Continuous Electrocoagulation Treatment of Wastewater from Copper Production

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Based on a former study regarding the use of electrocoagulation for treating metal containing effluents from copper production, the aim of the present study was to improve the economic feasibility concerning a continuous operation. Tests were carried out on a 10 L EC-reactor, using extrapolated parameters from a feasibility assessment performed in batch runs prior to this work. Electrocoagulation provides enough evidence of being not only environment-friendly and cost-effective, but also well suited for almost any kind of wastewater, even for sewage. All this can be employed at low or no chemical dosage and above all, with very low energy demand requirements. Findings on last development as well as an outlook for future research work are here presented.

Keywords:

Electrocoagulation – Energy demand – Heavy metal removal, – Precipitation – Sustainable wastewater treatment

Kontinuierliches Elektrokoagulationsverfahren zur Reinigung von Abwasser der Kupferproduktion

Basierend auf vorhergegangenen Untersuchungen zum Einsatz der Elektrokoagulation für die Abwasserreinigung im Rahmen der Kupferproduktion war das Ziel der vorliegenden Untersuchung eine ökonomische Optimierung bezüglich eines kontinuierlichen Betriebs. Die Experimente wurden anhand extrapolierter Parameter aus dem Batch-Betrieb in einem 10-Liter-Reaktor durchgeführt. Die Elektrokoagulation besitzt das Potential für hohe Umweltfreundlichkeit und Wirtschaftlichkeit für fast alle Arten von Abwasser, sogar im kommunalen Bereich. Der Prozess benötigt wenig oder gar keine Zugabe von Chemikalien und vor allem ist der Energieverbrauch sehr niedrig. Ergebnisse aus dem aktuellen Stand der Arbeiten am IME sowie die zukünftig geplante Forschung werden vorgestellt.

Schlüsselwörter:

Elektrokoagulation – Energieverbrauch – Fällung – Nachhaltige Abwasserreinigung – Schwermetallentfernung

Procédé d'electrocoagulation en contínu pour le traitement des eaux usagées dans la production du cuivre

Tratamiento continuo de electrocoagulación para aguas residuales de la producción de cobre

1 Introduction

Funded by the European Commission the INTREAT project, "Integrated treatment of industrial wastes towards prevention of regional water resources contamination" addresses research and development of novel and sustainable treatment methods for contaminated effluents [1]. As an active belonging member, IME is engaged with an international workgroup for the prevention of regional water resources contamination in the Balkan area, combined with an initiative for improving former attempts in the field of metal recycling done over the last years. Facing a need for environment-friendly and cost-effective solutions, a relative old and quite unpopular method known as electrocoagulation (EC) was assessed for treating metal containing effluents from copper production. The aim was to provide a sustainable wastewater treatment, which should also be able to meet challenges, like water reuse, hydric resources will face within the next years. Based on satisfactory results from a feasibility assessment carried out for batch operation, the present study explored the technical and economical viability from EC-process concerning a continuous operation. Tests series were implemented using real metallurgical wastewater supplied by RTB-Bor, a Serbian mining and smelting complex.

2 Water insights

Besides global warming, world water crisis is named to be the most worrying challenge human race will face in the fight for survival. With about two-thirds of Earth's surface covered by water, most is too salty for direct use (Figure 1). According to the World Health Organization less than 0.007 % of all the water on Earth, is readily available for anthropogenic activities [2]. With almost 70 % of water resources being used in agriculture, the World Water Council

believes that by 2020, 17 % more water than is available will be required in order to feed the world [3].

In regard to this scary forecast, there is no wonder why environmental protection technologies around desalination and water reuse processes have become more and more important lately. Regarding competing water uses (Figure 2), it is remarkable how essential water resources are for high-income industrial economies, and the compromise these industrializers got in protecting the economy of developing countries, mostly agricultural based. After all, with nearly 70 % of water resources required in agriculture it is irrational not to care for food on a shared ecosystem.

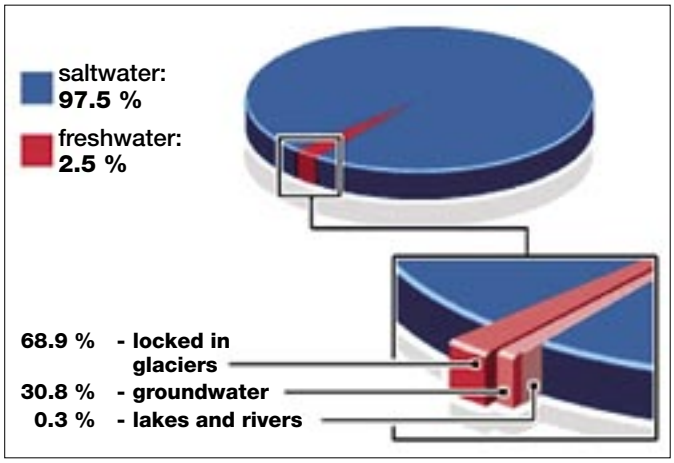

Fig. 1: Worldwide water supply [2]

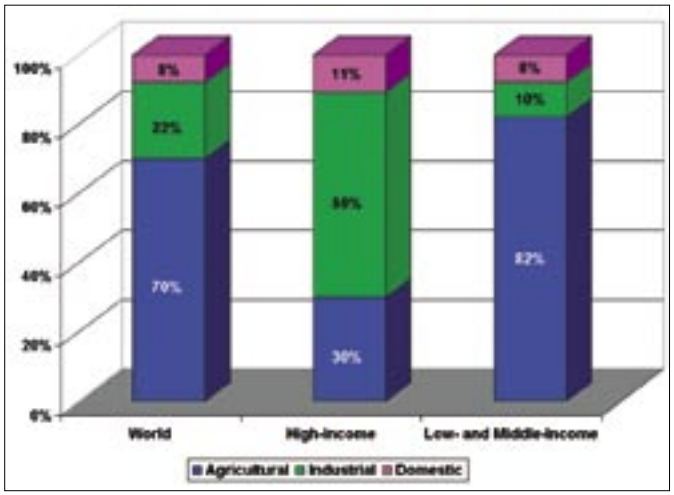

Fig. 2: Competing water uses for main income groups of countries [3]

3 Disadvantages of conventional technology

Precipitation is currently the most widespread industrial used technology as regards neutralization and metal removal. Hydroxide precipitation of soluble heavy metals can be reached by adding alkali-precipitating agents, where ions are converted to relatively insoluble metal-hydroxide precipitates, with caustic soda NaOH and lime $Ca(OH)_2$ as the most usual hydroxide-agents available [4]. A major disadvantage of this technology relies on the fact of adding impurities like sodium, in order to decrease hydrogen ion concentration (Figure 3), polluting effluents and impeding its reutilization in industrial process cycles. As a matter of fact, even sludge disposal turns complex, since there are no cost-effective issues for metal recycling.

4 Aqueous chemistry behind electrocoagulation

An EC-reactor is a simple arrangement of metal plates, which by means of electric current, get dissolved into water as charged ions, being responsible for neutralizing and required for destabilizing suspensions [6]. Production of polynuclear hydroxyl-aluminum particles is considered as a stepwise process involving deprotonation/dehydration mechanisms resulting in formation of six-member rings that may further coalesce by same mechanism [7] (Figure 4).

As a qualified electrochemical method, EC-technology enables the synergies from two powerful processes working on parallel to guarantee better results concerning neutralization and metal removal in industrial wastewater. On one hand, by means of electric field, electrochemical deposition takes place at the cathode, acting as a magnet, rapidly pulling all dissolved cations out from the solution.

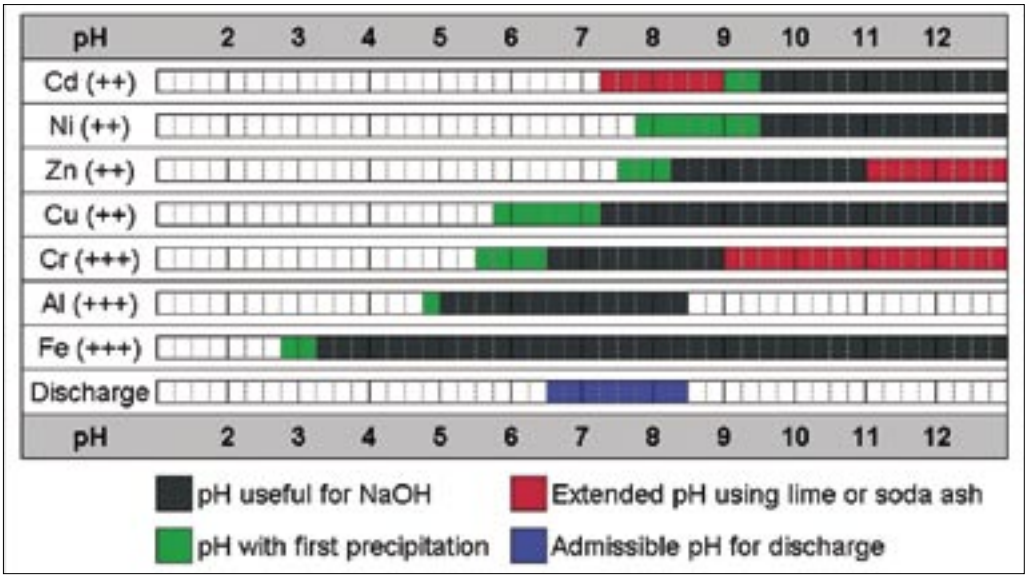

Fig. 3:
pH ranges for metal precipitation with NaOH [5]

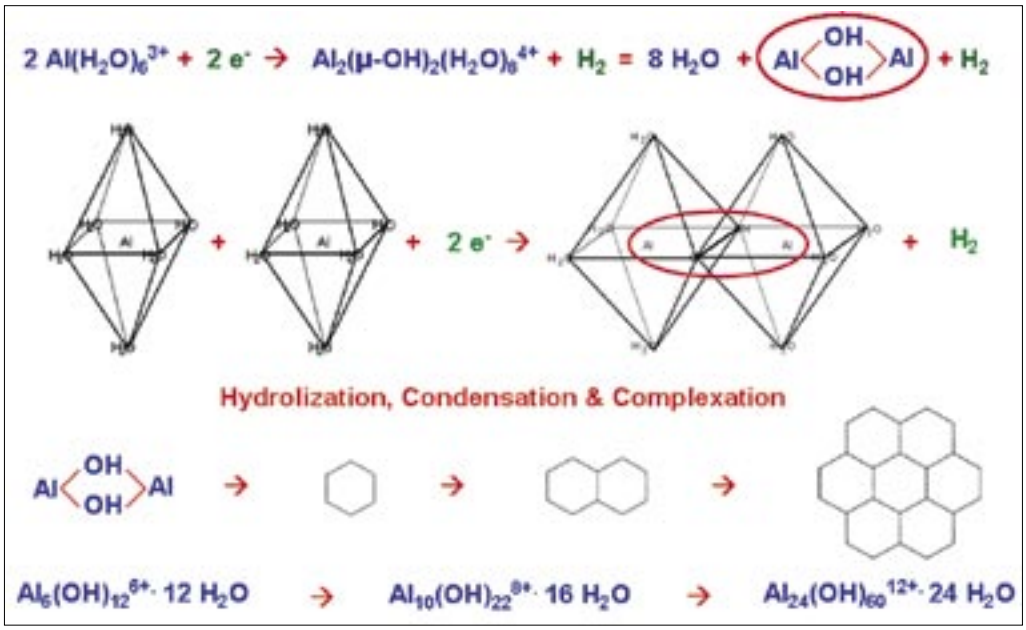

Fig. 4:
Proposed EC-mechanism in aluminum-based systems [6]

On the other hand, as byproduct from a hydrolysis, metal hydroxide flows from the anode into water, responsible for decreasing hydrogen ion concentration, providing an inexpensive neutralization, enabling like this a superior method to meet discharge requirements cost-effectively.

5 Materials and methods

Test series were conducted at IME hydrometallurgy lab in lab-scale using metal containing effluents supplied by RTB-Bor, a Serbian mining and smelting complex. Financially supported by INTREAT, this research looked for prevention alternatives as regards to water resources contamination at the river basin Saraka, where wastewater is discharged. Table 1 summarizes the effluents composition.

Tab. 1: Composition of Saraka wastewater from RTB-Bor (pH = 4.3)

Element	Copper (Cu)	Aluminium (Al)	Manganese (Mn)	Sulfate (SO_4^{2-})
Concentration [mg/L]	50	13	6	560

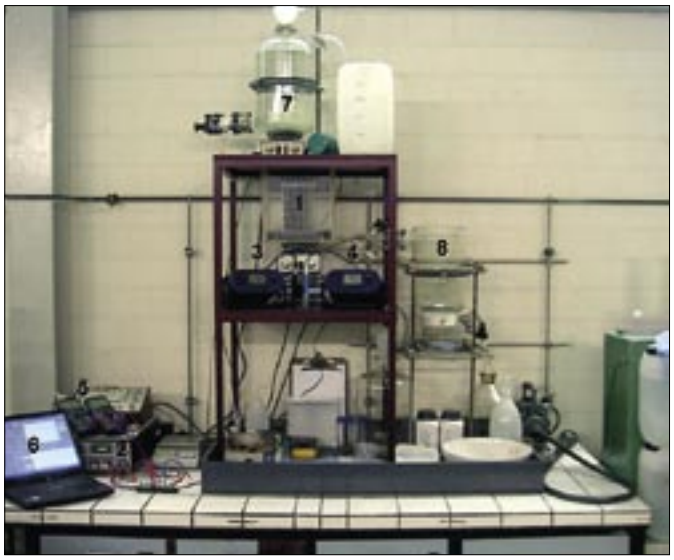

Fig. 5: Electrocoagulation system at IME RWTH-Aachen, Germany

Figure 5 presents the implemented electrocoagulation set up. In regard to used equipment, the most important parts are:

1 EC-reactor: 10 L-plexiglass tank ($200 \times 210 \times 245$ mm³),
2 Power supply: EA-PS7016-400, 0-16 V DC, 0-40 A,
3 Conductivity: WTW-LF197-S with probe head,
4 pH meter: WTW-pH197i with T-indicator,
5 Power control: Protek 506 with serial data port,
6 Data acquisition: Software from Protek on IBM T23,
7 Pretreatment: 10 L capacity with magnetic stirrer,
8 Filtration unit: Paper-based with sludge bifurcation.

The determination of suitable test parameters took place within test series performed in batch run prior to this work [6]. It was found according to Figure 6 as the best configuration, an arrange of six pair of Al-electrodes with total effective area of 0.57 m², powered at a current density of 30 A/m², and a minimum retention time of 15 minutes. Aim of this work was to optimize the EC-process in order to meet discharge requirements running in continuous op-

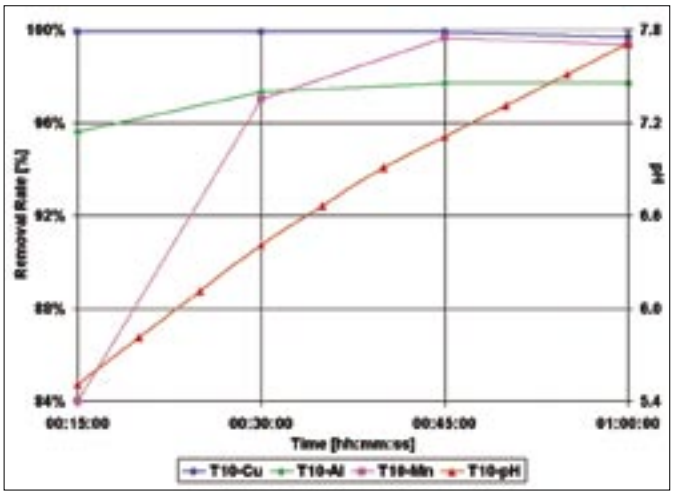

Fig. 6: Metal removal rates on batch operation [6]

Fig. 7: Continuous 3 reactor precipitation line at IME RWTH-Aachen, Germany

eration (metal concentration < 1 mg/L, pH = 7). Analyses were done at IME's chemical lab via ICP-OES.

Figure 7 presents the three reactor used in the precipitation line. The most important parts are:

1 Reactor 1: 10 L glass vessel (pH = 4.3 to 5.7),
2 Reactor 2: 10 L glass vessel (pH = 5.7 to 7.3),
3 Reactor 3: 10 L glass vessel (pH =7.3 to 9.3),
4 Agent dosing: Solenoid pumps BT4a 1005 ProMinent,
5 Stirring: e-drives with speed control (300 rpm),
6 pH-meter: Mettler-Toledo 2100e glass electrode,
7 Storage tank: 200 L capacity for untreated wastewater,
8 Product tank: 200 L capacity for treated effluents.

The retention time in each of the three reactors was about 15 min, while some particles were deposited at the bottom by means of centrifugation (300 rpm). Contrary to the significant change in pH (from 4.3 up to 9.3), a considerable change in temperature was not observed (ΔT = 6 °C).

6 Results and discussion

Table 2 summarizes the parameter settings for the conducted test series concerning the EC-process investigation in a continuous mode. Test series T17, T18 and T19 were intended to investigate the role that electrochemical deposition plays in metal removal, while T20 was intended for improving dynamics based on assumption of t0 ≠ 0 min, meaning a process taking place in the presence of enough aluminum hydroxide, compared to results from T10 after 15 min treatment time.

Tab. 2: Test series parameters for the EC-process on lab scale using 12 electrodes

Test No.	Electrode area [m²]	Time [min]	Flow rate [L/h]	Current density [A/m²]	Energy [kWh]	Al consumption [g/L]
T10	0.57	15	40	30	0.125	0.15
T17	0.57	1	600	30	0.125	0.01
T18	0.57	1	600	50	0.560	0.02
T19	0.57	5	120	30	0.125	0.05
T20	0.57	10	60	30	0.125	0.10

Table 3 summarizes configuration settings for test series concerning the reference conventional precipitation process running also in continuous operation.

Tab. 3: Summary of test series parameters for reference chemical precipitation tests

Test	Effluents treated	Time [min]	Flow [L/h]	Energy [kWh]	Active agent	Agent used	Final pH
CP	9.4 L	45	12.5	0.060	NaOH	0.375L	9.3

Table 4 presents all analyses and their related removal rates found after the EC-process.

Tab. 4: Summary of test results after EC-process found via ICP-OES

Time [min]	pH	Tests	Cu [mg/L]	Cu [%]	Al [mg/L]	Al [%]	Mn [mg/L]	Mn [%]
0	4.3	Origin	50	0	13	0	6	0
1	4.4	T17	32.8	34.4	6.9	46.9	5.2	13.3
1	4.5	T18	30.3	39.4	6.4	50.8	5.1	15.0
5	4.8	T19	22.2	55.6	5.5	57.7	4.9	18.3
10	5.1	T20	0.09	99.8	0.6	95.4	1.4	76.7
15	5.5	T10	0.009	99.9	0.57	95.6	0.97	84.0

Table 5 summarizes all analyses provided by chemical lab and their related removal rates found after treatment in the precipitation line.

Tab. 5: Summary of test results after chemical precipitation found via ICP-OES

Time [min]	pH	~~Test~~	Cu [mg/L]	Cu [%]	Al [mg/L]	Al [%]	Mn [mg/L]	Mn [%]
0	4.3	Origin	50	0	13	0	6	0
15	5.7	~~T17~~	34	32.0	12.3	5.4	5.5	8.3
30	7.3	~~T18~~	0.9	98.2	0.4	96.9	3.3	45.0
45	9.3	~~T19~~	0.9	98.2	0.3	97.7	0.1	98.3

6.1 Effect of aluminum hydroxide dosage on neutralization

Figure 8 shows electrolytic produced Al-hydroxide resulting from the anodic dissolution of aluminum plates by means of an electric current, which provides a comparable neutralization effect as regards chemical precipitation using NaOH.

In order to decrease hydrogen ion concentration towards the neutral range (6.5 ≤ pH ≤ 8.5), hydroxyl-particles (OH^-) dosage is required. Compared to chemical precipitation, the hydroxide dosage ratio in the EC-process is applied by means of current density. The higher the current density the faster Al-hydroxide gets into solution, caused by a process known as hydrolysis, an effect described as material decomposition into water. In doing so, solid aluminum develops into a floc or coagulant in the presence of electric current within three stages [8]: hydrolysis (Formula 1), followed by condensation (Formula 2), ending into a complexation of conglomerates (see Figure 4).

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

$$2Al(H_2O)_6^{3+} + 2e^- \rightarrow Al_2(\mu\text{-}OH)_2(H_2O)_8^{4+} + H_2 \quad (2)$$

Based on observations concerning reactivity from OH^- on hydrogen ion concentrations, even when effluents did not

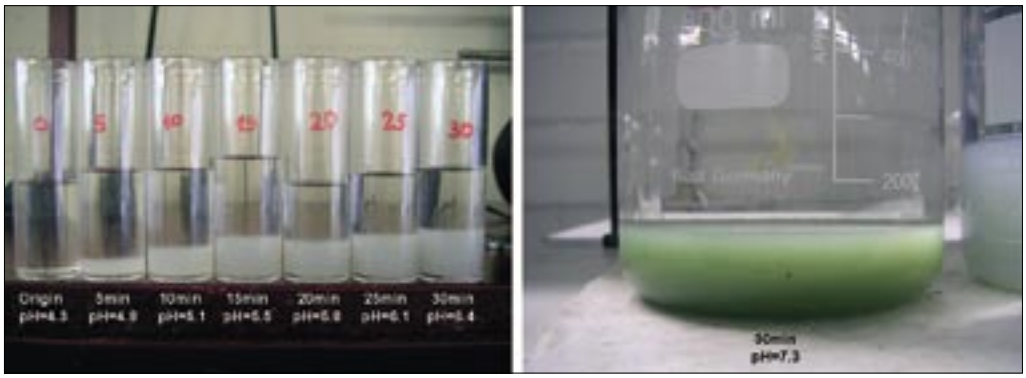

Fig. 8:
left: Sludge from EC-process within the first 30 min of operation; right: Sludge from NaOH dosage after 30 min, both using Saraka wastewater

reach pH range required for discharge after EC-process due to retention times over 30 min (see Figure 6), it was found that residual sludge remained reactive afterwards, pulling pH value towards the neutral range ($6.5 \leq pH \leq 7.5$). Therefore, since neutralization becomes a minor concern and it does not play a major role in metal removal (primary concern) due to electrochemical deposition, this was neglected in order to enhance the process at higher flow rates, improving cost-benefit issues (higher capacity, less consumptions).

6.2 Effect of electrochemical deposition on metal removal

Figure 9 shows a 32 % average removal rate after one minute retention time (test T17 with 600 L/h), while at lower flow rate after 5 min retention time (test T19 with 120 L/min) values ascend to 44 %. Since there is not enough time to reach a significant Al-hydroxide concentration in the solution, effects on metal removal due to the presence of OH^- can be neglected here.

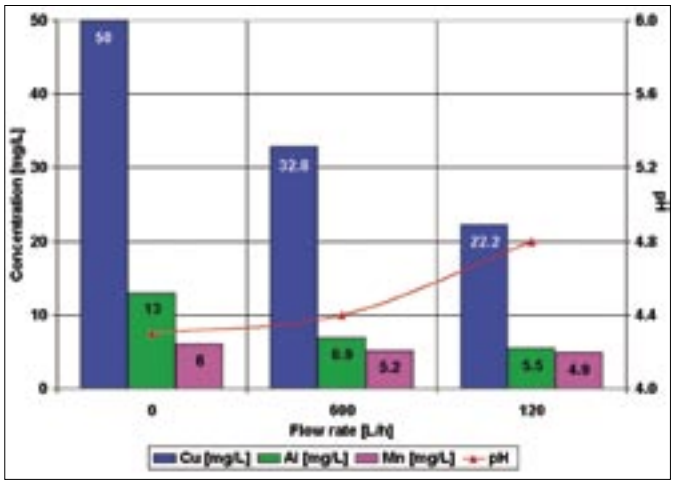

Fig. 9: Effect of electrodeposition at retention times of 1 and 5 min

Being the most significant advantage of EC-process over precipitation, electrochemical deposition largely contributes for the prompt and efficient removal of dissolved metals in metallurgical effluents. However, it does not represent the functional principle behind metal removal as a whole. Since values are far from meeting discharge requirements, it is likely to conclude that flow rates should be lower than 120 L/h for the given reactor, meaning a retention time of effluents higher than 5 min.

6.3 Effect of current density on metal removal

Another aspect under revision was the effect of current density as a force driving electrodeposition at the cathode, which then was expected to influence to a high extent the metal removal rates. Therefore, Figure 10 presents the effect of current density on metal removal for two different trials (T17 = 30 A/m², T18 = 50 A/m²), both at 1 min retention time.

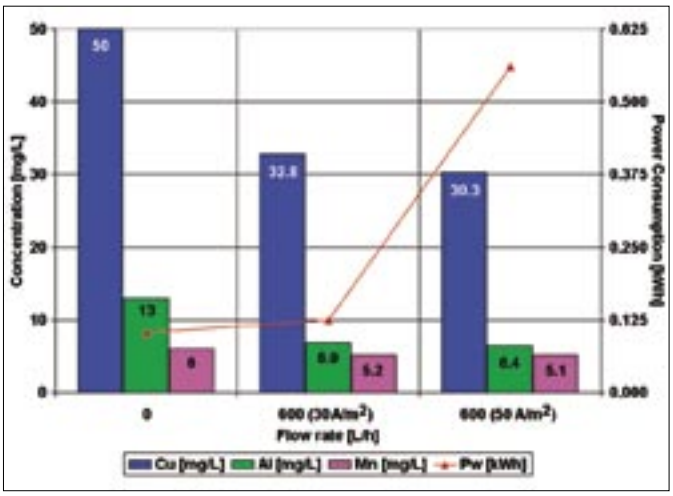

Fig. 10: Effect of current density on metal removal at equal flow rate

From the results it is likely to conclude that higher current densities may have positive influences on electrodeposition effect. But on the other hand, power consumption increases of around 4.5 times for comparable metal removal effects. This may not allow the EC-process to perform cost-effectively.

6.4 Effect of retention time on metal removal

Based on the previously presented results the electrodeposition effect was investigated for very low retention times at different current densities. The fulfillment of discharge requirements (metal concentration below 1 mg/L) was reached for retention times around 15 min (T10 = 40 L/h), and for 10 min (T20 = 60 L/h). So it can be assumed that a EC process taking place in the presence of enough aluminum hydroxide, serves the targets in the first 10 min of operation. Figure 11 only shows a value for Mn just over the limit (1.4 mg/L). By means of few minor upgrades, it is likely to conclude that after a retention time of 10 min EC-process is able to meet discharge requirement for this specific wastewater.

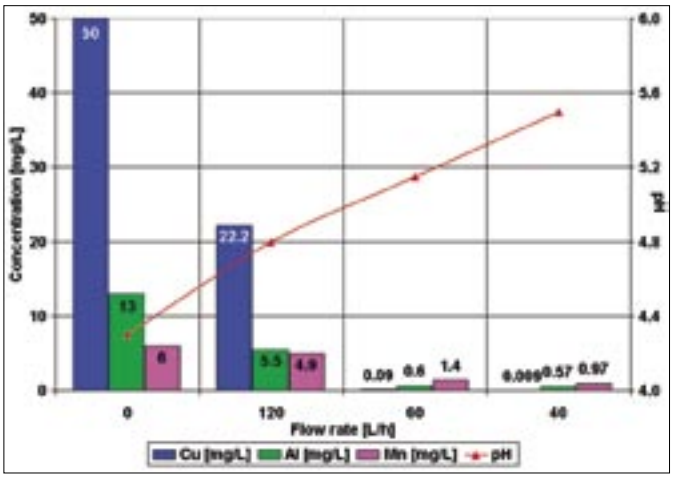

Fig. 11: Effect of retention time for 5, 10 and 15 min on metal removal

6.5 Electrocoagulation vs. chemical precipitation

Figure 12 shows the appearance of sludge recovered from conventional chemical precipitation along a continuous neutralization process.

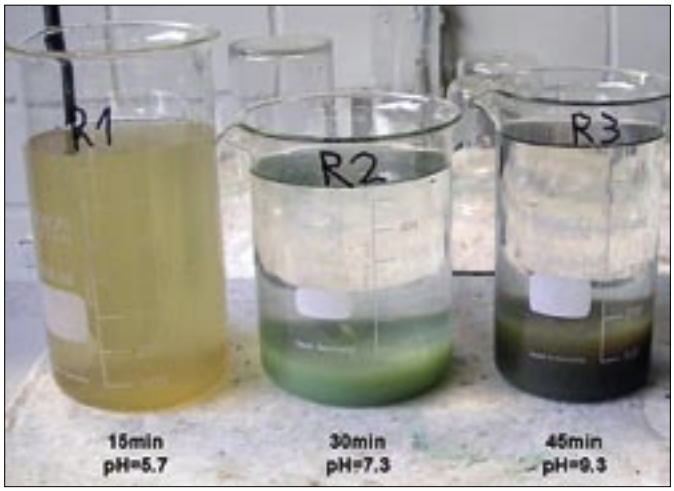

Fig. 12: Sludge resulting from chemical precipitation using NaOH [9]

Precipitation was carried out by means of 1 molar caustic soda dosage (NaOH-1M) and it took around 45 min to meet discharge requirements concerning metal removal (Figure 13). However, since the precipitation range for manganese starts above pH > 8.7 [10], an extra conditioning is required in order to meet neutralization requirement (6.5 ≤ pH ≤ 8.5).

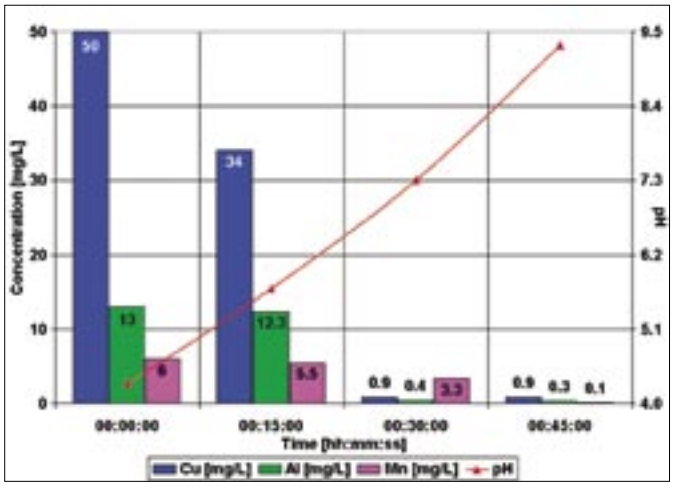

Fig. 13: Effect of neutralization degree on metal removal for NaOH [9]

Finally, since manganese compounds are less toxic than those of other widespread metals such as iron, nickel and copper compounds [11], in spite of manganese being just above the limit of 1 mg/L after 10 min (Figure 14), EC-process provides better removal rates for copper, at even higher flow rate (60 L/h), introducing an eco-friendly and cost-effective solution for industrial applications (Table 6).

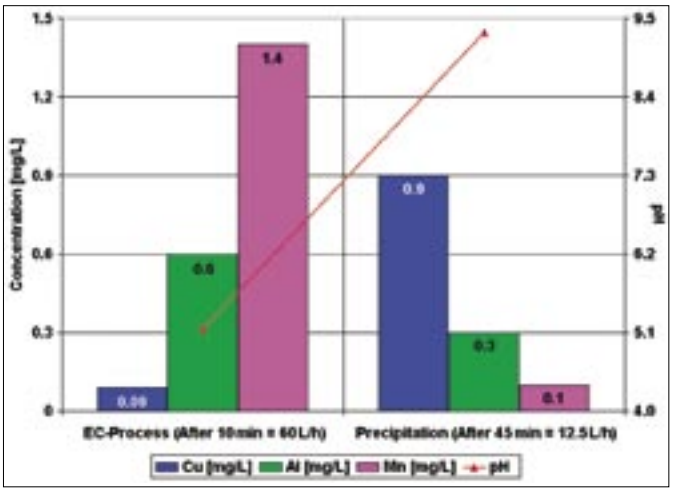

Fig. 14: Final concentrations after treatments found via ICP-OES

6.6 Energy demand and operational facts

In order to determine which process may be more cost efficient, a rough comparison between the conventional technology (continuous chemical precipitation) and the considered technology (continuous electrocoagulation) was undertaken. This comparison took place within a study prior to this work [9].

Formerly it was found that both processes require a hold-up time of 45 min (flow rate =12.5 L/h) to meet discharge requirements, including required neutralization of effluents. Since pH values are neglected for this particular study and taking into consideration that both processes require pH conditioning after treatment (see Figure 14), Table 6

Tab. 6: Energy demand and operational facts between CP and EC in continuous operation

Parameter	Chemical precipitation	Electrocoagulation
Effective flow rate	12.5 L/h	60 L/h
Annual capacity	110 m³/a	526 m³/a
Material added	Sodium liquor (NaOH)	Aluminum plates (Al)
Material cost	0.25 €/L (NaOH-1M)	4 €/kg (Al-plates)
Material used/m³	40 L (NaOH-1M)/m³	0.1 kg(Al)/m³
Material cost/m³	10 €/m³	0.4 €/m³
Annual material cost	1100 €/a	210 €/a
Power consumption	60 W (agitators, pumps)	125 W (EC-reactor)
Energy demand/m³	4.8 kWh/m³	2 kWh/m³
Annual energy cost	106 €/a (≈ 0.2 €/kWh)	220 €/a (≈ 0.2 €/kWh)
Annual total cost	1206 €/a	430 €/a
Treatment cost/m³	11 €/m³	0.82 €/m³

presents a comparison of energy demand and operational facts (neglecting assets and personal costs), between the chemical precipitation using NaOH-1M vs. electrolytic Al-hydroxide in EC-process by treating Saraka effluents.

Since neutralization of effluents requires higher retention times and chemical precipitation needs it for destabilizing suspensions, flow rate acceleration in order to increase annual capacity becomes unlikely to occur in this process. As mentioned before, since pH equals to $-\mathrm{Log10}\,|H^+|$ [12], decreasing hydrogen ion concentration can be reached by means of OH^- dosage, which then increases in logarithmic scale. Therefore, since operating range is around pH = 5.1, aluminum consumption remains as low as 0.1 kg/m^3, which combined with energy demand as low as 2 kWh/m^3, provides an effective treatment with costs below 1 €/m^3.

4 Conclusions and outlook

Based on figures and facts presented, it can be concluded that electrocoagulation technology provided enough evidence of being more environment-friendly with higher outstanding cost-efficiency potentials while running on continuous operation, than it was in batch-mode, and even more compared to conventional chemical precipitation. Technically speaking, the superiority of EC-process was demonstrated within the first minutes of operation due to the electrochemical deposition effect. Being able to handle higher volumes of effluents while meeting current discharge requirements, EC-technology may become a choice for wastewater treatment at metal industries within the next years (in this example 99.8 % copper removal). Economically speaking, EC-technology seems to provide the required synergies to achieve a rapid proliferation in the market. With potentially less than 10 times industrial treatment costs, a dried sludge with marketable properties (mostly Al_2O_3) and energy demand requirements as low as 2 kWh/m^3, further cost-efficiency issues will be matter of future research towards the first industrial prototype.

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