

**REMOVING THE ADSORBABLE ORGANIC HALIDES (AOX) FROM PULP & PAPER
INDUSTRIES EFFLUENTS BY USING ELECTRO-COAGULATION (EC)**

António J.S. Rodrigues, Carlos F. Oliveira

VentilAQUA SA, antonio.rodrigues@ventilaqua.com, +351 239 437 336

VentilAQUA SA, carlos.oliveira@ventilaqua.com

ABSTRACT

These days, major worries of mankind are focused on the negative effects of industrial effluents in the Environment. In pulp & paper industries the concern with AOX contaminants are high, these being subject to continuous monitoring, as part of the most toxic and harmful contaminants present in the wastewaters. Challenging limitations of conventional methods, project P2020 PROTEUS – Produtos e tecnologias para o sector do Eucalipto¹ is aimed to evaluate technologies based on Advanced Oxidation Processes (AOP) due is significant efficiency in removing AOX from those wastewaters. The main objective of Electro-Coagulation application is to remove the AOX, with other contaminants alongside, optimizing the operations and energy costs to reach an environmental sustainability and guarantee the Ecolabel standards.

The main feature within EC is an electro-chemical process, which is done by applying electrical current between electrodes inside a reactor. This study focused in the intermediate stream D0, the most concentrated source of AOX available. First, effluent enters the EC reactor after passing through a flowmeter and a pH meter. A current rectifier is introduced to supply a pre-defined voltage and current to the electrodes. The flow, the surface area, the distance between electrodes, the residence time are also operating parameters defined at several different conditions in order to optimize the ratio efficiency and cost. After EC the sample is collected the amount of AOX and other relevant parameters were evaluated. All materials used were prepared for industrial conditions and operation, such as high temperatures (>65°C) and a low range of pH. The trials were done with a modular reactor that could take electrodes with a variable gap between them. For this study trials, electrodes used were Iron (Fe) based electrodes for removing AOX, and also phosphorous. Because of their good electrical conductivity, one can optimize the energy consumption rate and from its easy availability their use creates an opportunity to add value to iron scrap wastes in the process, promoting a circular economy strategy. The pilot has a flowrate capacity of 1.5LPM and was installed in the bleaching sector of Aveiro Industrial Park.

The EC process returned impressive results on AOX removal with 93% efficiency. For optimized conditions, under industrial environment, pilot plant operated at 0.5-1.0LPM in a range of 10-35mA/cm² (j) with a very low average specific power consumption of 75W/g AOX removed. In this conditions the EC pilot reached the reduction objectives of 45%. The EC presented a good stability rate on AOX mass reduction independent of operating conditions and the results suggest that AOX removal by EC process could occur with reduced residence time.

Regarding the main objective one can conclude that EC is a viable technique for this purpose; in comparison, AOPs based on Fenton, nanomaterials and nanoparticles also present good efficiencies of removal but, in terms of cost-effective techniques, EC is a real breakthrough.

Key-Words: Advanced Oxidation Process (AOP), Adsorbable Organic Halides (AOX), Electro-Coagulation, Electro-Oxidation, Wastewater.

¹ This work is financed by Portugal 2020 through European Regional Development Fund (ERDF) in the frame of Operational Competitiveness and Internationalization Programme (POCI) in the scope of the project PROTEUS - POCI-01-0247-FEDER-017729

INTRODUCTION

These days, major worries of mankind are focused on the negative effects of industrial effluents in the Environment. In pulp & paper (P&P) industries the concern in AOX contaminants are high, these being subject to continuous monitoring, as part of the most toxic and harmful contaminants present in the wastewaters. Alongside with the toxicity associated to the AOX in wastewaters, their presence also interferes in the recovering and valorisation of other sub-products, reducing their environmental sustainability potential and guarantee the Ecolabel standards.

The P&P Industries are on the list of major industries with AOX contaminants [1], with levels that can reach 0,3 kg AOX [2] per air dried ton (ADt) of bleached pulp. The removal of recalcitrant contaminants, like AOX, is limited with traditional wastewater process. Therefore in 2014 a commission implementing decision referred in 2014/687/EU [3] recommended that advanced oxidation process (AOP) should be used to improve the removal of recalcitrant contaminants efficiency and biodegradability of the wastewaters [4].

This AOP has the capacity to form hydroxyl radicals that are highly reactive and can interact with recalcitrant contaminants. These radicals are also low selective forms that can oxidize other organic compounds as well. The study of AOP in P&P wastewaters are more focused on COD and colour removal ([4], [5]), so there is some scarcity on studies for AOX removal with AOP technologies ([6], [7]). In available studies, the most used AOP is the Fenton process, being used as benchmark in this study. The Fenton process forms hydroxyl radicals from external source (hydrogen peroxide) reacting with iron as catalyser, this leading to some drawbacks like consumables used, cost, and iron leachate in the sludge. This also led to the study of AOX removal with electrochemical AOP, designed by VentilaQUA SA.

The Electro-Chemical process is one of known Advanced Oxidation Processes (AOP) and is mainly composed by the following electrolysis sub-process represented in Figure 1.

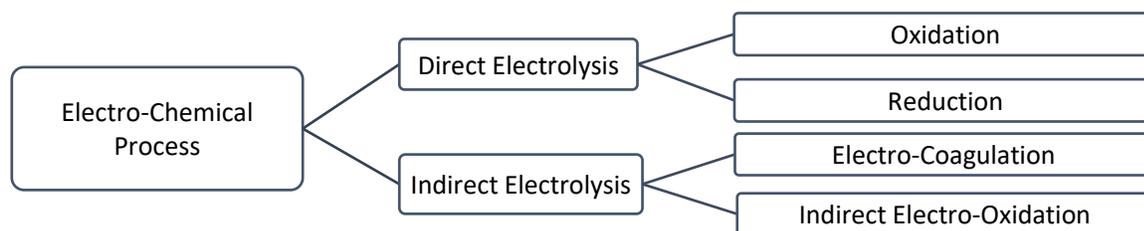


Figure 1. Electro-Chemical Process (Adapted from [8])

Depending on the type of wastewater, one or both technologies (electro-coagulation and/or electro-oxidation) can be applied, to achieve the defined objectives [8]. Electro-coagulation (EC) is rather advantageous as it is easy to implement and requires a minimum amount of chemicals, so it makes the process attractive and significant to replace old-fashioned, conventional processes, which require large volumes and/or a high number of chemicals, as well as large reactors under typical wastewater treatment displays. The electrochemical treatment process of effluents has been studied, but few authors have focused on the variables that are crucial for improving the performance [9].

Although EC technology is beneficial, the lack of a systematic approach to the operation/design of EC reactor and electrode reliability (the phenomenon of passivation of electrodes over time) have limited its application widely. However, recent technical improvements combined with the growing need for decentralized water treatment facilities, have led to a reassessment interest in the EC as AOP ([10][11]). EC application to wastewater treatment is currently growing considerably [9]. EC has been developed recently and turns to an alternative for industrial wastewater treatment like textile, food, mining, pharmaceutical, paper, detergent, and many others, which offer multiple comparative advantages over

traditional technologies (low maintenance costs and needless of using chemical agents) [12]. Most conventional treatment methods are becoming inadequate, due to the variability of wastewater compositions [13] and growing requirements and reject limitations, as commission implementing decision [3] supported. Therefore, the application of EC can be [14]:

- An alternative method for treating wastewater;
- A complementary technology (for increasing the efficiency of the conventional methods);
- Entire replacement of chemical and biological treatment plants.
- Electro-coagulation/electro-oxidation can be applied as an improvement for existing biological processes with excess organic load, avoiding expansion of existing biological reactors
- Electrochemical breakdown of complex organic compounds. This process results in improving yields and reducing treatment duration in a biological reactor, significantly [9].

EC is a process that uses principles of coagulation-flocculation in electrolytic reactors. Coagulation is defined as destabilizer of colloidal particles and flocculation is a process of increasing the particle size by particle collisions [8]. EC is a process of removing pollutants electro-chemically with a reactor equipped with a source of electric current that promotes the production of electromotive force, which results in a series of chemical reactions. This stage is consisting of electrodes – usually Iron (Fe) or Aluminium (Al) – contributing positively with charged ions (Fe^{3+} or Al^{3+} , respectively), which cause the neutralization of particles in the effluent ([14] e [15]). Due to the ions resulting from soluble anodes (coagulants produced “in situ”), suspended pollutants are destabilized, emulsified, or dissolved in an aqueous medium [16], aggregating to form larger particles (flakes), which can be removed by a physical separation method, like flotation, sedimentation (in case of sedimentary mud, instead of flotation) or filtration ([12] e [14]).

Figure 2 shows the interactions described, which occur within the electrocoagulation cell ([8] [17]).

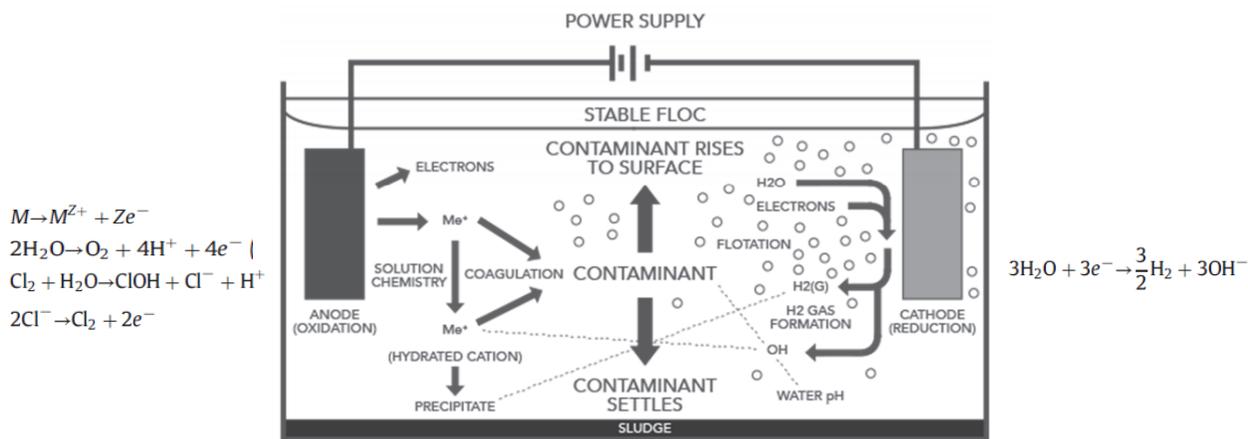


Figure 2. Interactions in Electro-Coagulation Reactor [17]

During an EC process, several chemical reactions occur within anode and cathode. An anode is a place where oxidation occurs, so electrons are released and forming cations (positively charged ions) while reduction takes place within a cathode that results in forming anions (negatively charged ions).

EXPERIMENTAL

Project experiments are divided into two sections, the laboratory preliminary experiments and the application of the pilot unit in an industrial environment. All trials were not only focused on efficiency

removal rates, but also on the energy consumption and costs associated with the technology.

Study case: AOX, the samples origin

AOX is one of the contaminants monitored in P&P industries, being a high priority parameter due to the high level of toxicity and interference in other sub-products. Also, removing AOX can grant a positive effect in produced products which guarantees low emissions of AOX per ADt produced, as this parameter is stated in the EU Ecolabel, and requires emissions below 0,17 kg AOX/ADt.

This study was focused in the intermediate stream D0, because it is the most concentrated source of AOX available. In the study case, D0 stream represent 68% of AOX produced at the factory and its volumetric weight is only 15% of all streams combined, making a better option for removing the AOX. This stream has higher levels of COD (chemical oxygen demand), low pH (around 1-2) and outputs at 75°C.

Laboratory trials:

The laboratory trials were performed on an electrocoagulation cell unit in batch mode. The first setup is composed by a 700 mL reactor and can use from 2 to 8 square electrodes with 90mm each side. The electrodes material tested was aluminium, iron and stainless steel, in a monopolar configuration. The power supply unit used is a 600 watts unit that can output a maximum of 20 Amperes. For proof of concept and evaluation of EC AOP performance, the trials were done with a configuration of 4 monopolar electrodes at a constant current density. Three types of electrodes were used separately for performance analysis.

Industrial environment trials:

The laboratory trials resulted in the design of a pilot unit scale that was placed in the source of the D0 stream and operated under industrial conditions. Industrial environment trials were done with a modular reactor that could take between 4-16 electrodes with a variable gap between them. For this study trials electrodes used were Iron (Fe) based for removing AOX. Because of its good electrical conductivity one can optimize the energy consumption rate and from its availability it creates one opportunity to make an added value from iron scrap wastes in the process, promoting a circular economy strategy. The pilot has a maximum flowrate capacity of 90 L/h and temperature and pH reading. For long period trials an automatic polarity change in the output of the power supply was installed to help to eliminate passivation effects on the electrodes.

The following a) Figure 3 represents the pilot unit installed in the bleaching sector of Aveiro (Portugal) Industrial Park, and b) its components.

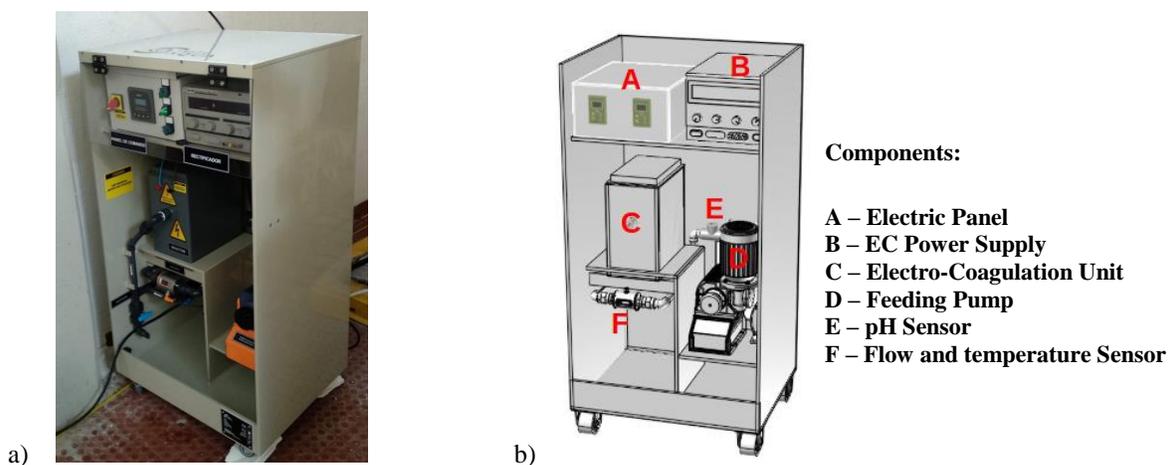


Figure 3. EC pilot unit. a) Pilot at industrial environment b) Pilot components description

The pilot was operating in real environment conditions, in the source of the stream, and Table 1 gathers the variations and configurations used in order to extract the most relevant operating conditions that can optimize relation between technical and economic performance, under a fine tuning operation.

Table 1. Trial operating condition resume for the EC industrial pilot unit

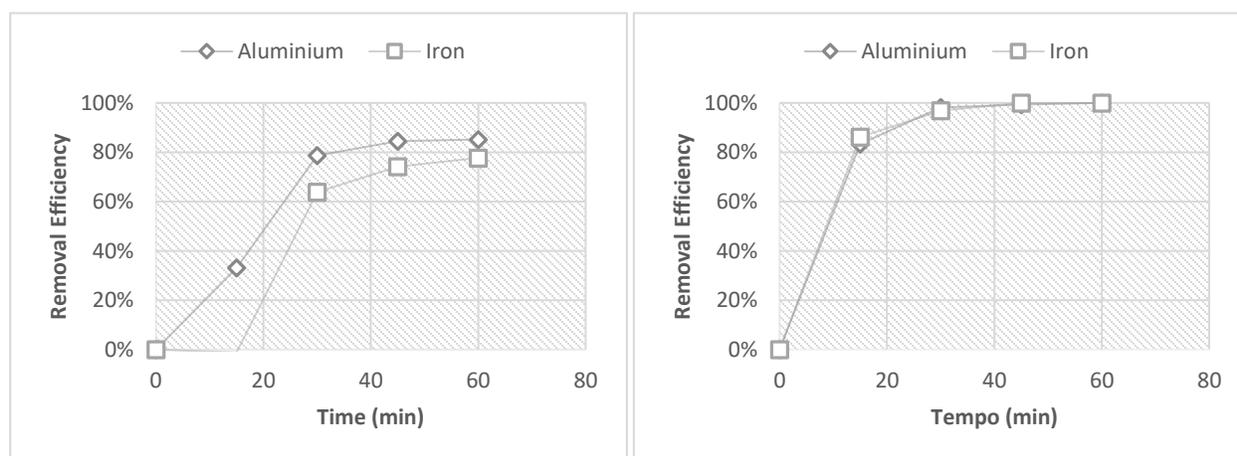
Trial Battery	Flow (l/h)	Tr (min)	S/V (m ² /m ³)	Gap (mm)	j (mA/cm ²)
E-E16P2-I	30-90	9 – 3	99	10	3,3 - 6,6
E-E8P2-I	30-90	12 – 4	36	25	7,1 - 14,3
E-E8P3-I	30-60	9 – 4	36	25	9,5 - 14,3
E-E6P4-I	30-60	12 – 6	25	40	13,3 - 20,0
E-E4P5-I	30-60	12 – 6	14	55	22,2 - 33,3
E-E8P3-I-B	30-60	12 – 6 (6 - 3)*	36 (99)	10	9,5 - 14,3
E-E6P4-I-B	30-60	12 – 6 (4 - 2)*	25 (99)	10	13,3 - 20,0
E-E4P5-I-B	30-60	12 – 6 (3 - 1)*	14 (99)	10	22,2 - 33,3

(*) – Real reaction time residence

RESULTS AND DISCUSSION

From laboratory trials several studies regarding the removal efficiency on the AOX, COD and phosphorous (P) were performed which also allowed to observe effect on pH and electrical conductivity.

From Figure 4 it is possible to verify the removal capacity in COD and P parameter with both types of electrodes. For P removal both have near 100% removal for 30 minutes operation. Regarding the COD levels the final result is similar between both electrodes types, 85,2% and 77,7% removal for aluminium and iron respectively, but aluminium electrodes showed a faster effect on COD reduction. This is due to the fact that iron electrodes are leaching some iron in the sample giving some coloration and only after 30 minutes the clarification, from coagulation, occurs.



**Figure 4. Left side) COD removal efficiency. Right Side) Phosphorous removal efficiency
Trials executed at $j=80$ A/m² on VentilAQUA Laboratory EC unit.**

For AOX removal, EC process was evaluated in terms of operating range and cost efficiency for the target parameter removal.

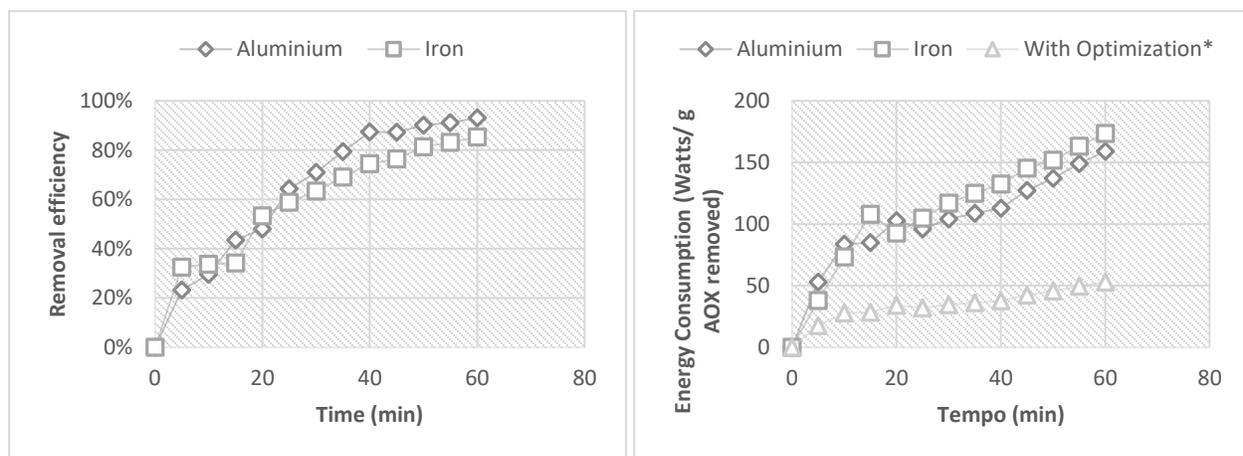


Figure 5. Left side) AOX removal efficiency. Right Side) Energy consumption per AOX mass removed. Trials executed at $j=80 \text{ A/m}^2$ on VentilaQUA Laboratory EC unit.

The laboratory results returned impressive results on AOX removal with 93% efficiency after EC process. We made an evaluation on energy consumption by mass of AOX removed and it's notorious that the increase of efficiency leads to an increase of power consumption in the process. In the right graphic of Figure 5 there is a line (With Optimization) that refers to a possible optimized energy consumption to be made in the reactor design, reducing the negative effects of the wastewater electrical resistance.

Iron electrodes showed slightly lower results in terms of removal performance, but in other parameters – including energy, acquisition, operation constrains (like passivation) – they overcome and compensate this gap, making the iron electrodes a more feasible solution for industrial scenario application, thus the ones to be selected for further developments.

The EC process also affects stream conductivity and pH. The decrease of conductivity could be related with some complexation of some salts and AOX. The hydroxyl radical species generated in the EC process induces a pH increase. Both this effects are considered positive on to the stream D0.

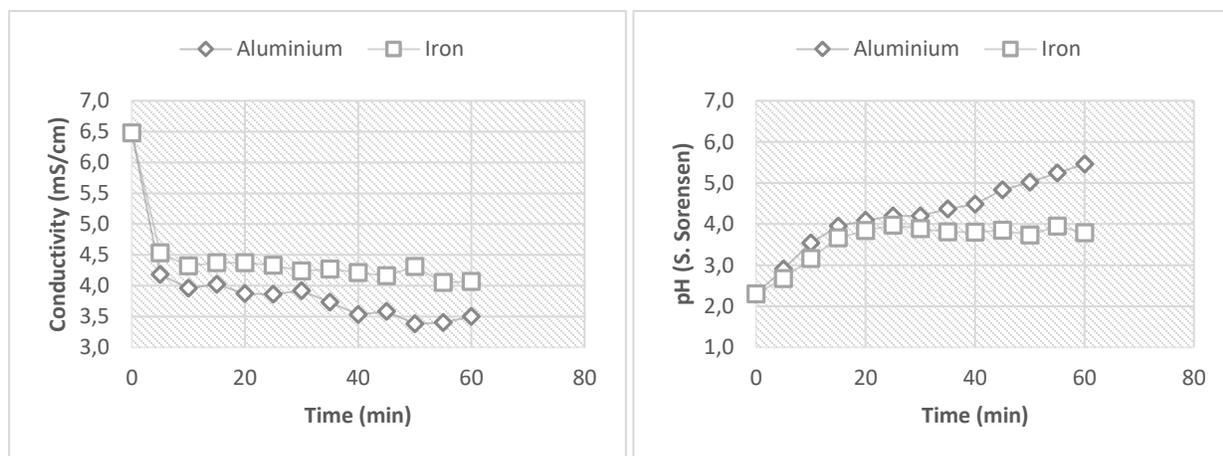


Figure 6. Effects of EC process on Conductivity and pH. Trials executed at $j=80 \text{ A/m}^2$ on VentilaQUA Laboratory EC unit.

**XXV TECNICELPA - Conferência Internacional da Floresta, Pasta e Papel XI CIADICYP
2020
10, 11 e 12 Março 2021 – COIMBRA, Portugal**

Table 2. Results for the EC industrial pilot unit trials. (*) Average Value (Best Value)

Trial Battery	Flow (l/h)	Electrodes Gap (mm)	j (mA/cm ²)	AOX Removal (%)	Energy per AOX removed (W/g)
E-E16P2-I	30-90	10	3,3 - 6,6	10 (22)	102 (46)
E-E8P2-I	30-90	25	7,1 - 14,3	19 (25)	168 (97)
E-E8P3-I	30-60	25	9,5 - 14,3	20 (28)	184 (127)
E-E6P4-I	30-60	40	13,3 - 20,0	23 (31)	200 (98)
E-E4P5-I	30-60	55	22,2 - 33,3	23 (30)	763 (397)
E-E8P3-I-B	30-60	10	9,5 - 14,3	N/A	N/A
E-E6P4-I-B	30-60	10	13,3 - 20,0	30 (44)	118 (58)
E-E4P5-I-B	30-60	10	22,2 - 33,3	32 (45)	134 (92)

Following the experimental protocol the results returned interesting outputs for AOX removal that normally are in the opposite side for other electro-coagulation studies, like solids or COD removal.

On the run trials it was observed that during the day there is a variance on the AOX values that could change significantly during a full day of trials. The results also demonstrated that the EC efficiency is more related with mass removal, and is not so dependent on the initial concentration. This leads to yield different efficiency removals, but similar mass removal with the variability of the AOX concentration in the D0.

Regarding design parameters for the EC AOP, results demonstrated that the current density is the most relevant parameter, but it also requires a reduced electrical resistance. By reducing the gap between electrodes this resistance was lowered and by balancing the density current and the reactor electrode surface and volume (S/V) ratio the desired removal efficiency was achieved, at a very low energy and electrode consumption. This also leads the experiment results to finding that the removal of AOX contaminant is a rather faster reaction which can take place in a range of less than 5 minutes residence time.

In the development of this study, alongside with the technical point of view there was always an implicit concern in the exploitation costs of the technology. Knowing this is a key factor for further developments and implementation it was carried an economical study based on the final results. **Table 3** summarizes the cost involved, and based on the following energy and electrode costs it was achieved interesting results. Keeping in mind that more than 60% of the cost is on the electrodes consumption side, is strongly recommended a supply of iron scrap to be used as electrode. This will reduce costs and improve the sustainability of the overall process, promoting a circular economy.

Table 3. Economic evaluation study of the EC AOP applied in the case of study

Parameter	Value	Unit
AOX removal target	45	%
Energy Cost	0,05	€/Kwh
Electrode Cost (Iron)	0,50	€/kg
AOX Removal cost by EC	0,011	€/g AOX
Cost in D0	0,587	€/m ³ D0
Cost per pulp produced	2,866	€/ADt

**XXV TECNICALPA - Conferência Internacional da Floresta, Pasta e Papel XI CIADICYP
2020
10, 11 e 12 Março 2021 – COIMBRA, Portugal**

CONCLUSIONS

This study aimed to the application of EC AOP in the removal of AOX contaminant in the P&P industries.

At a laboratory scale the EC technology proved a great performance into AOX removal achieving 93% removal capacity and promising to be an economical and sustainable solution to consider. Results obtained from the pilot unit at industrial environment clearly indicated a successful achievement of combining the needed efficiency removal rate defined in the project (45% AOX removal in the D0 stream) with a sustainability of the AOP operational conditions, meaning energy and electrode consumptions at a low level.

Comparing the costs to the BAT reference (Fenton AOP), the cost associated with EC technology is only 3% of the Fenton process cost. The difference in operational costs can justify further developments in this technology and into the application of AOX and other associated contaminants removal in the P&P Industries.

REFERENCES

1. W.H.W. Osman, S.R.S. Abdullah, A.B. Mohamad, A.A.H. Kadhum, R.A. Rahman. Simultaneous removal of AOX and COD from real recycled paper wastewater using GAC-SBBR. *Journal of Environmental Management* 12, 80-86 (2013).
2. M. Suhr, G. Klein, I. Kourti, M.R. Gonzalo, G.G. Santonja, S. Roudier, L.D. Sancho. Best Available Techniques (BAT) Reference Document for the Production of Pulp, Paper and Board. Joint Research Centre (2015).
3. Commission Implementing Decision of 26 September 2014 establishing the best available techniques (BAT) conclusions 2014/687/EU.
4. D. Hermosilla, N. Merayo, A. Gascó, Á. Blanco. The application of advanced oxidation technologies to the treatment of effluents from the pulp and paper industry: a review. *Environ Sci Pollut Res* 22, 168–191 (2015).
5. D. Pokhrel, T. Viraraghavan. Treatment of pulp and paper mill wastewater—a review. *Science of the Total Environment* 333, 37– 58 (2004).
6. E.C. Catalkaya, F. Kargi. Color, TOC and AOX removals from pulp mill effluent by advanced oxidation processes: A comparative study. *Journal of Hazardous Materials B* 139, 244–253 (2007).
7. A.S. Morais, A.H. Mounter, D.S.A. Silveira. Improvement of eucalyptus bleached kraft pulp effluent treatment through combined ozone-biological treatment. *TAPPI Journal*, 26–32 (2008).
8. METCALF&EDDY - Wastewater Engineering - Treatment and Reuse. 4 a . ed. [S.l.] : McGrawHill, 2003
9. CURINHA, J. V. C. M. - Adição de Produtos Químicos e Ensaio de Eletrocoagulação e Eletrooxidação para o (Pré) Tratamento das Águas Residuais Provenientes dos Lagares de Produção de Azeite. [S.l.] : Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, 2008
10. MOLLAH, M. Y. A.; MORKOVSKY, P.; GOMES, J.; KESMEZ, M.; PARGA, J.; COCKE, D. - Fundamentals, present and future perspectives of electrocoagulation. *Journal of hazardous materials*. . ISSN 0304-3894. 114:1-3 (2004) 199–210. doi: 10.1016/j.jhazmat.2004.08.009.
11. HOLT, P. K.; BARTON, G. W.; MITCHELL, C. A - The future for electrocoagulation as a localised water treatment technology. *Chemosphere*. . ISSN 0045-6535. 59:3 (2005) 355–367. doi: 10.1016/j.chemosphere.2004.10.023.
12. PÉREZ-SICAIROS, S.; MORALES-CUEVAS, J.; FÉLIX-NAVARRO, R.; HERNÁNDEZ-CALDERÓN, O. - Evaluation of the Eletrocoagulation Process for the Removal of Turbidity of River Water, Wastewater and Pond Water. *Revista Mexicana de Ingeniería Química*. 10:2011) 79–91.
13. CHEN, X.; CHEN, G.; YUE, P. L. - Separation of pollutants from restaurant wastewater by electrocoagulation. *Separation and Purification Technology*. . ISSN 13835866. 19:1-2 (2000) 65–76. doi: 10.1016/S1383-5866(99)00072-6.
14. KOBYA, M.; CAN, O. T.; BAYRAMOGLU, M. - Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes. *Journal of Hazardous Materials*. . ISSN 03043894. 100:1-3 (2003) 163–178.
15. MORANTE, G. - Eletrocoagulación de Aguas Residuales. *Revista Colombiana de Física*. 34:2 (2002) 484–487.
16. RUIZ, A. A. - Uso de electrocoagulación para la remoción de tartrazina en soluciones acuosas. *Producción+Limpia*. 6:2 (2011) 58–77.
17. H. Posavcic, I. Halkijevic, Application of electrocoagulation for water conditioning December 2019 *Environmental Engineering* 6(2):59-70