New Concept for Online Monitoring in Wastewater Treatment towards Pollution Control in Real-Time

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Abstract

Aim of present research work was to design and to implement an electromagnetic-sensor (EMS) for wastewater analysis of treated effluents after the electrocoagulation-process (ECP). The EMS should deliver a feedback signal able to perform online monitoring of treated effluents in order to control effectiveness and efficiency of the wastewater purification step. The main target is to improve the mass and energy balance of the ECP, while providing real-time protection against environment and water resource contamination. The experimental results confirmed the feasibility of magnetic permeability for the measurement of ionic content in metal containing fluids and introduced an efficient methodology for online monitoring. The project was realized within cooperation between RWTH Aachen University and its Colombian partner Pontificia Bolivariana University UPB, enabling joint projects towards process automation of industrial wastewater treatment using the electrocoagulation process, started with partial funding from the DAAD and COLCIENCIAS.

1 Introduction

The ”Zero-Waste-Strategy” involves reduction, reuse and recycling of industrial by-products like wastewater and it has become a major goal of the European Union. Since industry is an essential engine of economic growth, global annual water use due to industrialisation is expected to rise from an estimated 725 km^3 in 1995 to about 1,170 km^3 by 2025, by which time industrial water usage will represent 24 percent of all water abstractions [1]. Developing countries in Asia and South-America with abundant mineral and natural resources, now experiencing rapid industrial development, already face pollution control problems nowadays. Unfortunately current chemical precipitation technologies for wastewater treatment involve the dissolution of reactive agents impeding the reuse of treated effluents. Therefore, clean electrochemical technologies like the electrocoagulation process (ECP) become necessary, since they are able to remove dissolved elements like heavy metals and many other nocuous compounds from industrial effluents, based on metallic hydroxides electrochemically formed in-situ from dissolution of aluminium or iron electrodes.

The main advantage of ECP relies on the fact of having higher removal efficiencies than conventional precipitation technologies, without adding chemicals like sodium or calcium hydroxide, which increases the salinity of the solution, or metallic salts like aluminium or iron sulphate, which in reaction with water produce sulphuric acid, remaining as well in treated effluents. Besides these advantages, quality of residual sludge from ECP also simplifies the recycling path towards the recovery of metals dissolved in industrial effluents, as they develop into metallic hydroxides which might be used as raw materials for primary and secondary metallurgy processes.

For these reasons many electrochemistry projects have been carried out at IME in the last years in order to recover valuable metals from industrial effluents. Besides selective electrowinning, the electrocoagulation treatment was proven as suitable technology for purification, achieving ppb-levels for different metals (µg/l), far below the current discharge limits. In this paper, a novel treatment concept with online monitoring of effluents is introduced, using an electromagnetic sensor able to qualitatively determine the metallic content present after the purification step in real-time.

2 State-of-the-art

2.1 Chemical precipitation versus electrocoagulation

Chemical precipitation is a widespread technique for industrial wastewater treatment. Figure 1 describes the precipitation ranges for selected cations present in industrial effluents when using sodium hydroxide to effect formation of hydroxides while neutralising the solution. Since there is no other driving force effecting the formation of metallic hydroxides than the chemical energy released from the hydroxyl-ions when sodium gets dissolved, efficiencies in metal removal using chemical precipitation are lower in comparison to electrochemical treatments. The ECP is driven by two forces, a) the dissolution from the anode, caused by the hydrolysis of the positive charged electrode, and b) the electrodeposition at the cathode surface, effected by the formation of hydrogen gas (formula 1) describing a dissociation of water molecules based on sacrificial electrodes [2].

$$2H_2O + 2e^- \rightarrow 2OH^-_{(anodic)} + H_{2\,(cathodic)} \tag{1}$$

Technically electrocoagulation is not only more efficient, but it also decreases the salinity of the treated effluents. This allows the reuse of treated effluents in combination with standardised processes for water deionisation like the reverse osmosis. As the contamination levels do not remain constant, the conductivity of the solution can be used as a direct measurement of total ionic concentration present in solution. This enables a process control variable reliable enough to minimize the energy demand.

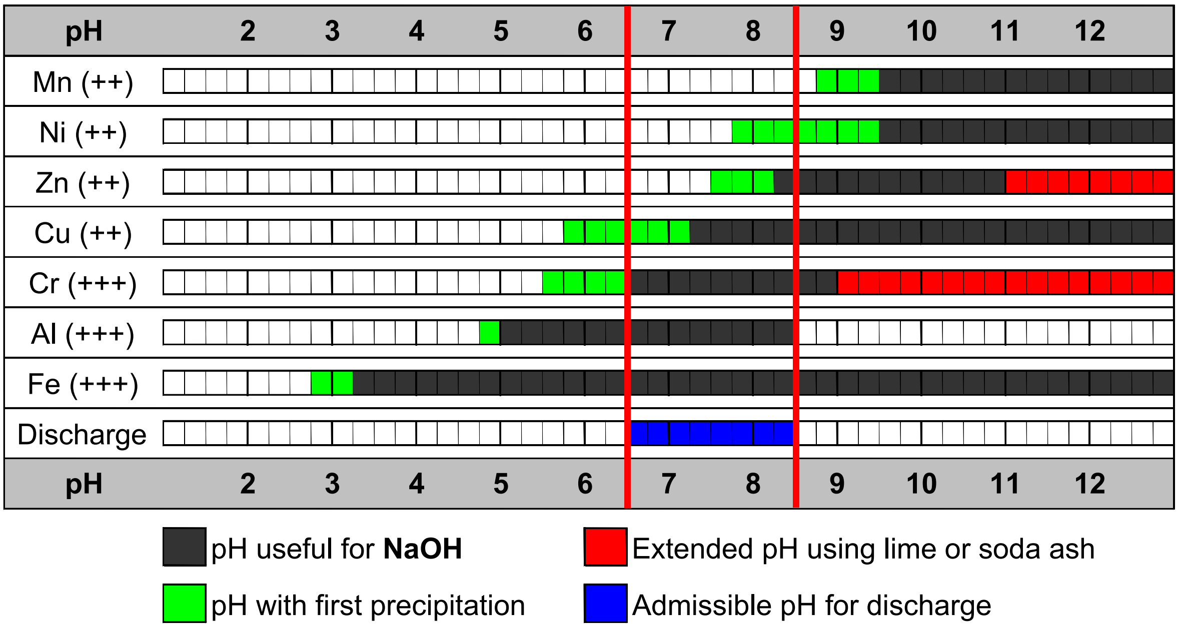

Figure 1: Precipitation ranges for metallic cations using sodium hydroxide NaOH [3]

Figure 2 shows the results of a wastewater purification test using the same industrial effluents, left after chemical precipitation with NaOH and right after electrocoagulation with Al-anodes. The effectiveness of electrocoagulation compared to chemical precipitation is higher with respect to the metal removal yield at pH values below the neutral range, i.e. manganese as well as for copper, where the values are 100 times higher reaching the ppb-level (µg/l) [3].

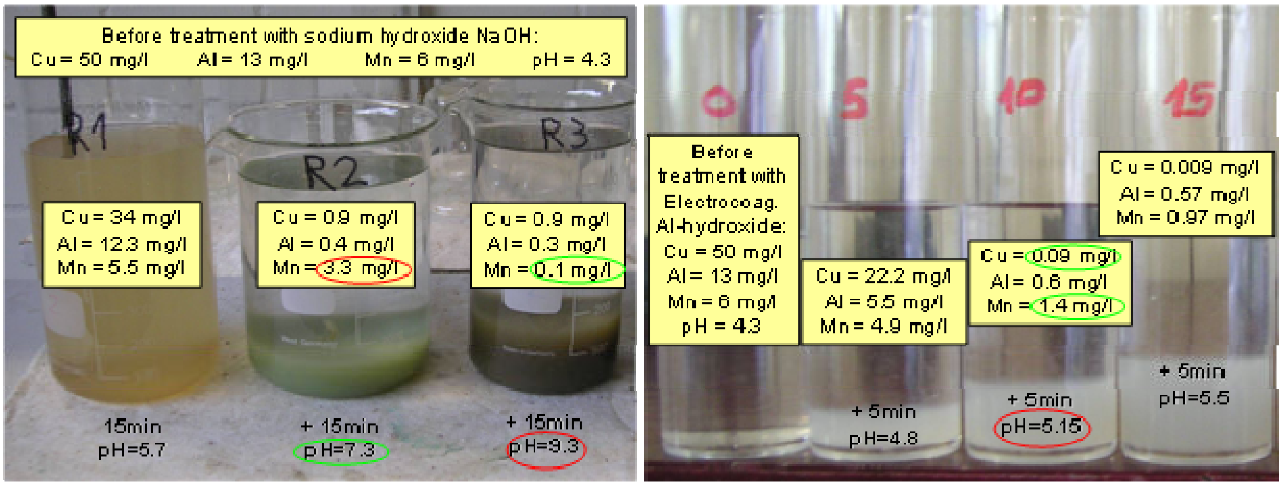

Figure 2: Appearance of treated effluents using chemical precipitation and electrocoagulation

Figure 3 shows the decrease in electrical conductivity of industrial wastewater as the pH value raises during purification. The conductivity value shall never reach values as low as from tap water (300 µS/cm) due to the presence of neutral salts and other impurities. But it can be understood how conductivity value provides a reliable and directly proportional measurement of the metallic content still present in the solution after treatment, since removed metals indicate a comparable portion of it.

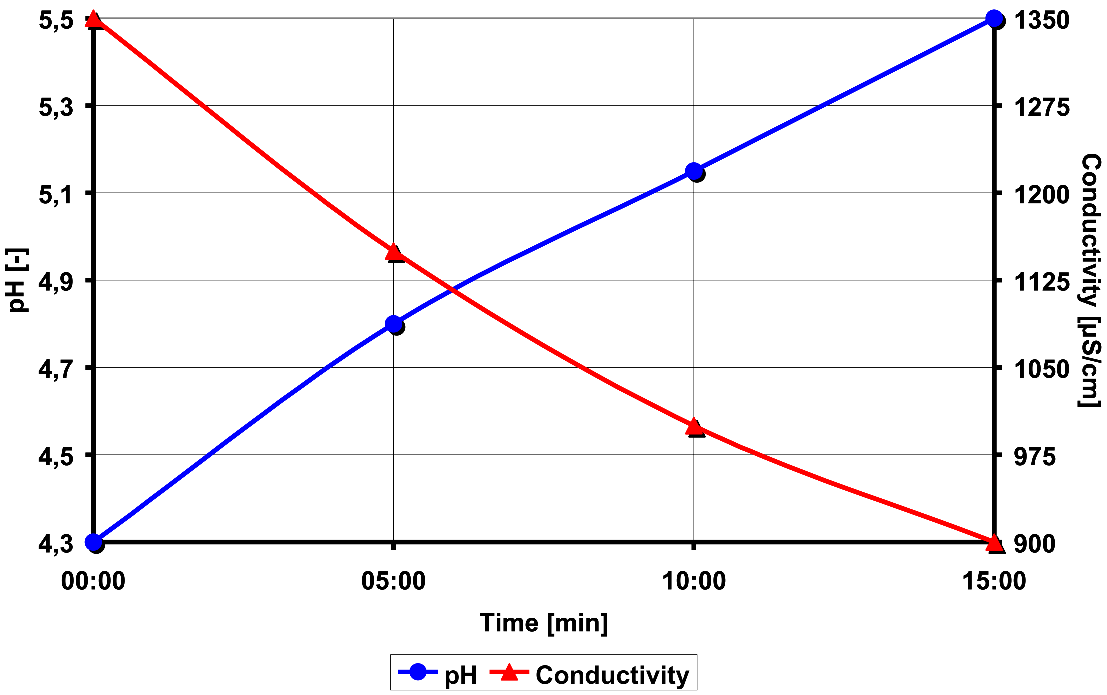

Figure 3: pH and electrical conductivity change during metal removal using electrocoagulation

2.2 Chemical analysis and proposed online monitoring approach

Although the electrical conductivity provides a qualitative measure regarding contamination level of industrial effluents, the proposed online monitoring approach is not intended for replacing conventional quantitative analytic methods such as AAS or ICP. Despite their reliability, they are labour demanding techniques, for which sampling requires preparation and expensive operating conditions, being unable to perform analysis in real-time. For this reason, alternative methods such as Electronic Tongues (ETs) have been investigated over the last 30 years. ETs can be described as semiconductor devices for liquid chemical analysis, which make use of electrochemical reactions in order to selectively detect elements dissolved in a sample, including metals. The functional principle is based on the conductivity variation effected by elements inducing changes on the semiconductor arrays, requiring several arrays of semiconductors for each particular element [4]. The specific elements dissolved react with these semiconductors depending on their affinity and induce a chemical reaction proportional to their concentration, varying like this their electrical properties. However, in regard to detection of metallic cations, errors were found to be from 5 to 30% from the literature, which seems to be acceptable for environmental monitoring, considering the capability of electronic tongues to work reliably at low ppb concentration levels [5].

In order to avoid chemical reactions with the sensor and thus replacement of measurement devices from time to time due to material corrosion and fatigue, an electrode-less and non-invasive measuring principle is proposed based on the magnetic permeability of the solution.

This Electro-Magnetic Sensor (EMS) operates like a conventional electric transformer (fig. 4). The EMS developed at IME consists of two coils acting as a transmitter-receiver system, based on a core of hollow glass filled with the solution. Just as the iron core the liquid is able to transport the magnetic flux responsible for the energy transfer from the primary into the secondary winding. The metallic content is able to transmit a comparable signal in the radiofrequency range (MHz), providing a proportional value to the electric conductivity of the solution, and like this to the total ionic concentration in the purified effluent.

In other words, the electric conductivity given by the total ionic concentration of the sample can be understood as the sum of all equivalent conductivities, represented by each element dissolved in wastewater before/after treatment. As the purification process takes place, dissolved metals start to be removed from the solution either by absorption on metallic hydroxides produced from the electrolytic dissolution of the sacrificial anode, or by means of electrodeposition at the surface of the cathode. For this reason the electric conductivity value decreases proportionally during wastewater treatment as described previously, and it represents like this a valid controllable variable in order to determine the contamination level after the purification step.

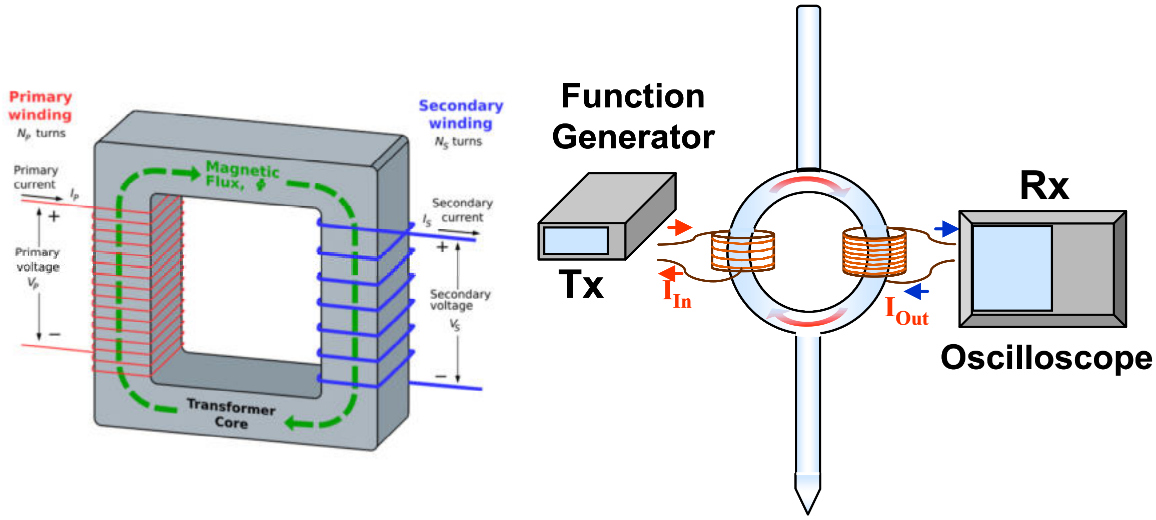

Figure 4: Process analogy between electric transformers and proposed electromagnetic sensor

The challenging target of this research is to identify parameter sets enabling identification of individual metal concentrations in complex solutions by varying frequency and projecting system response using multivariate analysis and pattern recognition techniques. Although this method shall not provide an absolute measurement of metallic contents, thus requiring calibration for each particular kind of effluent, process control and online monitoring of wastewater treatment during electrocoagulation can be performed using frequency response from signals obtained with the developed electromagnetic sensor.

3 Materials and Methods

In order to verify the technical feasibility of the proposed electrode-less and non-invasive approach for online monitoring of wastewater treatment, experiments were carried out in lab-scale. Figure 5 describes the hardware components used for the design, implementation and validation of the Electro-Magnetic Sensor. The EMS is based on a transmitter-receiver principle, for which the magnetic permeability of the medium, represented by the metallic content dissolved in industrial wastewater after treatment, providing a proportional value to the electrical conductivity of the sample. In this way, a prototype consisting of two coils mounted on a core of hollow glass was implemented as described in figure 4. Since electromagnetic radiation is a relevant issue for accurate measurements, proper isolation was provided by means of a Faraday cage connected to earth ground to isolate any interfering field. The transmitter (Tx) uses a radiofrequency signal, in form of a sinusoidal wavelength in the MHz range, provided by an arbitrary frequency generator 33250A from the company Agilent Technologies. At the receiver side (Rx), a portion of the sinusoidal signal transmitted over the ionic conductive content from the sample is then registered by a digital storage oscilloscope DSO7032A also from Agilent Technologies. These electronic devices were programmed for fully automated operation, using standard communication interfaces over USB interfaces, and they stored on Excel sheets using VBA (Visual Basic programming) all digital information regarding measurement of amplitude and phase of transmitted and received signals for further data mining.

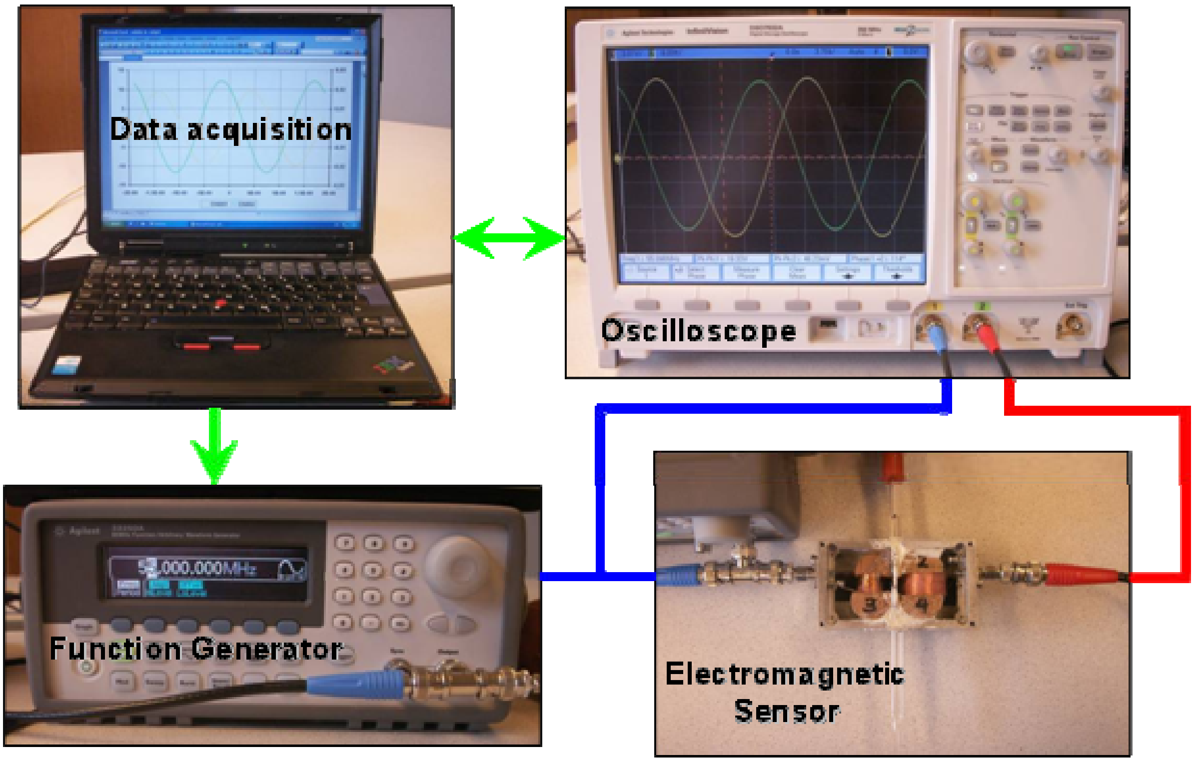

Figure 5: Hardware set-up for the design and validation of the electromagnetic sensor

In regard to validation of ionic concentration measurements using the proposed magnetic permeability principle, synthetic samples of about 1, 10, 100 and 1000 mg/l of dissolved copper, nickel and zinc were prepared (see figure 6), representing common metals present in regular industrial wastewater. Furthermore, real industrial effluents before and after the electrocoagulation treatment were used in order to assess the reliability of messing principle for its integration into the proposed online monitoring system towards pollution control in real-time.

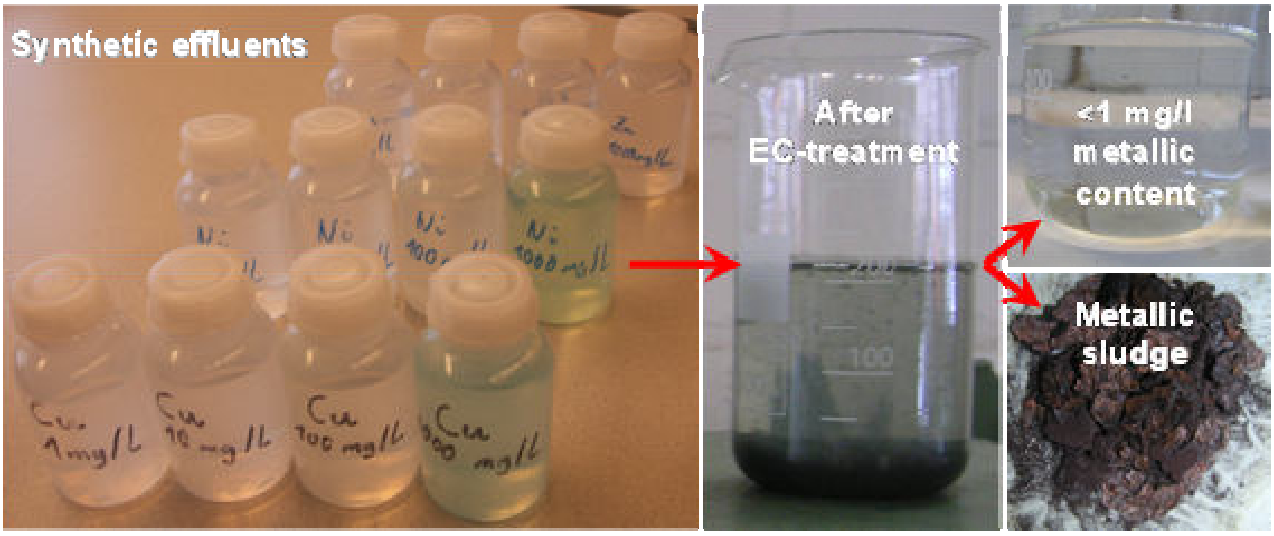

Figure 6: Synthetic and industrial wastewater before and after the electrocoagulation treatment

4 Results and Discussion

As described in figure 3, electrical conductivity provides a reliable indicator of contamination levels still present after wastewater treatment using electrocoagulation, as the physical property describing the total ionic content existing in industrial effluents. Taking into account that deionised water is considered to be an insulator and does not allow the transport of magnetic flux by itself, this can be seen from the frequency response of the electromagnetic sensor together with the synthetic samples shown in figure 7 (bottom line). Using this as a reference, proportional dependences of metallic content are clearly noticeable. This effect proofs the proposed principle which can be addressed to the magnetic permeability [6]. Further experiences using the electromagnetic sensor with real industrial effluents before and after the wastewater treatment also allowed validating the magnetic permeability as sensing principle towards the automation of electrocoagulation process. Despite the fundamental difference between the magnetic permeability based on the magnetic field and the electric conductivity based on the electric field, experimental results shown a remarkable correlation between these magnitudes. Although there is little theory regarding electromagnetic properties from aqueous solutions, a proposed hypothesis at this stage of research allows to think of the magnetic permeability and the electric conductivity as the same magnitude in the ionic range.

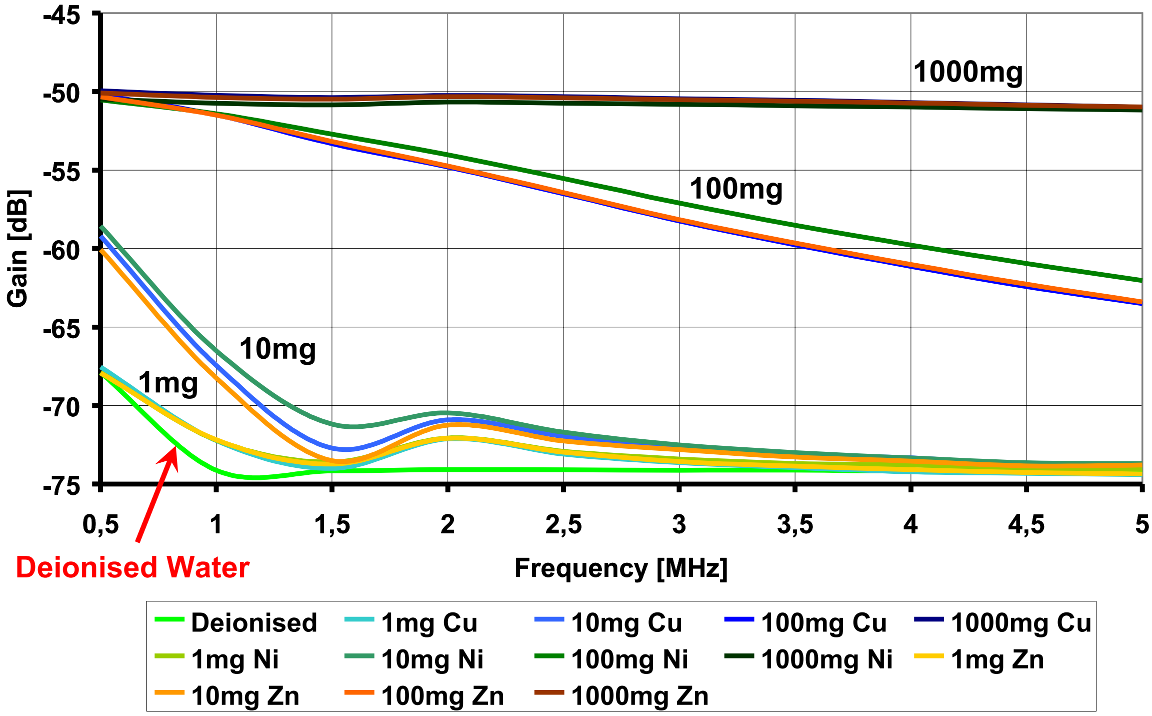

Figure 7: Frequency response from synthetic samples using the electromagnetic sensor at IME

In order to carry out an empirical validation of the proposed hypothesis, 20 different samples with defined conductivity values were prepared from 1 up to 20 mS/cm, and the measured results are presented in figure 8 against the gain magnitude from frequency response. From this logarithmic distribution is likely to confirm the technical feasibility of the proposed online monitoring using the electrode-less and non-invasive approach developed at IME towards pollution control in real time.

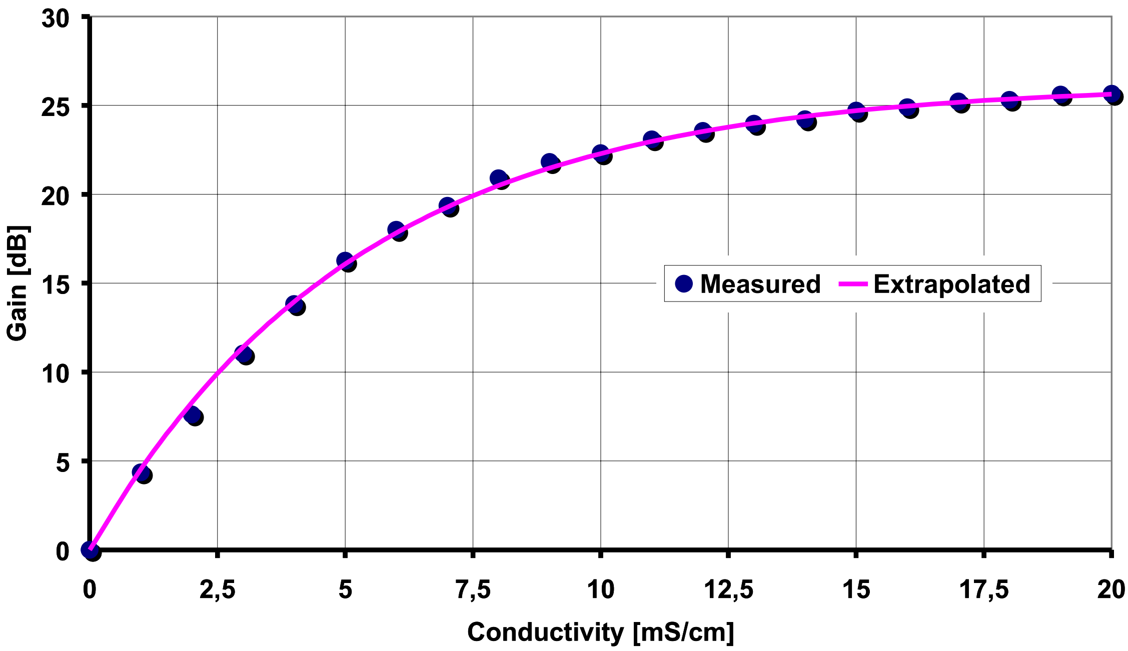

Figure 8: Frequency response from synthetic samples using the electromagnetic sensor

5 Conclusions and Outlook

The proposed model for the transfer of magnetic flux in wastewater contemplates a rearrangement of ionic content in the sample, building like this an infinitesimal wire in the nucleus of the toroidal core (hollow glass) filled with the solution, as represented in figure 9. Through this ionic wire arraged by the magnetic field, the magnetic flux is thought to flow from the primary to secondary winding, since water itself is a diamagnetic medium and therefore a poor conductor of electricity.

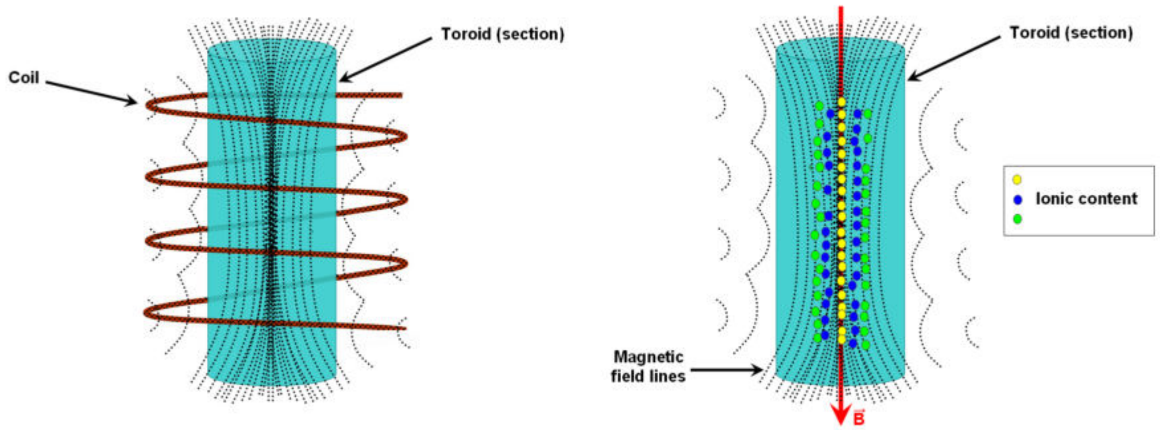

Figure 9: Proposed model for the transport of magnetic flux in electromagnetic sensor at IME

Figure 10 introduces a process scheme of the electrocoagulation treatment with integrated online monitoring using the proposed electromagnetic sensor for qualitative analysis of wastewater after the purification step. Using this approach, the electrocoagulation treatment shall perform adequately, while reducing the energy demand required to maintain a specific value of conductivity.

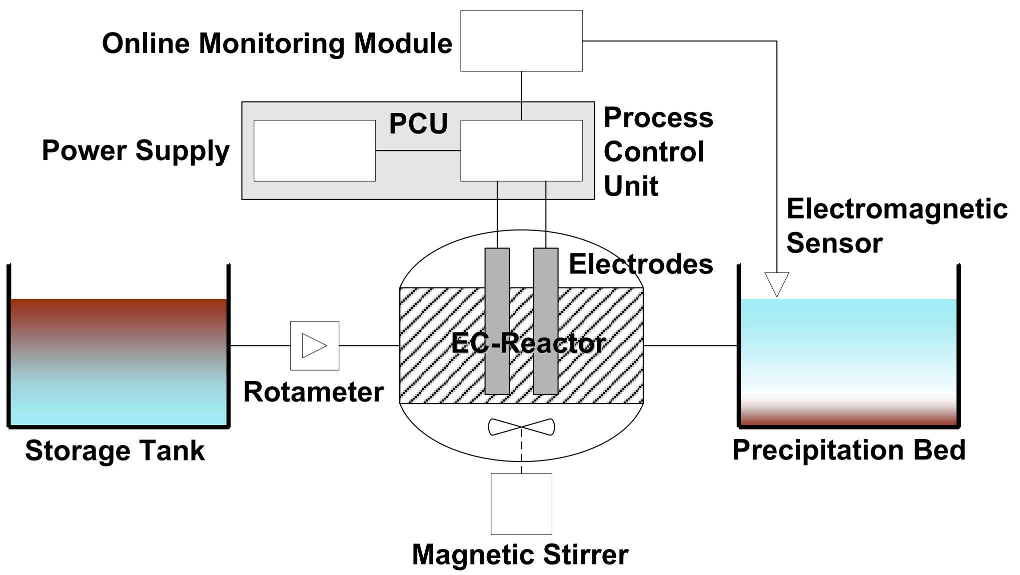

Figure 10: Process schematic of electrocoagulation treatment with integrated monitoring sensor

Even though that an additional characterisation of samples besides the determination of the electrical conductivity at the radiofrequency range (MHz) with current devices is very limited, it is though likely, that through additional parameterization, it shall be possible to differentiate two or more elements within the same sample. This will be a matter of further research at IME together with the Colombian partner Pontificia Bolivariana University UPB, within the R&D activities focused on the energy optimization of electrocoagulation treatment using the proposed electromagnetic sensor, which will be integrated to the automation process towards pollution control in real-time.

Acknowledgement

Authors would like to thank the German Academic Exchange Service DAAD and its Colombian counterpart COLCIENCIAS for the financial support on the Project Based Personnel Exchange Programme with Colombia PROCOL, as well as the Colombian Ministry of Environment MAVDT and the Colombian Institute of Energy Solutions IPSE for their interest and support to our research.

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