows the schematic representation of the EC system including the transfer function of inline reactor for EC treatment of G sample using closed-loop control. More information about the heuristic method used for PID tuning can be found in [72].

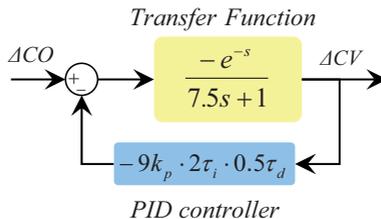


Figure XVII: Transfer function and PID coefficients defining the optimized closed-loop system response of the inline reactor for the EC treatment of G sample

All these mathematical abstractions become useful when operation of EC process must be performed in continuous flow within the “isoelectric point”, to achieve complete separation of metallic hydroxides through concomitant flotation. Opposite to chemical precipitation which predominant effect is the pH solubility, EC performance depends on the conditions nearby the “isoelectric point” or “point of zero charge”, given by the zeta potential. This enables the flotation effect promoted by the concomitant release of hydrogen gas. Figure XVIII describes this effect, as it is evident that the lowest turbidity value of 1 NTU (Nephelometric Turbidity Unit), shall always occur within the isoelectric range (0 mV), in this particular case with the anodic dosage of 160 mg/l Fe (EC-G3a), equivalent to a current density of 43.5 A/m².

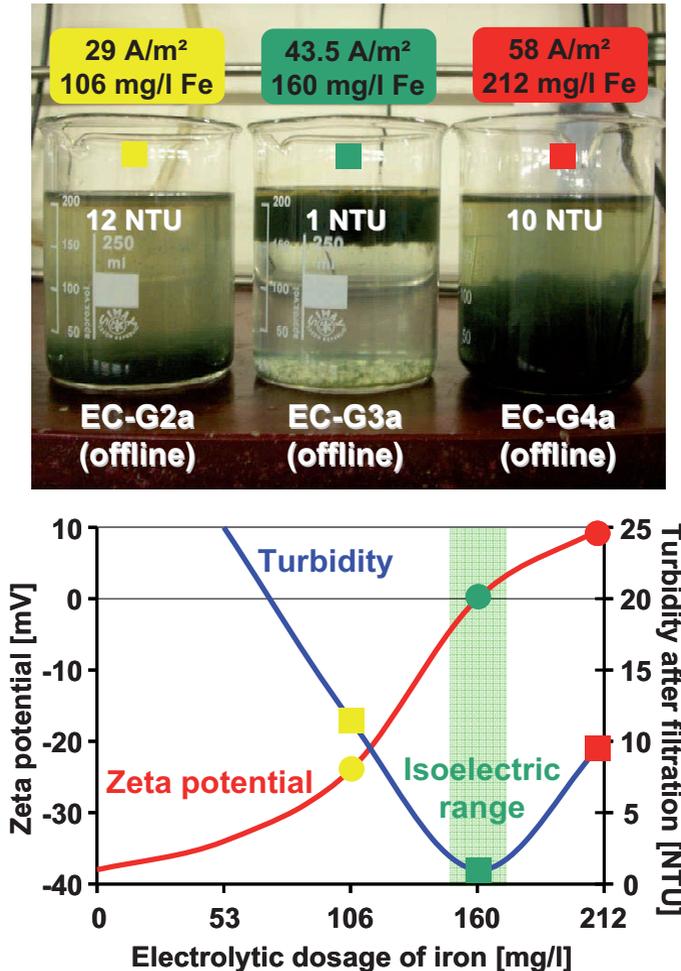


Figure XVIII: Effect of electrolytic dosage on zeta potential and turbidity during EC-G

Proof of principle of electrocoagulation technology in batch mode

A copper plant provided a wastewater sample (A) with high content of heavy metals, mainly copper, nickel and zinc. Table II summarizes the heavy metals content before and after treatment by chemical precipitation with lime (CP-Ali), and by EC treatment without pH-conditioning (direct), using the batch set-up, with regular steel (EC-Afe) and aluminium electrodes (EC-Aal), measured by the analytical lab. The expected discharge limit from the environmental authority is indicated for orientation purposes.

Table II: Heavy metals content in sample A before and after treatment by CP / EC

Element	Unit	A (before)	CP-Ali (lime)	EC-Afe (direct)	EC-Aal (direct)	Discharge limit
pH [-]	–	1.9	6.5	3.2	4.2	6.5 - 8.5
Conductivity	mS/cm	13.4	10.2	8.7	7.7	–
Free acid H ₂ SO ₄	mg/l	2 940	–	2 450	1 690	–
Copper (Cu)	mg/l	320	< 0.1	0.12	8.62	0.5
Nickel (Ni)	mg/l	56	< 0.1	20.8	27.0	0.5
Zinc (Zn)	mg/l	730	0.1	45.6	326.7	1
Aluminium (Al)	mg/l	0.7	< 0.5	0.03	240.7	2
Iron (Fe)	mg/l	10.4	< 0.1	1 312	7.48	2

Sample A presented a high level of contamination with acidic pH and high conductivity values, indicating a considerable amount of heavy metals dissolved, mainly zinc (730 mg/l) and copper (320 mg/l). After chemical precipitation with lime, pH value increased up to the alkaline range (pH 10.0), enabling reduction of some concentrations values below the detection range (< 0.1 mg/l). Then, additional neutralization was required to prepare the effluents for final discharge within neutral range (pH 6.5). Figure XIX summarizes all heavy metal removal yields after 1 hour of EC (direct) of sample A with steel (EC-Afe) and aluminium electrodes (EC-Aal), without pH-conditioning.

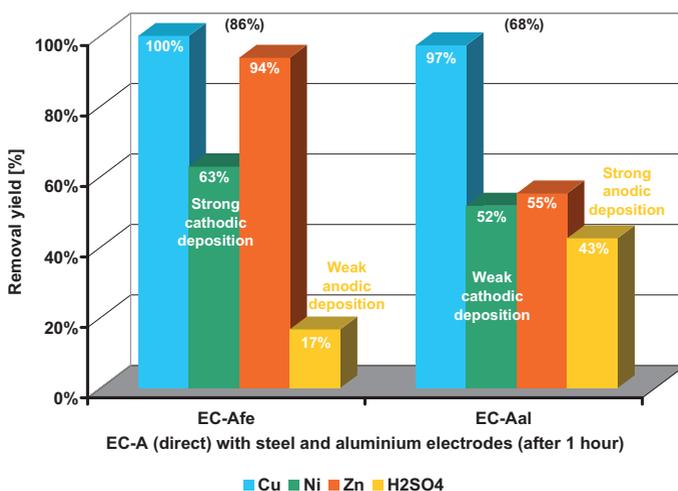


Figure XIX: Summary of metal removal yields after 1h EC (direct) of sample A using steel (EC-Afe) and aluminium electrodes (EC-Aal) without pH-conditioning

Steel EC-Afe were more effective in overall metals removal (86%), than aluminium electrodes EC-Aal (68%), despite lower pH and higher conductivity. This suggested passivation of Al-electrodes, due to deposition of mineral sulfates hindering electrons exchange, while contributing to higher power consumption and thus, less efficiency. Figure XX and XXI confirmed the passivation effect and higher sulfur content in sludge.

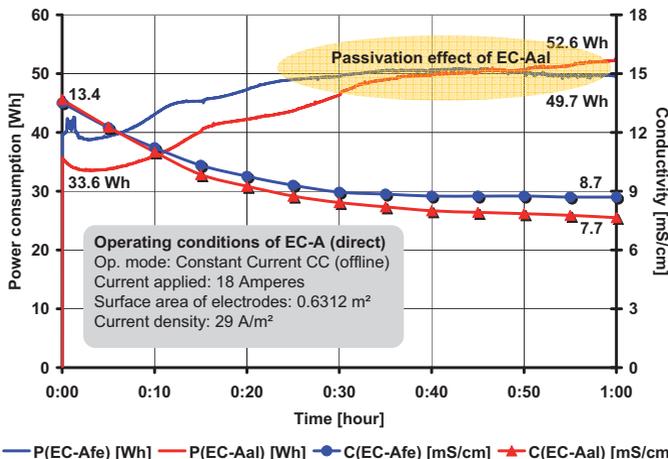


Figure XX: Effect of conductivity of sample A on the power consumption during EC (direct) with regular steel (EC-Afe) and aluminium electrodes (EC-Aal)

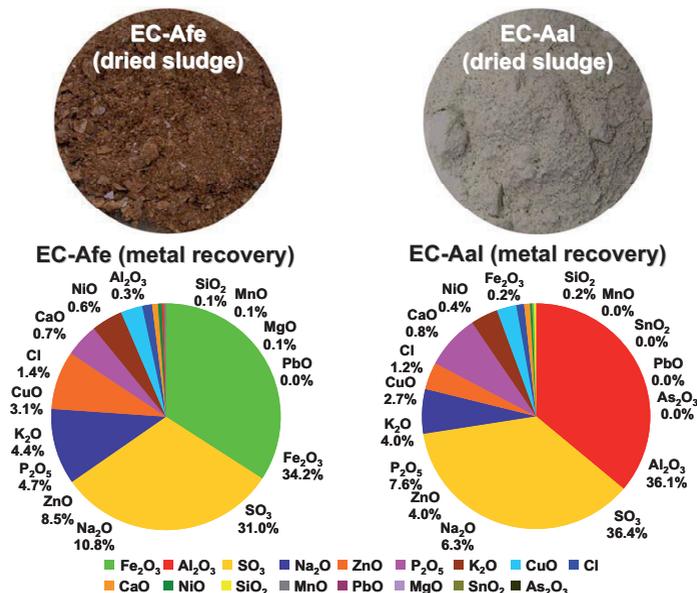


Figure XXI: XRF analysis and physical appearance of dried sludge recovered after EC (direct) of sample A with steel (left) and aluminium electrodes (right)

A copper plant provided a highly polluted wastewater sample (B) with high content of heavy metals, mainly copper, nickel and zinc. Table III summarizes the heavy metals content in all samples before and after treatment by chemical precipitation with lime (CP-Bli), and by EC treatment without pH-conditioning (direct), using the batch set-up, with regular steel (EC-Bfe) and aluminium electrodes (EC-Bal), measured by the analytical lab. The expected discharge limit from the environmental authority is indicated.

Table III: Heavy metals content in sample B before and after treatment by CP / EC

Element	Unit	B (before)	CP-Bli (lime)	EC-Bfe (direct)	EC-Bal (direct)	Discharge limit
pH [-]	–	0.8	6.5	3.0	3.9	6.5 - 8.5
Conductivity	mS/cm	117.4	14.3	41.6	35.8	–
Free acid H ₂ SO ₄	mg/l	26 700	–	18 200	14 500	–
Copper (Cu)	mg/l	3 800	< 0.1	< 0.01	62.4	0.5
Nickel (Ni)	mg/l	780	< 0.1	714	770	0.5
Zinc (Zn)	mg/l	1 800	0.4	1 472	1 697	1
Aluminium (Al)	mg/l	3.7	< 0.5	< 0.5	3 191	2
Iron (Fe)	mg/l	26.1	< 0.1	8 952	45.7	2

Sample B presented an extremely high level of contamination with copper, zinc and nickel values exceeding the discharge limit from the environmental authority in 7600, 1800 and 1560 times, respectively. Figure XXII summarizes all heavy metal removal yields after 1 hour of EC (direct) of sample B with steel (EC-Bfe) and aluminium electrodes (EC-Bal), without pH-conditioning. In this case, aluminium electrodes described the same strong anodic deposition behaviour, as seen on the EC (direct) of sample A.

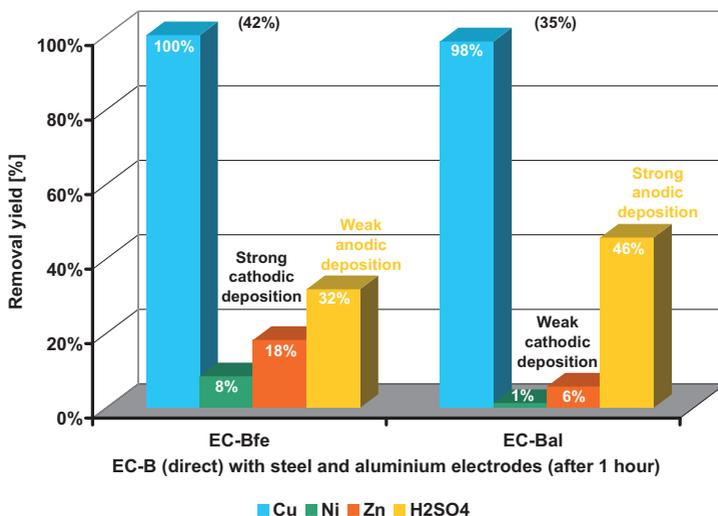


Figure XXII: Summary of metal removal yields after 1h EC (direct) of sample B using steel (EC-Bfe) and aluminium electrodes (EC-Bal) without pH-conditioning

Based on the low content of metal oxides introduced in Figure XXI, one can conclude that EC treatment in batch mode does not represent a feasible solution for metal recovery, technically and economically speaking. As widely described in the scientific literature reviewed for this research, EC treatment in batch mode often requires hours to achieve the discharge requirements enforced by the environmental authorities.

This was the main reason why it was decided to focus research on the design and optimization of EC treatment in continuous flow. However, and for the purpose of this exploratory research in batch mode, technically interesting figures can be seen as well, in particular cases when samples contain higher metal concentrations. Figure XXIII introduces XRF analysis and appearance of precipitates recovered after EC without pH-conditioning of sample B with regular steel (left) and aluminium electrodes (right). This result confirmed the strong anodic deposition behaviour of aluminium electrodes, based on a higher sulfur trioxide removal, by a significant lower heavy metal removal.

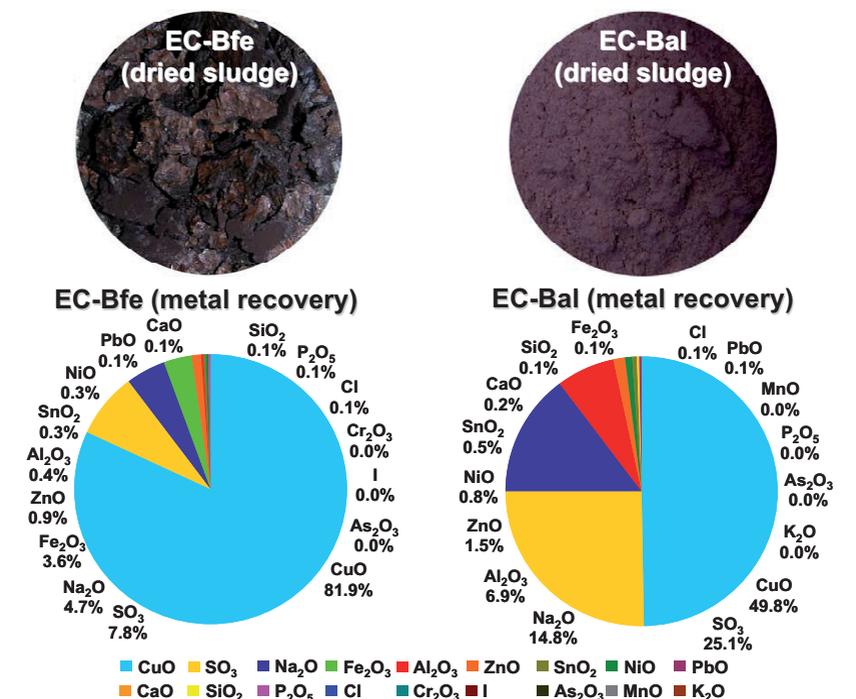


Figure XXIII: XRF analysis and appearance of dried sludge after EC (direct) of highly polluted wastewater (B) using steel (left) and aluminium electrodes (right)

Despite of 100% removal yield of copper metal using regular steel electrodes without previous neutralization, removal of zinc (18%) and nickel (8%) were less satisfactory. This is due to the extreme acidic conditions of the sample (pH 0.8), which do not allow complexation of iron-hydroxide flocs. In other words, heavy metals removal relies on a pure electrodeposition effect when using EC (direct) procedure outside the neutral pH value. However, taking into account the 81.9% content of copper oxide (CuO), this could represent a feasible, yet quite expensive path for heavy metals recovery.

In order to evaluate the effect of pH-conditioning on EC performance, this part of the experiments took place with wastewater sample (C) with high content of heavy metals, mainly copper, nickel and zinc, with previous neutralization using calcium hydroxide $\text{Ca}(\text{OH})_2$ (36% lime milk). Table IV summarizes all heavy metals content found before and after pH-conditioning from pH 2.0 to 6.0 using lime (pHc-C), and subsequent treatment by EC using the batch reactor with steel electrodes (EC-Cfe), including the heavy metal content found in suspended solids, measured by ICP and XRF analysis.

Table IV: Heavy metals content in sample C before and after EC treatment (batch) with pH-conditioning and XRF analysis of suspended solids from filtrate

Element	Unit	C (before)	pHc-C (lime)	EC-Cfe (batch)	Discharge limit	Suspended solids [%]
pH [-]	–	2.0	6.0	6.5	6.5 - 8.5	–
Conductivity	mS/cm	16.5	7.0	6.5	–	–
Copper (Cu)	mg/l	423	160	0.14	0.5	0.4%
Nickel (Ni)	mg/l	56.7	50.1	7.1	0.5	1.7%
Zinc (Zn)	mg/l	624	550	37.2	1	6.3%
Iron (Fe)	mg/l	60.8	0.07	379	2	62.0%

Figure XXIV shows cumulative removal yield after pH-conditioning (pHc-C) and subsequent EC-Cfe (batch) of sample C, including the expected percentage left in suspended solids that remained in treated sample after filtration. Figure XXV introduces the appearance of sample C before and after each treatment step, together with the XRF analysis of dried sludge, indicating percentage of metals and minerals recovered after pH-conditioning (left), by EC treatment (center) and left in filtrate (right), dried at 120 °C.

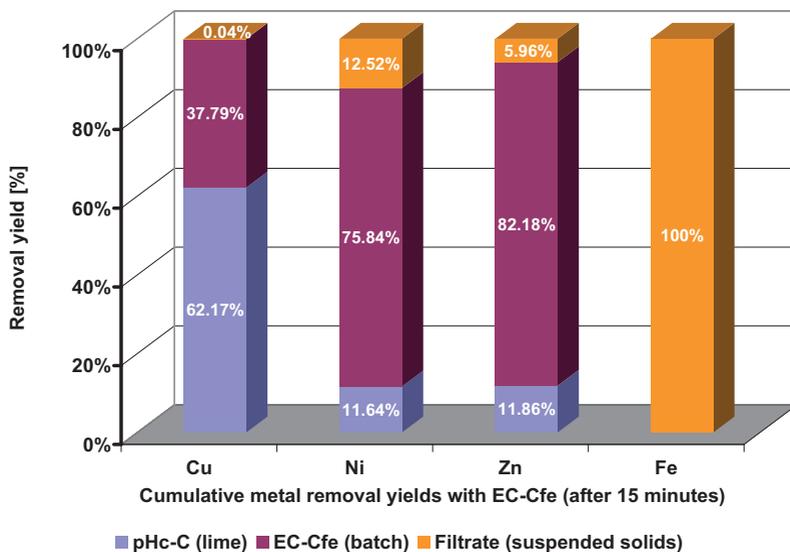


Figure XXIV: Cumulative removal yields after EC-Cfe (batch) of sample C with steel electrodes after pH-conditioning and including suspended solids left

Sample C presented a high level of contamination with heavy metals, mainly zinc (624 mg/l), copper (423 mg/l) and nickel (56.7 mg/l). During this experiment, suitability of EC technology in combination with conventional chemical precipitation was confirmed. On one hand, chemical precipitation required higher pH values than neutral range (pH 7.0), up to high alkaline levels (pH > 10.0), to remove heavy metals like nickel or zinc. On the other hand and as seen on previous experiments, electrolytic hydroxides generated by the EC treatment required neutral pH conditions in order to promote ideal agglomeration and effective adsorption conditions, as described before. Thus, it is only through the combination of both processes, which are not effective enough if operated separately, that is possible to design an efficient treatment path which is more sustainable, requiring less precipitating chemicals (lime) and electricity.

Like this, it was possible to achieve 99.96% removal of copper, 94.04% removal of zinc and 87.48% removal of nickel within 15 minutes, after previous neutralization using a reduced quantity of lime to reach only pH 6.0, and subsequent EC treatment using the batch reactor with regular steel electrodes. At this point iron content was still high, but its amount left in suspended solids was optimized using EC in continuous flow. The relevance of the suspended colloidal particles remaining in the filtrate after the EC treatment is very critical, due to agglomeration of remaining metals as hydroxides such as nickel Ni(OH)₂ or zinc hydroxide Zn(OH)₂, that get bound into the iron hydroxide particles as fine dispersions. Removing them would not only improve the appearance of cleaned effluents (a yellow dispersion observed after EC treatment), but it also prevents wrong measurements of dissolved content during the water analysis.

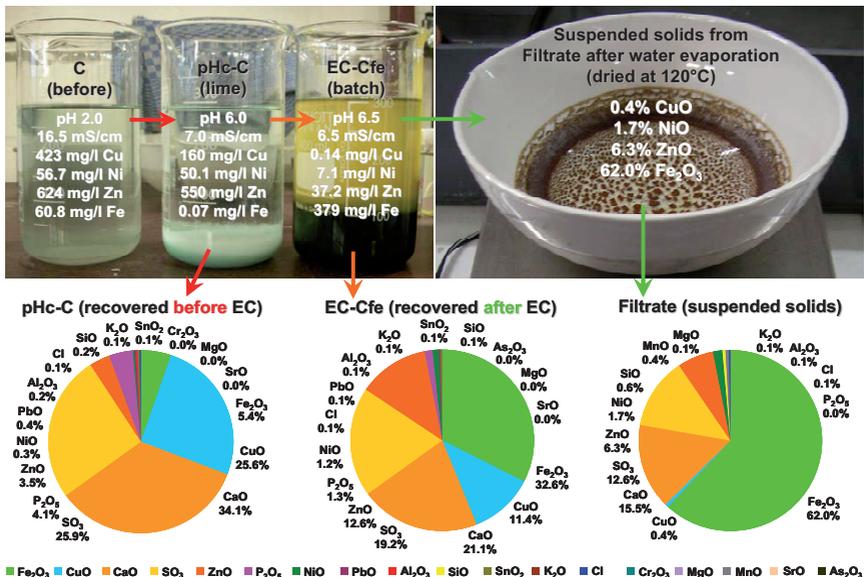


Figure XXV: Appearance of sample C and XRF analysis of sludge recovered after pH-conditioning (left), EC-Cfe (center) and filtrate (right)

A lead plant provided wastewater sample (D) with high content of heavy metals, mainly lead, arsenic, thallium, cadmium and zinc. Table V summarize the heavy metals content before and after treatment by chemical precipitation with soda (CP-Dso) and by EC treatment using steel electrodes EC-Dfe, without previous neutralization (direct), and after pH-conditioning (batch) with soda (pHc-D), measured by the analytical lab.

Table V: Heavy metals content in sample D before and after treatment by CP / EC

Element	Unit	D (before)	CP-Dso (soda)	EC-Dfe (direct)	pHc-D (soda)	EC-Dfe (batch)	Disch. limit
pH [-]	-	2.0	8.0	3.3	6.0	6.6	6.5 - 8.5
Conductivity	mS/cm	25.8	10.6	12.9	13.7	13.6	-
Lead (Pb)	mg/l	8.7	< 0.05	1.4	0.2	< 0.05	0.1
Arsenic (As)	mg/l	504	0.28	36.3	406	26	0.15
Thallium (Tl)	mg/l	88	0.65	60.9	84	57	0.05
Cadmium (Cd)	mg/l	8.9	< 0.05	4.53	7.9	2.1	0.05
Zinc (Zn)	mg/l	63	0.11	60.2	57	2.5	1
Iron (Fe)	mg/l	53	< 0.05	2 518	< 0.05	134	2

Sample D presented a high level of contamination with acidic pH and high conductivity values, in particular the arsenic content (504 mg/l), which exceeded in 3360 times the discharge limit. After chemical precipitation with sodium hydroxide NaOH (soda), pH value raised up to 8.0, which then allow to remove up to 99.94% of arsenic (0.28 mg/l). Despite such a good removal yield, soda was not able to meet the discharge requirements of 0.15 mg/l for arsenic and 0.05 mg/l for thallium (0.65 mg/l Tl).

FigureXXVI shows the appearance of D samples before and after EC treatment without neutralization (direct), and after pH-conditioning with soda (batch). Here it was possible to appreciate the condensation and complexation effect induced by the pH value of samples. After 60 minutes of EC treatment without pH-conditioning (direct), sample seemed to be cleaner that before, lead and arsenic values were lower, but iron value skyrocketed (2 518 mg/l Fe). A more efficient approach was then implemented after pH-conditioning (batch), reducing treatment time to only 10 minutes, and achieving higher removal yields, while consuming less power and anode material (134 mg/l Fe).

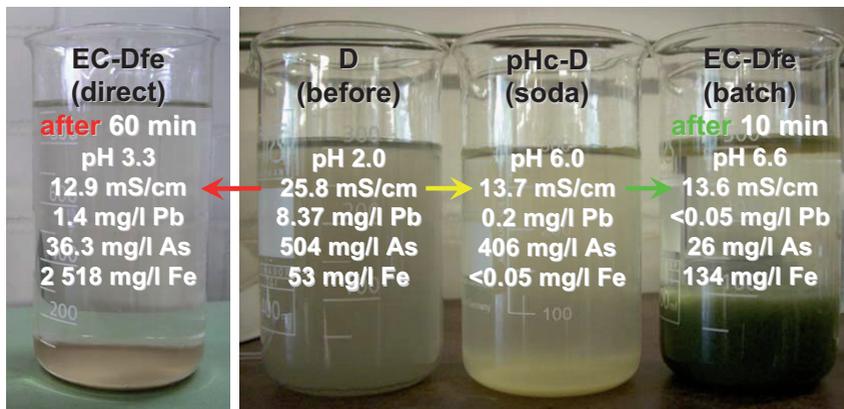


Figure XXVI: Physical appearance of sample D before and after EC treatment without neutralization (direct) and after EC treatment with pH-conditioning (batch)

Figure XXVII shows the Draeger® gas detector pump and sampling tubes used for the detection of arsine AsH₃ after EC treatment without previous neutralization (direct) and after pH-conditioning (batch). First experiment carried out without previous neutralization (pH 2.0), confirmed the release of vast amounts of arsine gas AsH₃ (more than 3 ppm). Further experiments performed after conditioning of pH to 6.0 with sodium hydroxide NaOH (soda), confirmed arsine emissions below 0.05 ppm.

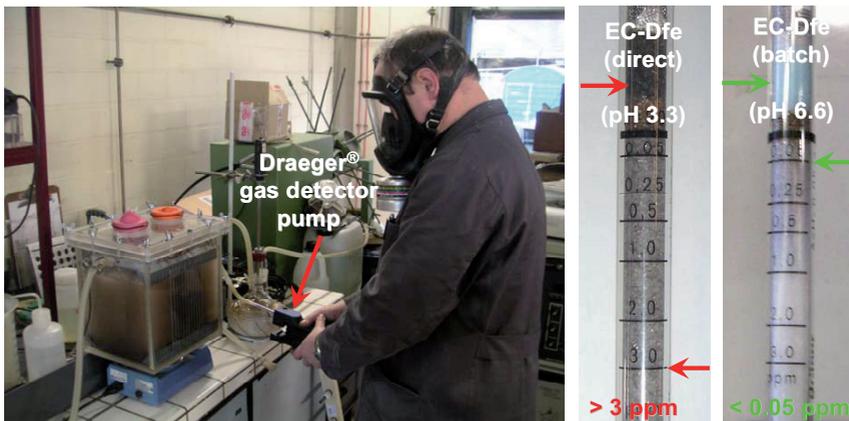


Figure XXVII: Draeger® gas detector pump and sampling tubes used for arsine AsH₃ detection during EC-Dfe before (direct) and after pH-conditioning (batch)

Figure XXVIII shows cumulative removal yield after pH-conditioning (pHc-D) and subsequent EC-Dfe (batch) of sample D, including the expected percentage left in suspended solids that remained in treated sample after filtration.

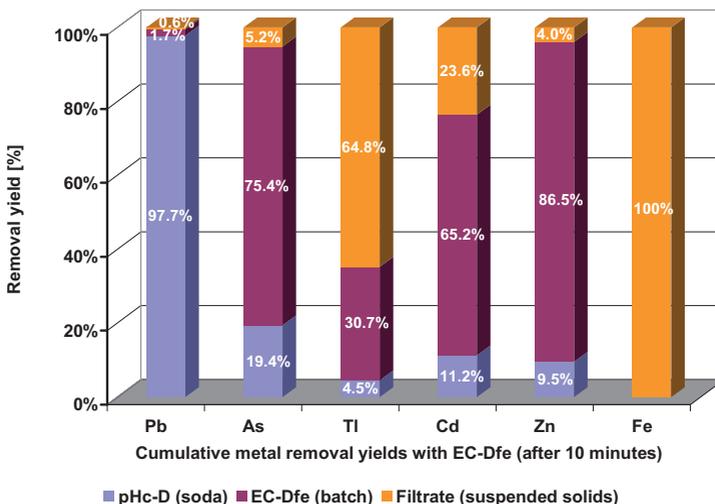


Figure XXVIII: Cumulative removal yields after EC-Dfe (batch) of sample D with steel electrodes after pH-conditioning and including suspended solids left

Flue-gas FGT wastewater sample (F) was provided by a waste incineration facility processing large amounts of industrial waste loaded with lead, mercury, copper, nickel, cadmium, chromium and zinc. Due to their bad performance, aluminium electrodes were no longer tested on this sample. Table VI summarizes its heavy metals content, before and after treatment by chemical precipitation with lime (CP-Fli), and by EC treatment in batch mode, using steel electrodes, after previous neutralization with calcium hydroxide up to pH 6.7 (pHc-F), measured by the analytical lab.

Table VI: Heavy metals content in sample F before and after treatment by CP / EC

Element	Unit	F (before)	CP-Fli (lime)	pHc-F (lime)	EC-F10 (batch)	EC-F20 (batch)	EC-F30 (batch)
pH [-]	-	0.5	9.0	6.7	6.8	6.9	7.0
Conductivity	mS/cm	190	52.2	52.7	50.2	50.1	50.0
Temperature	°C	21.0	26.1	25.8	21.3	21.5	21.7
Lead (Pb)	µg/l	500 000	< 10	48	< 10	< 10	< 10
Mercury (Hg)	µg/l	401	29	269	2.7	< 1	< 1
Copper (Cu)	µg/l	63 000	< 50	170	52	< 50	< 50
Nickel (Ni)	µg/l	8 500	< 50	3 100	210	< 50	< 50
Cadmium (Cd)	µg/l	780	< 50	470	130	68	< 50
Chromium (Cr)	µg/l	2 600	< 10	< 10	< 10	< 10	< 10
Zinc (Zn)	µg/l	490 000	400	10 000	110	< 50	< 50

Figure XXIX shows the physical appearance of sample F after EC treatment with previous pH-conditioning with lime milk. According to theory regarding concomitant flotation, there is an optimum operational window within the isoelectric range that was reached after 10 minutes of EC treatment. Evidence of this was given by the flotation effect, which then vanished and was no longer present in samples after 20 and 30 minutes, as a result of an electrolytic overdosage of iron-hydroxides by the sacrificial anodes.

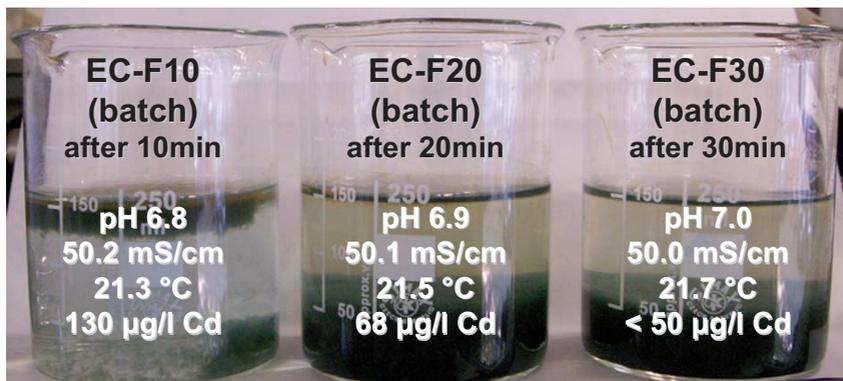


Figure XXIX: Appearance of sample F after EC treatment with previous neutralization

From the effect of power consumption on conductivity of sample F shown in Figure XXX, since there was no change, it was likely to confirm the described isoelectric range, indicating that batch process could be stopped after 10 minutes to prevent overdosage.

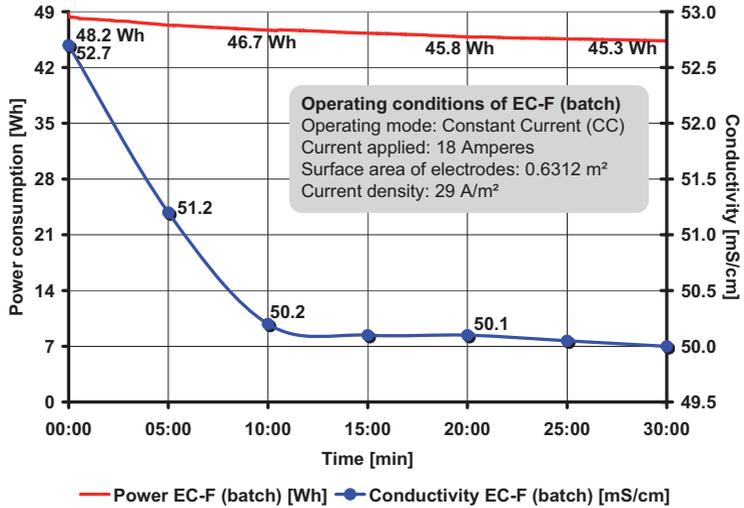


Figure XXX: Effect of power consumption on the electrical conductivity of sample F during EC treatment after pH-conditioning (batch) with steel electrodes

Figure XXXI shows cumulative removal yield after pH-conditioning (pHc-F) and subsequent EC-F10 (batch) of sample F, including the expected percentage left in suspended solids that remained in the treated sample after filtration.

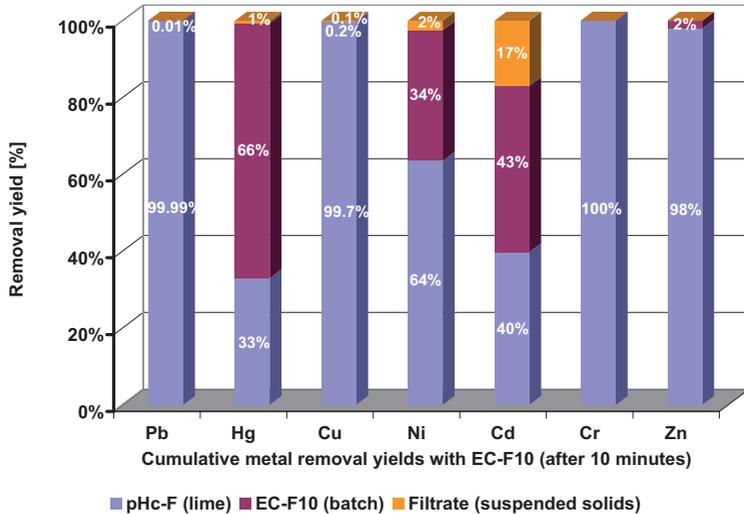


Figure XXXI: Cumulative removal yields after EC-F10 (batch) of sample F with steel electrodes after pH-conditioning and including suspended solids left

Experimental work with continuous EC using online process control

Main goal of this last set of experiments was to compare the EC performance using the closed-loop process control (online), with the results observed during offline mode. Table VII summarizes the heavy metal contents before and after treatment by chemical precipitation with lime (CP-Gli), by EC treatment in offline (EC-G45) and in online mode (closed-loop control), after pH-conditioning, measured by the analytical lab.

Table VII: Heavy metals in G before and after treatment by CP and EC (off/online)

Element	Unit	G (before)	CP-Gli (lime)	pHc-G (lime)	EC-G45 (offline)	EC-G45 (online)	Disch. limit
pH [-]	–	0.2	10.0	7.3	7.0	6.8	6.5 - 8.5
Conductivity	mS/cm	330	70.2	71.6	69.8	68.5	–
Temperature	°C	20.0	27.8	20.0	20.8	20.5	–
Lead (Pb)	µg/l	92 000	< 10	< 10	< 10	< 10	< 100
Mercury (Hg)	µg/l	67	5	55	< 1	< 1	< 30
Copper (Cu)	µg/l	41 500	< 50	< 50	< 50	< 50	< 500
Nickel (Ni)	µg/l	950	< 50	630	70	< 50	< 500
Cadmium (Cd)	µg/l	490	< 50	280	130	< 50	< 50
Chromium (Cr)	µg/l	1 100	< 10	< 10	< 10	< 10	< 500
Zinc (Zn)	µg/l	95 300	< 50	380	90	< 50	< 1 000

Figure XXXII shows the appearance of sample G after EC using inline reactor in offline mode (open-loop control for PID tuning), with previous pH-conditioning using lime milk. From this result it was possible to visualize that the synergic flotation observed after 45 minutes in EC-G45 (offline), could be achieved within 30 minutes in online mode (see Figure XXXIII). Despite of achieving relatively similar conductivity values, removal of cadmium (130 µg/l Cd), nickel (70 µg/l Ni) and zinc (90 µg/l Zn) was unsatisfactory.

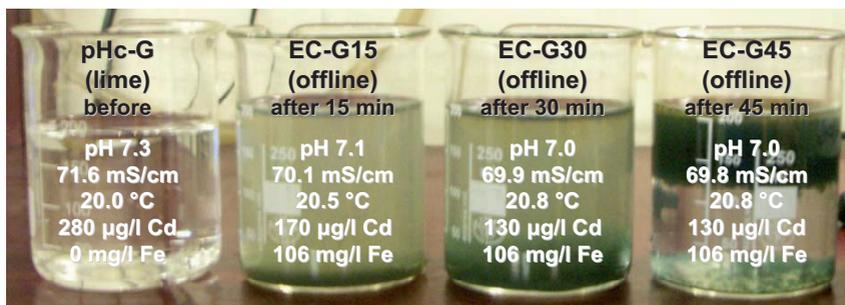
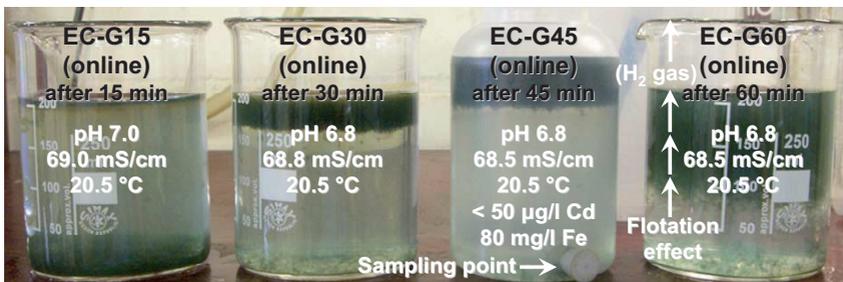


Figure XXXII: Physical appearance of sample G after pH-conditioning and continuous EC using inline reactor in offline mode (open-loop control for PID tuning)

Figure XXXIII shows the appearance of sample G after EC using inline reactor in online mode (close-loop process control), with previous pH-conditioning using lime. During online control, conductivity set-point of 68.5 mS/cm was achieved within 30 minutes with flotation effect. According to measurement of anode consumption, once process reached the desired set-point, electrolytic dosage of sacrificial anode was estimated about 80 mg/l Fe, which is nearly 25% less than in offline mode (106 mg/l Fe with 2 A).



FigureXXXIII:Physical appearance of sample G after pH-conditioning and continuous EC using inline reactor in online mode (closed-loop process control)

Compared to removal yields after pH-conditioning with lime (pHc-G), from these values it is likely to conclude that in addition to lead (< 10 µg/l Pb), copper (< 50 µg/l Cu) and chromium (< 10 µg/l Cr), online process achieved total metal removal of mercury (< 1 µg/l Hg), nickel (< 50 µg/l Ni), cadmium (< 50 µg/l Cd) and zinc (< 50 µg/l Zn) using 1.5 amperes (21.7 A/m²). This significant improvement in heavy metal removal yields could be related to the way sampling was performed from the bottom of the vessel, avoiding sample contamination, due to filtration problems with small colloidal particles.

Figure XXXIV shows cumulative removal yield after pH-conditioning (pHc-G), which accounts for 70% heavy metal removal, and the subsequent EC-G45 (online), with the remaining 30% metal removal of sample G, including the expected percentage left as suspended solids that remained in the treated sample after filtration. It is worth noticing that all metal content values are below the detection limits, therefore, there are no suspended solids expected other than colloidal iron, which was not accounted here.

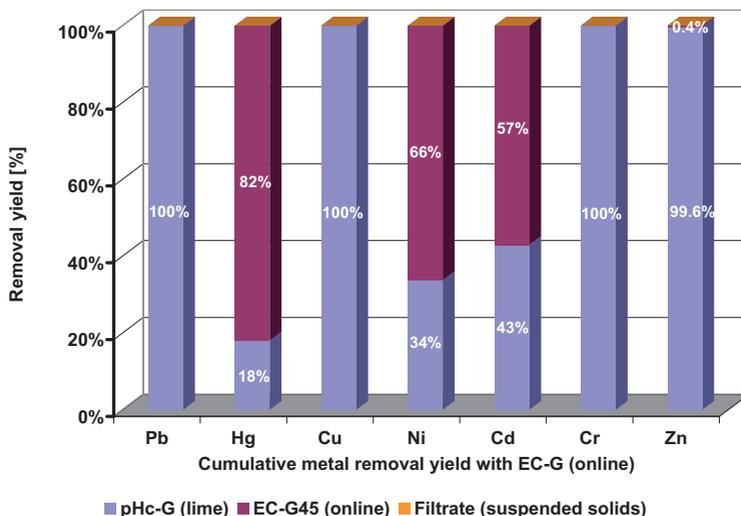


Figure XXXIV: Cumulative removal yields after pH-conditioning and EC-G45 (online) of sample G with steel electrodes including any suspended solids left

Figure XXXV introduces the conductivity response of the EC treatment of sample G in continuous flow with open-loop control (offline), used to calculate the transfer function of the inline reactor. The whole mathematical procedure to define the transfer function and the coefficients of PID controller for online control can be found in previous section.

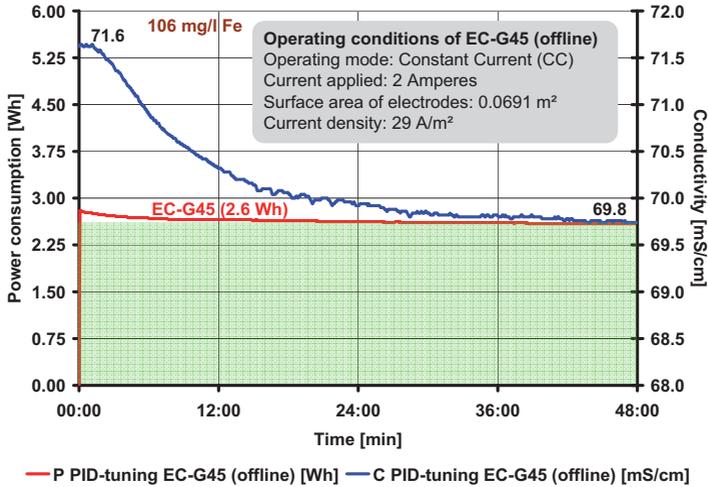


Figure XXXV: Conductivity response to continuous EC-G45 of sample G in offline mode (open-loop control) used to calculate the transfer function of inline reactor

Figure XXXVI shows the conductivity response to continuous EC of sample G in online mode (closed-loop) and its effect on the electrical power and electrode consumptions.

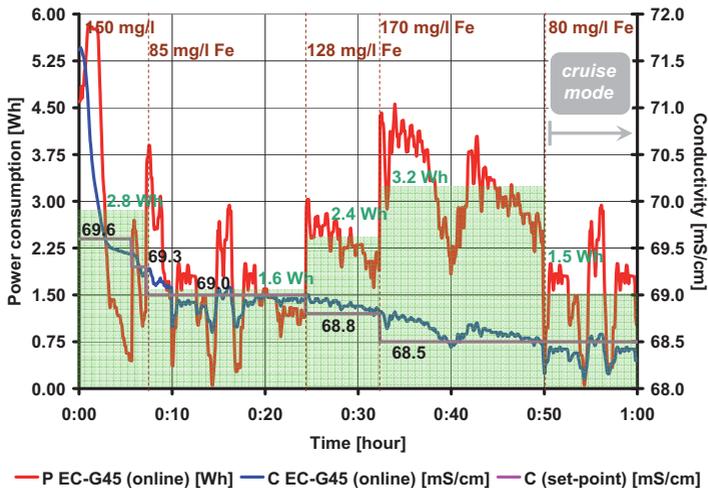


Figure XXXVI: Conductivity response to continuous EC of sample G in online mode (closed-loop control) and its effect on anode and power consumptions

For the first time in this research work and thanks to the implemented online control, it was possible to visualize the inertia from the electrolytical reactions during EC process. Like this, electrical conductivity of sample G followed the conductivity set-point given, and remained below this value by applying as much electrical energy as required from EC reactions. In doing so, change of set-point from 68.8 to 68.5 mS/cm required as much as 3.2 Wh over a period of 18 minutes to achieve the desired value. Once this value is reached, it is likely to see that only 1.5 Wh of power is required (**cruise mode**), to maintain operation at the isoelectric range, where flotation of colloids is perceivable.

Likewise, online process control allowed to reduce the sacrificial anodic dosage by 25% to 80 mg/l Fe, compared to 106 mg/l Fe required in offline mode (EC-G45), with improved heavy metal removal yields. This is due to the fact that in online mode, energy supply can be temporarily powered down, once the conductivity set-point has been reached. Then, it powered up again once the conductivity value rose over the set-point. Like this online process control takes advantage of the inertia in EC reactions. Compared to Figure XXXV, Figure XXXVI provided evidence that in order to drive EC reactions, power supply must be adjusted in real-time in order to save energy (1.5 Wh instead of 2.6 Wh) and anode material (80 mg/l Fe instead of 106 mg/l Fe). This effect of inertia shall depend on the flow capacity of the inline reactor, which in this case was very low, only 20 L/h. Unfortunately, there was not enough sample available from the waste incineration facility to perform EC treatment with higher flow capacities.

Figure XXXVII shows the effect of power consumption on the conductivity response to continuous EC of sample G in online mode (closed-loop), including the amount of energy released as hydrogen in EC off-gas (H₂-Energy). The PID controller lowered the electrical conductivity of sample G from 71.6 to 68.5 mS/cm during one hour of operation, consuming a total amount of power of 2.2 Wh, from which 55% (1.2 Wh) of it was released as hydrogen in EC off-gas. This hydrogen gas might play a significant role in the direct reduction of iron hydroxides during incineration of sludge towards a proposed zero-waste concept, described in the concluding remarks of this research.

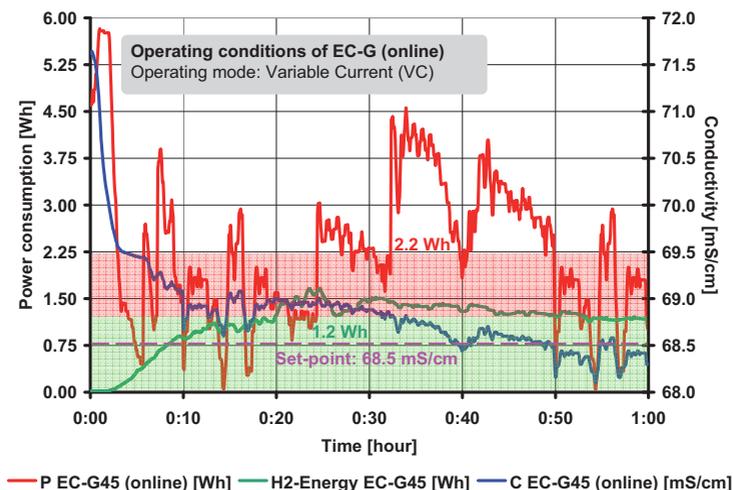


Figure XXXVII: Conductivity response to continuous EC of sample G in online mode (closed-loop control) and amount of energy released as hydrogen gas

Techno-economical assessment of continuous EC with online control

Since at the time of this research work it was not possible to perform extended runs of more than 1 hour (20L/h effective flow), due to the limited availability of wastewater samples, this section provides theoretical estimations about the expected performance of continuous EC for maximum operating time without anode renewal by the operator (maintenance-free time). Based on the anodic dosage required by the EC-G45 (online) test, the physical dimensions of the sacrificial bar (0.550 kg for 85 cm long) allow an extended run of maximum 12 days (288 hours), for which initial diameter of 10.2 mm, reduces its size to 3.3 mm, while inducing dynamic decline of SA:V ratio of inline cell. From these figures it is then possible to estimate the amount of generated iron scrap left after 12 days of continuous operation (0.09 kg), which could be sold later on.

Figure XXXVIII provide graphic representation calculated for anodic dosage of 80 mg/l for EC-G45 (online) test with closed-loop control. For the sake of economical interpretations, a colored rule is now introduced, intended for the analysis of process figures at given periods of time. Like this, green range covered from day 1 to day 7 (until 168 hours), yellow from day 7 until day 9 (until 216 hours), orange from day 9 until day 11 (until 264 hours), and finally, red one covered last day, until a maximum of 288 hours of EC treatment in continuous flow.

EC power requirements increased substantially with respect to SA:V, for instance EC-G45 (online) had a power consumption of 1.5 Wh (cruise mode) for SA:V 5.63 cm^{-1} , while EC-G (batch) had a power consumption of 40.0 Wh for SA:V 2.50 cm^{-1} . Since SA:V ratio is related to the reactor geometry, this heuristic approximation is based on the mathematical simulation of future power consumption with changing geometry, using power value reported from batch reactor, as if it were the worn out inline reactor.

Figure XXXIX provides graphic representation of simulated power consumptions, based on a changing geometry with the corroded anode, over a time period of 12 days. Like this, power consumption at day 1 started at 1.5 Wh (cruise mode), by 5.63 cm^{-1} SA:V, and by day 7, SA:V declined to 3.90 cm^{-1} , thus increasing power consumption to 21.3 Wh. By the end of the maximum maintenance-free time of 12 days (after 168 h), SA:V declined to 2.85 cm^{-1} , leading to a maximum power consumption of 34.2 Wh.

From these figures is then possible to perform the techno-economical assessment of continuous EC, starting with the amount of wastewater treated, total energy demand of EC with respect to each cubic meter treated, and last but not least, the economic figures on the anode material demand, including possible revenues from scrap sales. Figure XL shows the estimated cumulative energy demand vs. the amount of wastewater treated. Taking into account some economical considerations, like personnel cost and the expenses regarding electrodes replacement, as well as the uncertainties around handling and selling the iron scrap left after treatment, estimations towards this techno-economical assessment are based on maximum operation time of 12 days.

Like this, it has been estimated a maximum treatment capacity of 5.8 cubic meters of wastewater, after a time period of 12 days (288 hours), with a total energy demand of 5.5 kW, which means 0.95 kW for each cubic meter. Finally, Figure XLI introduces the variable treatment cost, based on three anticipated scenarios concerning the revenue from the sales of iron scrap, C1 based on a resell price per ton of 200 EUR/t, C2 of 100 EUR/t, and C3 in the case when there is no demand for remaining anode (0 EUR/t).

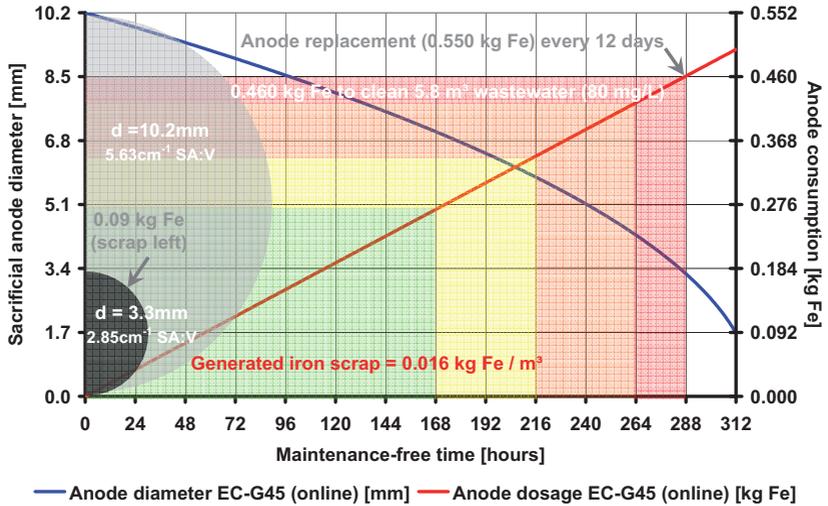


Figure XXXVIII: Behaviour of anode consumption vs. diameter for EC-G45 (online)

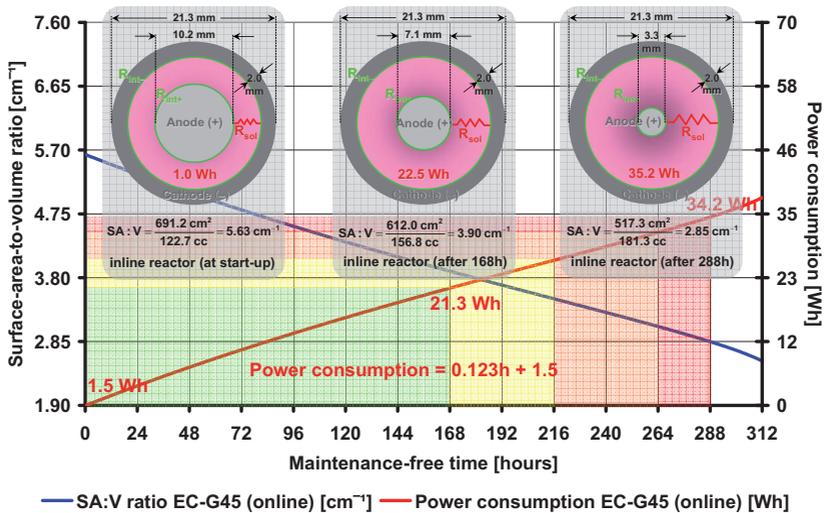


Figure XL: Effect of the inline reactor geometry (variable SA:V ratio) on the power consumption of EC-G45 (online)

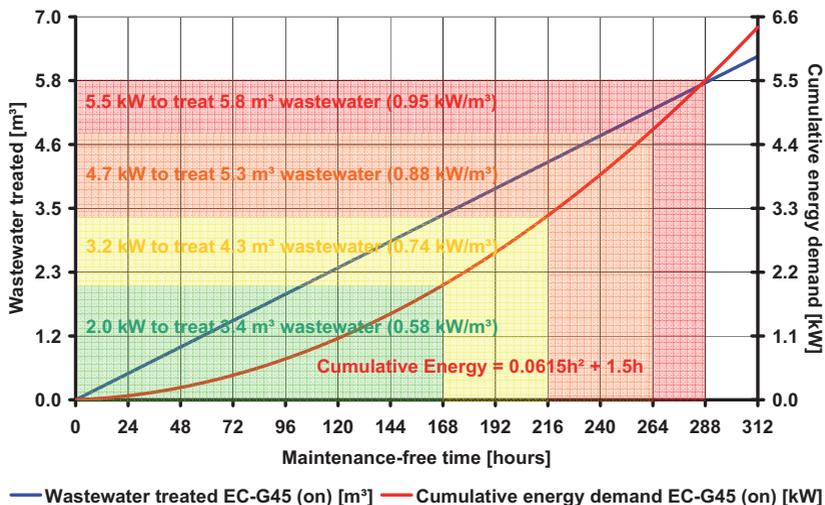


Figure XL: Cumulative energy demand of EC-G45 (online) versus the amount of wastewater treated

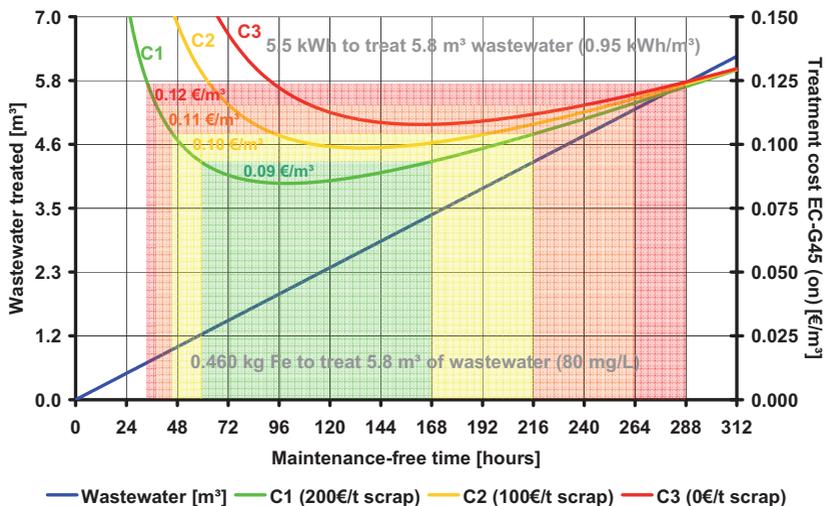


Figure XLI: Treatment cost based on EC-G45 (online) performance for three different iron scrap sales scenarios

Table VIII summarizes process economics relevant for the calculation of treatment cost between chemical precipitation using pHc-G + CP-Gli (5.11 €/m³), electrocoagulation with open-loop process control with pHc-G + EC-G45 (offline) (5.02 €/m³), and EC final closed-loop process control optimization with pHc-G + EC-G45 (online) (4.97 €/m³), on the basis of 20 m³/h effective flow, the actual rate at the waste incineration facility.

In the case of chemical precipitation of sample G, chosen neutralization reagent was hydrated lime, which has a commercial value of 100 €/t, and required a total amount of 37 kg/m³ to reach pH 7.3 (pHc-G), plus additional 1.2 kg/m³ to reach pH 10.0 (CP-Gli). Process cost per cubic meter of wastewater treated was estimated in about 5.10 €/m³. Taking into account that this process was performed to remove some micrograms per liter of heavy metals (µg/l), applying grams per liter of lime generated a considerable amount of sludge, which then required disposal, with estimated cost of 0.67 €/m³. Since wastewater cannot be discharged in the environment with pH 10.0, acidification using hydrochloric acid (HCl) required additional 0.12 €/m³. Finally, based on energy price of 0.10 €/kWh and energy demand of 5 kWh/m³, energy cost was 0.50 €/m³.

In the case of continuous electrocoagulation of sample G after pHc-G (4.83 €/m³) using the optimized closed-loop process control EC-G45 (online), anodic dosage of about 80 mg/l took place from regular steel rods, which have a commercial value of 300 €/t. Such a small amount of electrode material used, generated an equally small amount of sludge, only 0.3 kg/m³, which effected a sludge disposal cost of 0.01 €/m³ treated. EC process does not require acidification, and depending on the amount of scrap left, a minimum annual revenue of 280 € can be reached with a price of 100 € per ton. Finally, with energy demand calculation of 0.95 kW/m³ (5.5 kW/5.8 m³ see Figure XL), energy cost of 0.09 €/m³, rounded the process treatment cost to a total of 4.95 €/m³.

Based on the small difference of total treatment cost between CP-Gli and EC-G45 of only 0.15 €/m³, it is worth noticing that continuous EC introduced a more sustainable approach, since it was not only cheaper, but it also reduced the amount of chemicals required, which mitigate the impact of excessive calcium and chloride in water bodies. From the economic figures in CWW BREF about EC treatment [9], it was remarkable to find out that reported economical data from this research work were slightly better. For instance, energy use amounts reported in CWW BREF are about 1 kW per cubic meter, and from this research work ranged from 0.58 to 0.95 kW/m³ (see Figure XL). Likewise, CWW BREF anticipated a minimum of 0.15 €/m³ of wastewater cleaned, while reported data from Figure XLI anticipates costs between 0.09 and 0.12 EUR/m³.

Last but not least, since additional expenses on personnel, overhead and the annual depreciation of installation facilities also effect a significant impact on total operational cost calculation, Table IX takes into account all these figures, in order to provide a more realistic estimation. Like this, personnel expenses were estimated in 200.000 €/a, including four (4) operators to run the facility 24/7 in 8 hours shifts (50.000 €/a each). Overhead expenses of 100.000 €/a included a plant manager, a secretary and the accountant. Depreciation was estimated in five years time (20% annual depreciation), for a total installation expenses of 200.000 €, which included the neutralization and the electrocoagulation plant with the construction of storage tanks, pipelines, pumps, process reactors and online control instruments. All these raised total operational cost of about 40% from 4.95 to 6.9 €/m³, 6.15 €/m³ for pH-conditioning and 0.75 €/m³ for EC. As a concluding remark, it should be noted that EC represents 11% of operational cost (0.75 €/m³), but it is accountable for 30% of heavy metals removal (see Figure XXXIV).

Table VIII: Process treatment cost based on CP and EC-G45 treatment of sample G

Process treatment cost	Unit	pHc-G (pH 0-7)	CP-Gli (pH7-10)	EC-G45 (offline)	EC-G45 (online)
Effective flow rate	m ³ /h	20			
Annual treatment capacity	m ³ /a	175 200			
Material used	–	hydrated lime		steel rods (iron)	
Material price per ton	€/t	100		300	
Material demand per m ³	kg/m ³	37	1.2	0.106	0.080
Annual material demand	t/a	6 482	210	19	14
Annual material cost	€/a	648 200	21 000	5 700	4 200
Material cost per m ³	€/m ³	3.70	0.12	0.03	0.02
Generated sludge per m ³	kg/m ³	21.6	0.7	0.4	0.3
Generated sludge per year	t/a	3 784	123	70	53
Sludge disposal cost per ton	€/t	30			
Annual sludge disposal cost	€/a	113 520	3 690	2 100	1 590
Sludge disposal cost per m ³	€/m ³	0.65	0.02	0.01	0.01
HCl acid for pH-neutralization	g/m ³	–	0.2	–	–
Annual HCl acid demand	t/a	–	35	–	–
HCl acid price per ton	€/t	–	600	–	–
Annual HCl acid cost	€/a	–	21 000	–	–
Acidification cost per m ³	€/m ³	–	0.12	–	–
Generated scrap per m ³	kg/m ³	–	–	0.021	0.016
Generated scrap per year	t/a	–	–	3.68	2.80
Scrap sale revenue per ton	€/t	–	–	100	
Annual scrap sale revenue	€/a	–	–	-368	-280
Annual scrap sale revenue	€/m ³	–	–	-0.002	-0.002
Energy demand per m ³	kWh/m ³	4.84	0.16	1.28	0.95
Annual energy demand	kWh/a	847 968	28 032	224 256	166 440
Energy price per kWh	€/kWh	0.10			
Annual energy cost	€/a	84 797	2 803	22 426	16 644
Energy cost per m ³	€/m ³	0.48	0.02	0.13	0.09
Annual process treatment cost	€/a	846 517	48 493	29 858	22 154
Process treatment cost per m³	€/m³	4.83	0.27	0.17	0.12

Table IX: Operational expenses based on CP and EC-G45 treatment of sample G

Operational Expenses (OPEX)	Unit	pHc-G (pH 0-7)	CP-Gli (pH7-10)	EC-G45 (offline)	EC-G45 (online)
Annual process treatment cost	€/a	846 517	48 493	29 858	22 154
Process treatment cost per m ³	€/m ³	4.83	0.27	0.17	0.12
Annual personnel expenses	€/a	150 000	50 000	50 000	50 000
Personnel cost per m ³	€/m ³	0.86	0.29	0.29	0.29
Annual overhead expenses	€/a	50 000	50 000	50 000	50 000
Overhead cost per m ³	€/m ³	0.29	0.29	0.29	0.29
Installation expenses	€	150 000	–	50 000	50 000
Annual depreciation cost (20%)	€/a	30 000	–	10 000	10 000
Depreciation cost per m ³	€/m ³	0.17	–	0.05	0.05
Total annual operational cost	€/a	1076517	148 493	139 858	132 154
Total operational cost per m³	€/m³	6.15	0.85	0.80	0.75

Conclusions and transfer potentials

According to the theory and the experimental results provided in this research work, electrocoagulation technology shall play a significant role in the future of wastewater treatment, for industrial but also for domestic purposes. EC technology provides safe and reliable operation with no side-effects or collateral damages to environment and public health. EC technology is a polishing treatment, which means, it does not suit for every sort of wastewater, but in combination with an adequate conditioning of pH, EC delivers unparalleled performance, far better than any other technology on the market.

As discussed in the theory and confirmed in the experimental part of this research work, to highlight some of the best features of electrocoagulation technology, these include:

- Easier and cheaper separation of colloidal particles through synergic flotation
- Higher sustainability due to less dependency on questionable chemical reagents
- Robustness and flexibility to potential changes of wastewater quality in real-time
- Less chance for human-induced failure due to online process control operability
- Unparalleled cost/performance ratio thanks to the inertia of electrolytic reactions

Bearing in mind that nothing is perfect, the main drawbacks of EC technology include:

- As a polishing treatment, EC requires previous conditioning to pH neutral value
- Dependency on the electrical power to drive wastewater treatment reactions
- Regardless of extremely low dosage rates, sacrificial anodes must be replaced
- Despite low maintenance, it requires trained personnel for anode replacement
- Closed-loop process control requires sophisticated and expensive equipment

In regard to the inertia of its electrolytic reactions, the need for such sophisticated and expensive online control equipment is due to the fact that hydrolysis, condensation and complexation of colloidal particles occur at a much slower velocity, than the dissolution of sacrificial anode is effected by the electrical current applied to it. In other words, closed-loop control enables the power supply to shut down, in order to allow enough time for the removal of heavy metals from wastewater to take place, through coagulation and adsorption of dissolved elements into small colloidal particles (flocs).

Since these colloidal mechanisms require previous conditioning of pH to the neutral range (pH \approx 7.0), this provides the best isoelectric conditions for synergic flotation with the concomitant release of hydrogen gas. It is worth noticing that according to off-gas measurements, gas being released from the EC reactor is pure hydrogen, without any toxic (arsine) or oxygen content, which also eliminates the risk of explosion.

Removing heavy metals from industrial wastewaters is certainly one of the most challenging environmental issues nowadays, mostly because of the difficulty effected by the pH solubility relationship, as the single mechanism ruling their precipitation from water (see Figure V). In this regard, continuous EC have demonstrated throughout many experiments performed with several types of wastewater (industrial, municipal, petrochemical), to provide the best and most efficient mechanisms for the removal of organic and inorganic pollution. To summarize evidence of this, Figure XLII and XLIII compared the process flowcharts and the associated techno-economical assessment of conventional chemical precipitation and continuous electrocoagulation of sample G.

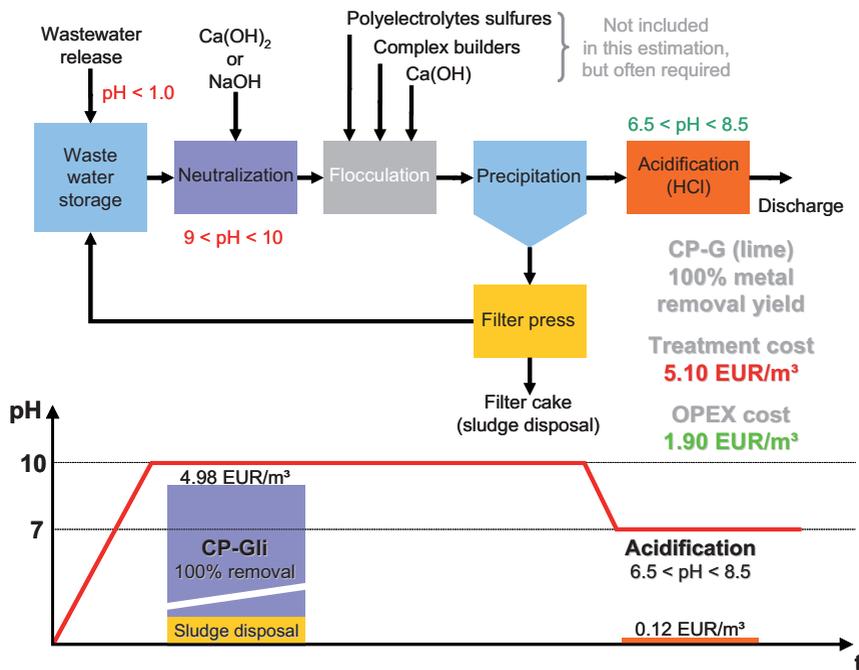
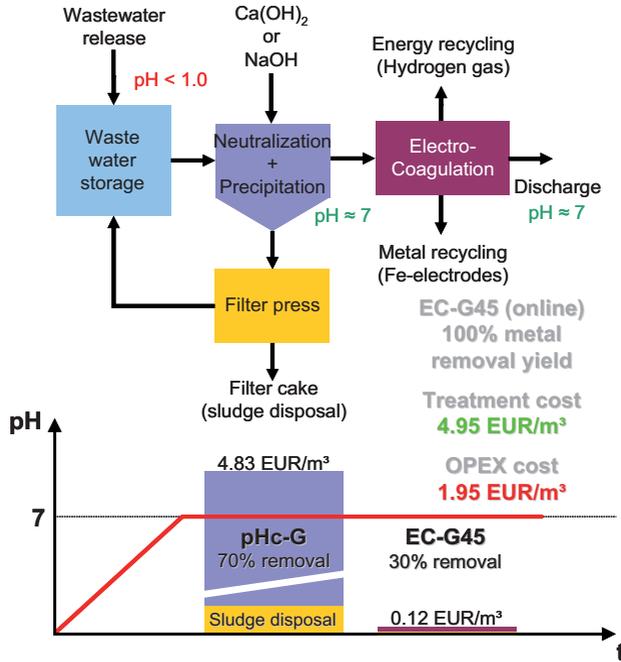


Figure XLII: Process flowchart of conventional chemical precipitation (CP-Gli) and associated techno-economical assessment of treatment and operational cost

From Figure XLII it is likely to conclude that industrial wastewater sample G required vast amounts of lime in order to raise the pH from 0.2 to 10.0, to induce precipitation of heavy metals below the discharge requirements from the environmental authority. But then, since it is not allow to discharge treated effluents outside the neutral range ($6.5 < \text{pH} < 8.5$), acidification of effluents with hydrochloric acid (HCl) must take place.

Compared to Figure XLIII, online electrocoagulation required less lime because pH must be raised only up to 7.0 (pHc-G). From there, EC-G45 (online) takes over and removed the remaining 30% of heavy metals spending the same amount of money as acidification ($0.12\text{€}/\text{m}^3$) used after chemical precipitation (see Figure XLII). Even though money savings are only $0.10\text{€}/\text{m}^3$, the fact of using less chemical products, which will invariably end up increasing the concentration of salts in water bodies (Ca^{2+} , Cl^-), should be enough motivation to go for for a more sustainable technology, like the EC.

Figure XLIV provides graphical representations of all technical and economical figures concluded from the techno-economical assessment of continuous EC with sample G. Technically speaking, EC is a sustainable technology that enables the cost-effective removal of heavy metals within neutral pH (7.0). Compared to chemical precipitation, CP-Gli only reached 70% removal at this pH, the remaining 30% was achieved by continuous EC, from which 7% was accountable to online control (see Figure XXXIV). Economically speaking, it is clear why pH-conditioning is more expensive than EC.



FigureXLIII:Process flowchart of online electrocoagulation (pHc-G / EC-G45) and associated techno-economical assessment of treatment and operational cost

Considering the amount of lime required by CP-Gli to raise the pH value up to 10 (1 200 mg/l lime), compared to 80 mg/l dosage from sacrificial anode in EC-G45, it represents 15 times more material demand. Despite of high installation costs (200k€ for 20m³/h), subtracting 9% (0.63 €/m³) of EC operational expenses (opex), EC treatment cost only represents 2% (0.12 €/m³) of this abstraction (0.75 €/m³). The 89% left is accountable to pH-conditioning, 70% treatment (4.83 €/m³) and 19% operational expenses (1.32 €/m³). All these provide enough evidence about the feasibility of EC for heavy metals removal.

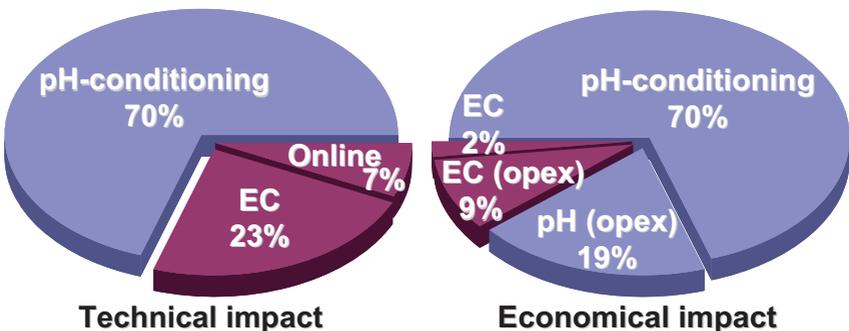


Figure XLIV: Summary of technical and economical impacts for pHc-G/EC-G45(online)

Zero-waste concept of EC technology towards a circular economy

Based on the encouraging results for bacteria removal from municipal wastewater, and taking into account the disturbing figures about the 2.4 billion people worldwide lacking of access to adequate sanitation, final part of this research work dealt with the design of a zero-waste concept for decontamination of water based on EC treatment. Figure XLV introduces the proposed zero-waste concept for the integral management of water, energy and resources, based on the principles of the circular economy.

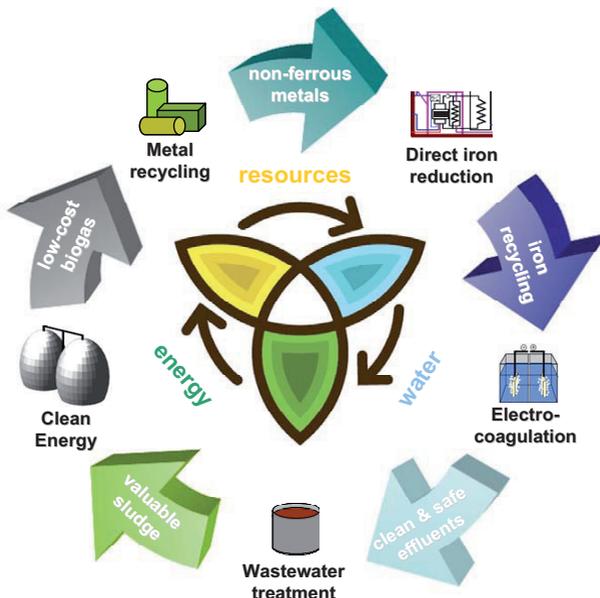
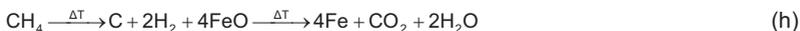


Figure XLV: Zero-waste concept of EC technology towards a circular economy [80]

This concept proposes the implementation of EC technology for the effective removal of pollution from municipal wastewater, while replacing the need for chemicals like aluminium or iron sulfate. This has the advantage of producing sewage sludge with low sulfur content, which can be tapped for energy production in the form of biogas (CH₄) through biodigestion. Based on this energy resource, incineration of digested sludge could enable the reduction of iron hydroxides, to allow the regeneration of EC sacrificial anode, with concomitant reduction of greenhouse gas emissions, like this:



Furthermore, this concept could be the only feasible solution to the problem of landfills and their vast amounts of biosolids being generated and disposed by nearly every municipal wastewater treatment plant around the world. This analogue concept towards the Direct Iron Reduction DIR of electrolytic hydroxides from EC treatment, still needs further research, since there are several technical constraints that need to be addressed, such as the wet content, removal of trace elements and the recycling of phosphorus, certainly one of the most valuable resources for the years to come.

To provide further insight into this concept, Figure XLVI introduces a typical process flowchart describing the most relevant steps within the proposed zero-waste concept. Like this, municipal wastewater from a community can be cleaned by EC treatment with subsequent biological treatment, enabling safe reuse of water free from bacteria and heavy metals. Then, sewage sludge recovered from EC can be tapped for biogas production in biodigestors, which could deliver the energy for the direct iron reduction.

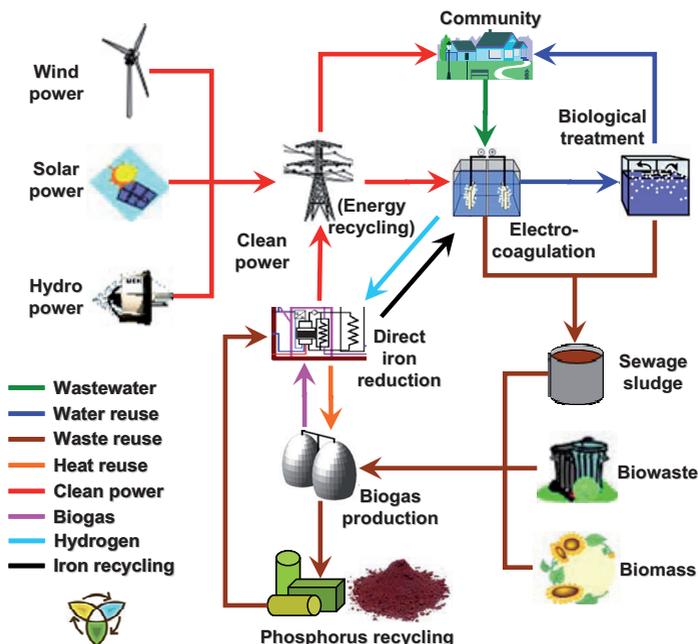


Figure XLVI: Process flowchart of the proposed zero-waste concept based on EC [80]

At this point it is worth noticing four potential synergies from this concept towards direct reduction of iron oxides (dried hydroxides) back into iron sponge material: (1) reducing gas, namely biogas CH_4 , (2) reducing atmosphere, namely hydrogen gas H_2 from EC, (3) heat, enabling water evaporation from sludge prior to reduction, and last but not least, (4) co-generation of electrical power to recycle energy from combustion process. In addition to the challenges of these four potential synergies, further research can be anticipated on the hydrometallurgical routes enabling phosphorus recycling and removal of trace elements (heavy metals) from digested sludge, prior to incineration.

Even though this zero-waste concept proposes quite ambitious tasks (like trying to kill three birds with one stone), solving pollution of water, tapping unconventional and yet renewable energy sources, and enabling reuse and recycling of valuable resources, these are certain ways in which sustainability will be seen for future generations, if they still want to survive with the limited resources of the only planet Earth available.