Subject Area 5.1: Microbial studies and technologies supporting waste disposal, management, and remediation of municipal and industrial hazardous wastes

Research Article

Feasibility Assessment of Electrocoagulation Towards a New Sustainable Wastewater Treatment*

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DOI: http://dx.doi.org/10.1065/espr2007.05.424

Please cite this paper as: Rodriguez J, Stopić S, Krause G, Friedrich B (2007): Feasibility Assessment of Electrocoagulation Towards a New Sustainable Wastewater Treatment. Env Sci Pollut Res 14 (7) 477–482

Abstract

Background, Aim and Scope. Electrocoagulation (EC) may be a potential answer to environmental problems dealing with water reuse and rational waste management. The aim of this research was to assess the feasibility of EC-process for industrial contaminated effluents from copper production, taking into consideration technical and economical factors. EC-technology claims to offer efficient removal rates for most types of wastewater impurities at low power consumption and without adding any precipitating agents.

Materials and Methods. Real wastewater from Saraka stream with high concentrations of heavy metals was provided by RTB-BOR, a Serbian copper mining and smelting complex. Runs were performed on a 10 l EC-reactor using aluminum plates as sacrificial electrodes and powered by a 40 A supply unit. Results concerning key factors like pH, conductivity and power consumption were measured in real time. Analysis of dissolved metal concentrations before and after treatment were carried out via ICP-OES and confirmed by an independent test via AAS.

Results. Several aspects were taken into account, including current density, conductivity, interfacial resistivity and reactor settings throughout the runs, in order to analyze all possible factors playing a role in neutralization and metal removal in real industrial wastewater.

Discussion. Electrode configurations and their effects on energy demand were discussed and exemplified based on fundamentals of colloidal and physical chemistry.

Conclusions. Based on experimental data and since no precipitating agents were applied, the EC-process proved to be not only feasible and environmentally-friendly, but also a cost-effective technology.

Recommendations and Perspectives. The EC-technology provides strategic guidelines for further research and development of sustainable water management processes. However, additional test series concerning continuous operation must be still performed in order to get this concept ready for future large-scale applications.

Keywords: Aqueous chemistry; electrocoagulation; energy demand; metals removal; sustainability; wastewater treatment

Introduction

Despite the fact that electrocoagulation (EC) technology was patented a century ago [1], the absence of any significant know-how concerning this technology is quite disappointing. Given the world water crisis forecasted by UNO and the World Water Council, there are reasons to believe that by 2020, 17% more water than is readily available will be required in order to feed the world [2]. Therefore, the urgent need for sustainable solutions is recognized. While EC-systems provide environment-friendly and cost-effective results for sustainable water reuse, it is disconcerting to realize how many places in the world still remain using freshwater for cleaning purposes.

Furthermore, using renewable energies to operate EC-process would avoid any concern related to global warming due to the electrical power from fossil resources. Since metallurgical wastewater treatment is one key aspect involving hydrometallurgy, this research in EC-technology carried out over the few last years at IME, provides an improvement to former attempts in this field. The drawbacks and opportunities of EC-method were technically and economically assessed, including the neutralization and removal of heavy metals, within current discharge requirements as stipulated by law.

1. State of the Art

1.1 Generalities

The operating principle behind electrocoagulation involves colloidal chemistry concepts, dealing with the formation, characterization and modification of colloids. Those particular structures with singular properties, with sizes within the 1 nm to 1 μm range, are considered big enough to disregard quantum mechanical effects, but conserving largely the thermodynamical properties of the bulk [3]. The passage of dispersed colloidal particles through typical membrane filters is much more restricted than the passage of dissolved ions or molecules which get absorbed by means of surface bound OH-groups and then it becomes easier to separate them from a solution.

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Since colloidal wastewater contaminants (organic and inorganic) are retained in solution due to their charged surfaces (ξ-potential), opposite charged ions are required to absorb on the particle surface in order to effect a destabilization with concomitant agglomeration and precipitation. To achieve this, solid aluminum is dissolved anodically into a hydroxide gel or coagulant by means of an electric current within three stages: *hydrolysis*, followed by *condensation* and *complexation* of agglomerates [4].

1.2 Disadvantages of conventional technology

Neutralization and precipitation as hydroxides is currently the most widespread industrially used technology for the removal of heavy metals from wastewater. Hydroxide precipitation of soluble heavy metals can be effected by adding bases such as caustic soda NaOH or lime $Ca(OH)_2$ as the most readily available precipitating agents, converting ions to relatively insoluble metal-hydroxides [5]. A major disadvantage of this method is due to the fact of adding impurities like sodium in order to decrease hydrogen ion concentration (**Fig. 1**), polluting effluents and impeding their reutilization in industrial process cycles. In addition, sludge disposal becomes complex since there are no cost-effective issues for metal recycling from residual Na-hydroxide.

1.3 Proposed electrocoagulation mechanism

An EC-reactor is an arrangement of metal plates, based on sacrificial anodes, which get dissolved into water as ions by means of an electric current. Previous research in aqueous chemistry has shown that polynuclear formation of hydroxyl-aluminum particles is a stepwise process involving a deprotonation-dehydration mechanism (**Fig. 2**), resulting in the formation of six-membered rings, which may further coalesce by the same mechanism [7].

As a working hypothesis $Al^{3+}_{(aq)}$ ions are formed in a first step (**Eq. 1**). At the cathode hydrogen is evolved with formation of OH^- (**Eq. 2**) thereby raising the pH of the solution, which leads to hydrolysis and condensation of $Al(H_2O)_6^{3+}$ in a stepwise fashion (**Eq. 3**) through $Al_2(OH)_2(H_2O)_8^{4+}$, $Al_6(OH)_{12}(H_2O)_{12}^{6+}$, $Al_{10}(OH)_{22}(H_2O)_{16}^{8+}$, $Al_{24}(OH)_{60}(H_2O)_{24}^{12+}$ [8] leading finally to an amorphous insoluble polymeric hydroxide $[Al(OH)_3]_n \cdot (H_2O)_x$.

$$Al_{(s)} + 6H_2O \rightarrow Al(H_2O)_6^{3+} + 3e^- \tag{1}$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{2}$$

$$2Al(H_2O)_6^{3+} \rightarrow Al_2(OH)_2(H_2O)_8^{4+} + 2H_3O^+ \tag{3}$$

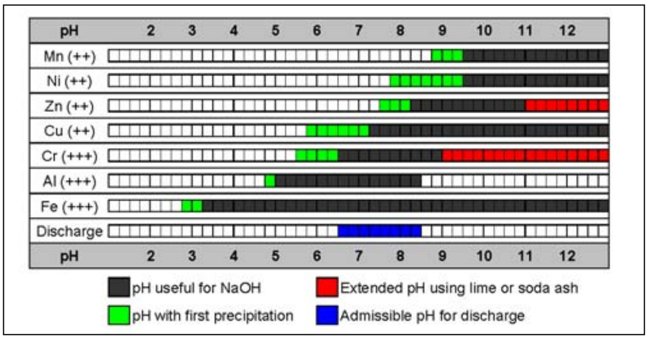

Fig. 1: pH ranges for metal precipitation with NaOH [6]

Besides being known as an effective mordant, aluminum hydroxide is also an important adsorbent of organic and inorganic ions, molecules and colloidal particles [8]. Based on this adsorption property, a mechanism known as Ostwald-Ripening in colloidal chemistry, is responsible for small particles in heterogeneous colloidal dispersions to decrease in size and disappear at the expense of larger ones [3]. The final product is a colloidal agglomerate based on hydroxide bridges shown as hexahedrons (see Fig. 2), which binds and helps to precipitate impurity particles. This enlarged impurities, cations which did not reach the cathode area as well as some other inorganic and organic species, become easier to retain during filtration.

The synergetic effects of EC-technology minimize the need for precipitating agents, enabling water reuse and reducing the amount of residual sludge, thus providing additional reasons to upgrade wastewater treatment processes. As a matter of fact, current implementations of EC-systems used in washwater treatment or wash rack applications provide ecological and economical benefits, while detergents and soaps remain in effluents for reuse.

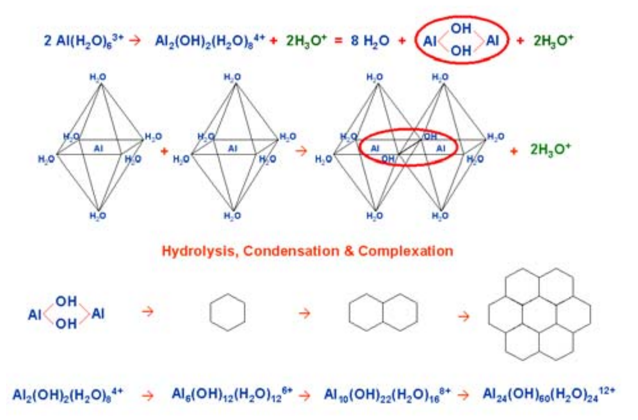

Fig. 2: Proposed EC-mechanism in aluminum-based systems

2 Materials and Methods

Experiments were run at IME hydrometallurgy lab, on a test facility engineered for this purpose (**Fig. 3**). The EC-

Fig. 3: Electrocoagulation system at IME RWTH-Aachen, Germany

system was tested on small-scale using real wastewater from Saraka stream provided by RTB-BOR, a Serbian mining and smelting complex. Samples were taken before and during runs. Metal concentrations were determined via ICP-OES method at IME chemical lab. Results were confirmed by an independent analysis via AAS method, supplied by the chemical lab at the Institute for Inorganic Chemistry IAC at the RWTH Aachen University.

Fig. 3 shows most significant parts of equipment being:

1. **EC-reactor**: 10 l Plexiglas tank (200x210x245mm^3).
2. **Power supply**: EA-PS7016-400, 0-16V DC, 0-40A.
3. **Conductivity meter**: WTW-LF197-S with probe head.
4. **pH meter**: WTW-pH197i with temperature indicator.
5. **Power measurement:** Protek 506 with serial data port.
6. **Data acquisition:** software from Protek on IBM T23.
7. **Pretreatment unit:** 10 l capacity with magnetic stirrer.
8. **Filtration unit:** paper-based with sludge bifurcation.

Table 1 presents the composition of industrial effluents (Saraka wastewater) provided by RTB-BOR.

Table 2 summarizes relevant parameters of the test runs and the aluminum consumption reported after treatment.

Test runs T2 and T3 prove power consumption related to the gap or distance between electrodes. T4, T5 and T6 provide information on the efficiency of the treatment with regard to the electrode surface area given by the number of electrodes. In T9 and T10 optimization of the EC-process with respect to current density, electrode geometry and temperature, was attempted.

Table 1: Composition of Saraka wastewater from RTB-BOR (pH=4.3)

Element [Symbol]	Copper [Cu]	Aluminum [Al]	Manganese [Mn]	Sulfate $[SO_4^{2-}]$
Concentration [mg/l]	50	13	6	560

Table 2: Parameters of the test runs with initial pH=4.3

Test No.	Elect No.	Gap [mm]	Area [m^2]	Cur. Den. [A/m^2]	Final pH	Al-use [g]
T2	12 (reg.)	8	0.80	15	7.0	9.9
T3	12 (reg.)	18	0.80	15	6.8	8.6
T4	24 (reg.)	8	1.60	15	6.3	22.8
T5	18 (reg.)	8	1.20	15	6.5	21.4
T6	12 (reg.)	8	0.80	15	7.0	21.3
T9	12 (reg.)	8	0.80	30	4.9	17.0
T10	12 (perf.)	8	0.57	30	7.1	10.7

3 Results and Discussion

The main objective of this lab-scale feasibility study was to find optimal parameters to neutralize metallurgical wastewater using different configurations and evaluating their efficiency in terms of metal removal rate and energy demand. Starting from concentrations of Cu (50 mg/l), Al (13 mg/l) and Mn (6 mg/l), discharge requirements as regards final metal concentrations of less than 1 mg/l and a pH value in the neutral range were met.

3.1 Effect of electrode material on metal removal and pH

Based on previous research, two different electrode types, aluminum (Al) and iron (Fe), were selected. Although Fe electrodes had shown satisfactory removal rates in the treatment of leachates containing pulp and paper mill [9], results obtained in metallurgical wastewater treatment were unsatisfactory. It seems that stronger basic polymeric $Al(OH)_3$ as opposed to ferrihydride is more effective in metal ion absorption. This may be due to the more acidic pK_a of $Fe(III)_{(aq)}$ aqua ion (2.2) as opposed to $Al(III)_{(aq)}$ (5.2), which prevented a significant change in pH. Thus the raise in hydroxide ion concentration was insufficient for the destabilization and removal of metal cations M^{2+}.

On the other hand, Al-electrodes have provided excellent results not only for neutralization, but for metal removal rates as well, achieving a pH increase from 4.3 to neutral range (pH=7) in about 40 to 45 minutes (**Fig. 4**), reaching removal rates over 99.1% (average), Cu < 0.005 (99.9%), Al = 0.3 (97.7%) and Mn = 0.02 (99.7%), in mg/l each.

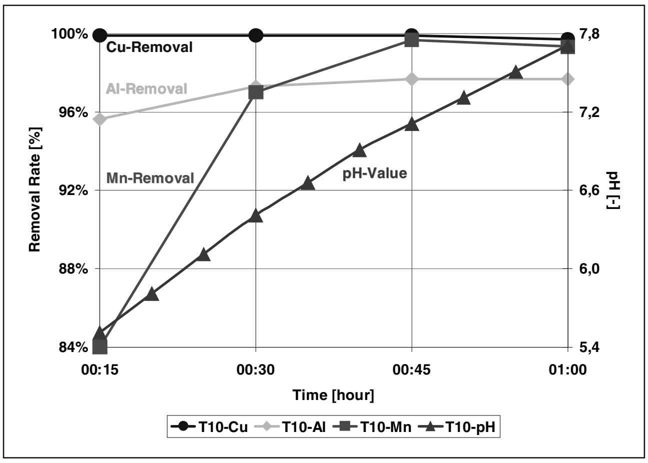

Fig. 4: Effect of Al-electrodes on metal removal and pH

3.2 Effect of neutralization on wastewater conductivity

Before assessing EC-process efficiency in terms of energy demand, one must consider the effect that neutralization induces on solution conductivity. Ultra pure water is used in industrial applications as insulator with conductivity values below 0.06 µS/cm. In contrast to metallurgical wastewater, conductivity values are above 1000 µS/cm. This is due to dissolved salts and metals, which beside to other impurities like atmospheric carbon dioxide for instance, contribute substantially to increase conductivity (e.g. domestic tap water conductivity is about 250 µS/cm).

A gradual decrement of conductivity was observed during neutralization, with a value decreasing from 1350 down to 390 µS/cm (**Fig. 5**). Though conductivity does not play an important role for discharge requirements, it does for operational costs since power consumption increases inversely proportional to it (**Fig. 6**).

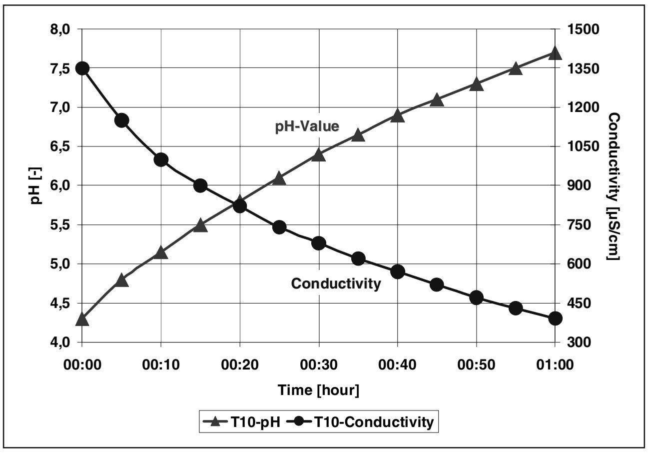

Fig. 5: Effect of neutralization on wastewater conductivity

3.3 Effect of wastewater conductivity on energy demand

A significant part of the energy demand in the EC-process is attributable to a decrement of conductivity value in the solution, notably at the end of a run, though the fraction of energy consumed by the interfacial resistance related to anodic metal dissolution (faraday energy) still exerts the major part of the overall power consumption.

From the extrapolation of curve T10-PT(ideal) in **Fig. 6**, neglecting the overshoot during the first 30 minutes in T10-PT(real), and since current density is set constant during runs, the total resistance from the electrical current value is derived using Ohm's law (RT=PT/I^2). RT is also equal to the sum of the specific solution resistance (RS), and the interfacial resistance at the electrodes surface (RE). Since RE cannot be easily determined by physical means, it is possible to assume RE=RT-RS, where RS is given by the measured wastewater conductivity (C), and the dimensions of the electrode array (RS=gap/area*C).

The small deviations presented in the real power consumption T10-PT(real) in Fig. 6, are traced back to the fact that sampling points taken during runs induced changes to the system response.

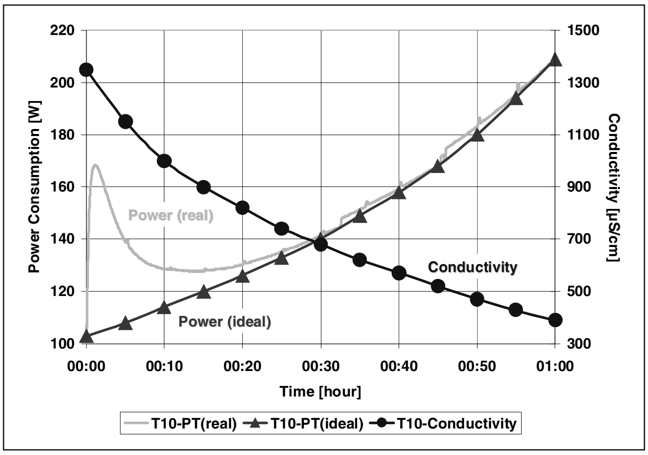

Fig. 6: Effect of wastewater conductivity on energy demand

3.4 Effect of interfacial resistivity on energy demand

Due to the phase transition from liquid wastewater to the solid electrodes, an interfacial resistance is introduced in the space region covering the Helmholtz layer as well as the steeper part of the Guy-Chapman layer, which exerts an additional opposition to the electric current flow [10]. Taking this concept into consideration and the electrical description of an electrode array as outlined above (RT=RS+RE), **Fig. 7** illustrates the partition of total energy demand due to changes of solution (RS) and interfacial resistivity (RE) and total resistance (RT) throughout a run.

According to Fig. 7 one may conclude that nearly 40% of the dynamic energy demand is attributable to an increase of solution resistivity T10-RS, while 60% went at the expense of interfacial resistivity and its increasing resistance T10-RE, due to the fact that a portion of cations is removed by electrodeposition on the cathode plates.

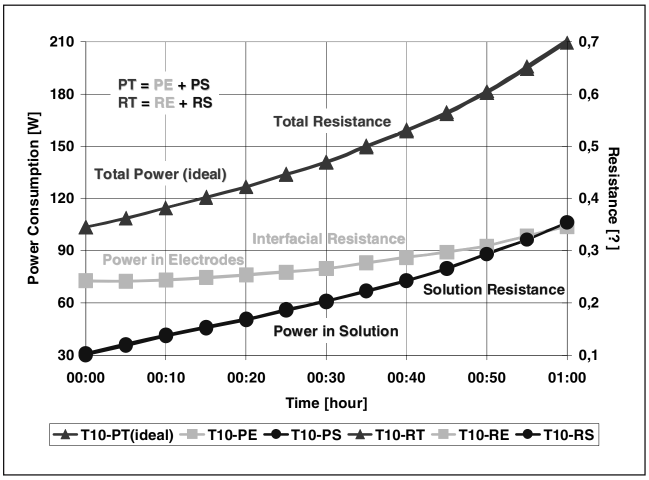

Fig. 7: Effect of interfacial resistivity on power consumption

3.5 Effect of electrode gap on energy demand

Concerning issues related to process efficiency influenced by reactor design, in particular cell ratios from electrode configurations, it is necessary to describe their effects on power consumption and metal removal. One of the first experiments in the search for optimal operating parameters was to establish the gap or space between the electrodes.

From results obtained in test runs with 12 Al-electrodes setting gaps between 8 mm (T2) and 18 mm (T3), using the same wastewater and current density (15 A/m^2), power consumption and voltage in **Fig. 8** show a 40% energy demand increase, from 60 (T2) to 100Wh (T3) on increase of electrode gap, thus allowing to select 8mm as the optimum separation for similar neutralization reactions.

3.6 Effect of electrode area on pH and energy demand

The next target was to determine the amount of electrode pairs necessary for effective neutralization. For this reason, test runs were conducted using 24 (T4), 18 (T5) and 12 Al-

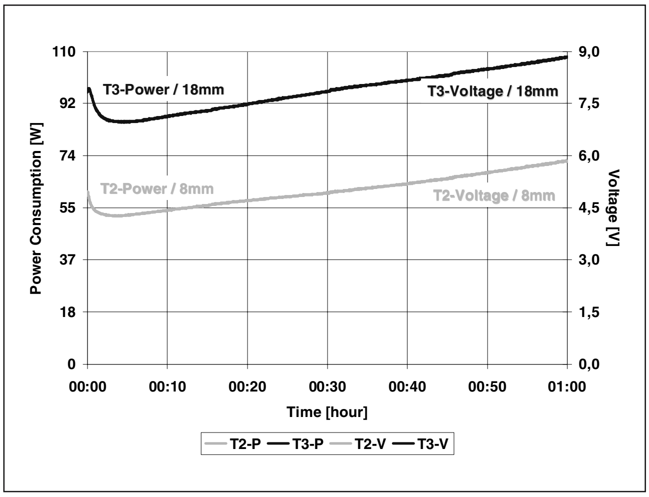

Fig. 8: Effect of electrode gap on power consumption

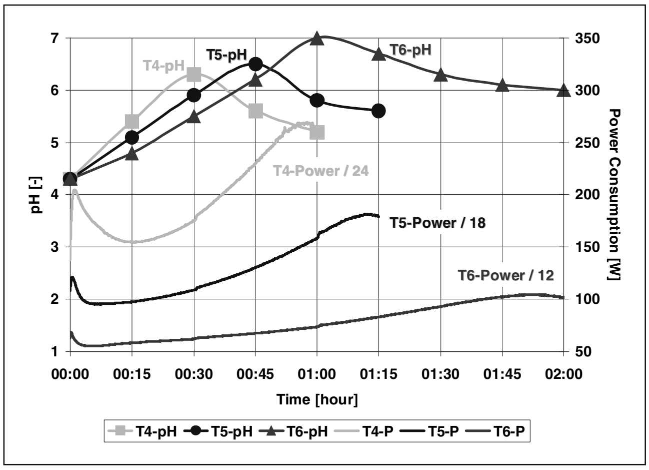

Fig. 9: Effect of electrode surface on pH and power consumption

electrodes (T6), with otherwise identical parameters (electrode gap 8mm, current density 15A/m², the same wastewater). Since electrodes are connected in parallel, more electrode pairs simply increase the total surface area.

By using an array of 12 electrodes pH=7 was reached after 1 hour with a total energy demand of 63.2 Wh, while arrays of 18 and 24 electrodes lead to a maximum pH value of 6.5 and 6.3, with total energy demand of 116.1 Wh and 197.7 Wh respectively (**Fig. 9**). Shortly after reaching their maximum pH value, solutions also reached saturation in Al-hydroxide. This state resulted in a modification of all operating conditions with loss of current voltage linearity from Ohm's law as well as an increase in temperature rises, leading to many other undesirable effects.

3.7 Effect of temperature on metal removal

As conductivity decreases temperature rises. Under galvanostatic conditions an increase in solution resistance leads to higher voltage and thus greater power consumption (V=I*R). While current is set to drive constant, voltage increases as resistance does, forcing the system to dissipate extra power (P=V*I) in the very same space mostly as heat, leading to a temperature increase (**Fig. 10**).

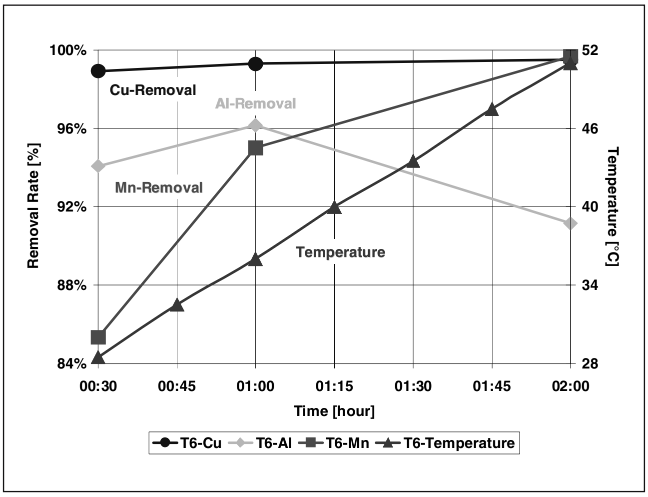

Fig. 10: Effect of temperature on metal removal

Regarding this increase of temperature, it was observed that part of the precipitated Al-hydroxide is redissolved, as shown by T6-Al after one hour (Fig. 10). For this reason, EC-process should never be run up to saturation.

3.8 Effect of flow direction on pH and temperature

A strategy to avoid sizeable temperature gradients in the bath was to improve the flow characteristic in EC-reactor. A better circulation of the solution should lead to more effective results in terms of retention time and metal removal, and thus helping to meet discharge requirements faster, improving parameters towards continuous operation.

Interpreting data in **Fig. 11**, a change of vertical streaming (T9 using regular electrodes), to a horizontal one (T10 using perforated electrodes), otherwise applying the same electrical and geometrical parameter basis (8 mm, 30A/m², the same wastewater), this change led to an improvement of

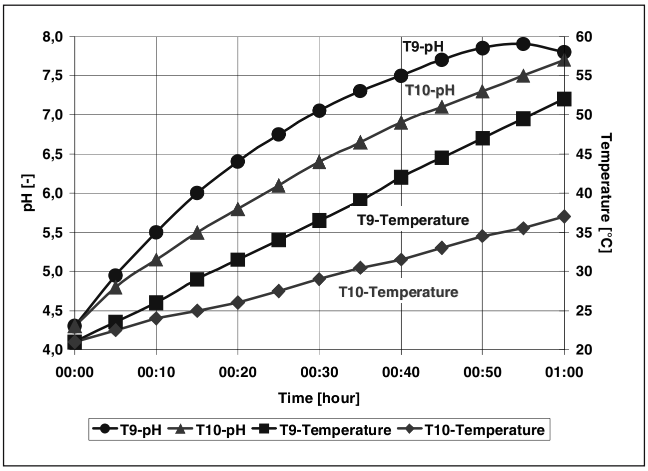

Fig. 11: Effect of flow direction on pH and temperature

temperature gradient from 0.50°C/min (T9) down to 0.25°C/min (T10). A temperature overshoot above 35°C at neutral pH effected a negative outcome for T9, namely a failed neutralization detected after filtration (pH <5).

3.9 Effect of current density on metal removal

While in chemical precipitation, dosage of base required to neutralize effluents is done by means of pumps [11], in electrocoagulation it is the current density (A/m^2) that determines dosage rate for the release of aluminum ions required to form Al-hydroxide. Equally, cathodic hydrogen evolution and metal deposition increase proportional to the electric field strength, driven also by the current density.

Comparing metal removal rates in Fig. 4 and 10, a slight improvement in average removal rate from 96.8% (T6) to 99.1% (T10) was observed at neutral pH of 7 after 60 and 45 minutes respectively. Since current density was doubled, from 15 (T6) to 30 A/m^2 (T10), it is possible to accelerate metal removal, but temperature issues like failed neutralization or redissolutions must be handled with care.

3.10 Energy demand and operational facts

Based on a techno-economical comparison performed on the same metallurgic wastewater provided by RTB-BOR using chemical precipitation (CP) and EC-process [12], both with 12.5 l/h effective flow rate, a roughly estimation of 110 m^3 can be treated yearly while meeting discharge requirements (metal concentrations below 1 mg/l, pH=7).

Based on concentration analyses carried out via ICP-OES, both CP and EC-process met the discharge requirements. However, the presented technical and economical facts all together provide enough evidence about the sustainability and superiority of EC-process over chemical precipitation. **Table 3** compares figures regarding energy demand and operational facts (neglecting assets and personal costs), between chemical precipitation using the cascade line and EC-process for cleaning the same metallurgic wastewater.

Table 3: Energy and operational facts between CP and EC [12]

Parameter	Chemic. Precipitation	Electrocoagulation
Effective flow rate	12.5 l/h	12.5 l/h
Annual capacity	110 m^3/y	110 m^3/y
Material used	Sodium liquor (NaOH)	Aluminum plates (Al)
Material cost	0.25 €/l (NaOH-1M)	4 €/kg (Al-plates)
Material used / m^3	40 l (NaOH-1M) / m^3	1 kg (Al) / m^3
Material cost / m^3	10 €/m^3	4 €/m^3
Annual material cost	1,100 €/y	440 €/y
Energy demand	60 Wh (agitator, pump)	125 Wh (EC-reactor)
Energy demand / m^3	4.8 kWh/m^3	10 kWh/m^3
Annual energy cost	106 €/y (0.2 €/kWh)	220 €/y (0.2 €/kWh)
Annual treatm. cost	1,206 €/y	660 €/y
Treatment cost / m^3	11 €/m^3	6 €/m^3

4 Conclusions and Perspectives

From the results of these studies, electrocoagulation may prove to be not only feasible and environmentally-friendly, but also technically and economically superior to conventional technology like chemical precipitation.

However, employing an EC-reactor is not simple. There are many parameters to be adjusted and optimized for a more reliable and cost-effective operation regarding neutralization and metal removal. Moreover, test series must be performed using different configurations and settings before EC-technology can become widely accepted for industrial applications. Therefore, testing and improvements involving continuous operation, for industrial and municipal wastewater treatment applications, will be subject of future research.

Acknowledgements. We would like to thank the European Commission for the financial support on the project INTREAT, INCO-CT-2003-509167, as well as Prof. Dr. Ulrich Koelle from the Institute for Inorganic Chemistry IAC and PD Dr. Michael Schroeder from the Institute for Physical Chemistry IPC at RWTH Aachen University, for their kind and valuable scientific support.

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Received: February 27th, 2007
Accepted: June 7th, 2007
OnlineFirst: June 8th, 2007