

EDER CARLOS LOPES COIMBRA

**ELECTROCOAGULATION OF KRAFT PULP BLEACHING FILTRATES TO
IMPROVE BIOTREATABILITY**

Dissertation submitted to the Civil Engineering Graduate Program of the Universidade Federal de Viçosa in partial fulfillment of the requirements for the degree of *Magister Scientiae*.

Adviser: Ann Honor Munteer

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ABSTRACT

COIMBRA, Eder Carlos Lopes, M.Sc., Universidade Federal de Viçosa, February, 2020. **Electrocoagulation of kraft pulp bleaching filtrates to improve biotreatability.** Advisor: Ann Honor Munteer.

Bleached kraft pulp mills are well known for high water consumption throughout the production process. Bleaching filtrates, with high color and organic loads, are responsible for the largest volume of total mill wastewater. These filtrates contain many high molecular weight compounds of low biodegradability (BOD₅/COD ratio). Electrocoagulation as pretreatment of the high-volume bleaching filtrates to lower their organic loads and improve their biodegradability before biological treatment is one approach to improving overall bleached kraft pulp mill effluent treatment. The response surface methodology can be used to develop models to predict effects of the combined electrocoagulation operating factors. In this study, the main objective was to evaluate the potential of electrocoagulation with iron and aluminum electrodes for increasing biological treatability of acid and alkaline eucalypt kraft pulp bleaching filtrates, and to optimize operating conditions (pH, current density and electrolysis time), in order to achieve maximum dissolved BOD₅/COD ratios. Electrocoagulation with iron and aluminum electrodes was effective for removing recalcitrant dissolved organic matter from acid and alkaline bleaching filtrates and under optimal conditions the biodegradable fraction was always greater than 75% of the total dissolved organic matter after treatment. Electrocoagulation with aluminum electrodes was more efficient in removing true color and estrogenic activity, while filtrates treated with iron electrodes were less toxic to *Daphnia similis*. Electrocoagulation of at least one filtrate before their combination was more advantageous in removing dissolved organic matter during aerobic biodegradability tests than no pretreatment of either filtrate. Electrocoagulation of both filtrates separately before their combination led to 90% DOC in a five-day biodegradability test, while only 30% DOC removal was achieved in the combined raw filtrates in the same test. Treatment of alkaline filtrate, with aluminum electrodes, followed by combination with raw acid filtrate prior to biological treatment is recommended to reduce additional pH adjustment costs, since only alkaline filtrate needs pH adjustment before electrocoagulation. Finally, electrocoagulation with aluminum electrodes is the more expensive option because of the higher cost of this metal and the higher optimum treatment time and current density. However,

electrocoagulation with aluminum electrodes was more efficient in removing recalcitrant organic matter.

Keywords: Biodegradability. Response surface. Toxicity. Wastewater.

RESUMO

COIMBRA, Eder Carlos Lopes, M.Sc., Universidade Federal de Viçosa, fevereiro de 2020. **Eletrocoagulação de filtrados de branqueamento de polpa kraft para melhorar sua biotratabilidade.** Orientadora: Ann Honor Mounteer.

A fábrica de polpa kraft branqueada é bem conhecida pelo alto consumo de água dentro dos seus setores sequenciais de fabricação. Como fonte de uma variedade de poluentes orgânicos, os filtrados da unidade de branqueamento são responsáveis pelo maior volume, quantidade de cor e matéria orgânica dos efluentes da fábrica. Além disso, esses filtrados são constituídos por compostos com alta massa molar que levam a uma baixa relação DBO_5/DQO e, portanto, resistência à degradação biológica. O uso do pré-tratamento por eletrocoagulação dos volumosos filtrados de branqueamento para reduzir suas cargas orgânicas e melhorar sua biodegradabilidade antes do tratamento biológico é uma abordagem para melhorar o tratamento geral de efluentes da fábrica de polpa kraft branqueada. A metodologia da superfície de resposta pode ser usada para o desenvolvimento de modelos para prever os efeitos dos fatores operacionais combinados de eletrocoagulação. Nesse estudo, o objetivo principal foi avaliar o potencial da eletrocoagulação com eletrodos de ferro e alumínio para a melhora da biotratabilidade de filtrados ácido e alcalino de branqueamento de polpa kraft de eucalipto, otimizando as condições operacionais de densidade de corrente, pH e tempo de eletrólise para alcançar as respostas máximas de DBO_5/DQO dissolvida, por meio da metodologia de superfície de resposta. Os resultados mostram que a eletrocoagulação com eletrodos de ferro e alumínio foi extremamente adequada para remover a matéria orgânica dissolvida recalcitrante dos filtrados de branqueamento ácido e alcalino e, nas condições ideais, a fração biodegradável foi superior a 75% da fração total da matéria orgânica dissolvida remanescente. Os tratamentos envolvendo o eletrodo de alumínio mostraram-se mais eficientes na remoção da cor verdadeira e da atividade estrogênica, enquanto aqueles com ferro apresentaram menor toxicidade à *Daphnia similis*. Os testes de biodegradabilidade aeróbia mostraram que o tratamento de pelo menos um filtrado com eletrocoagulação é mais vantajoso na remoção de matéria orgânica dissolvida dos filtrados combinados, sob condições aeróbias, do que nenhum tratamento usado em quaisquer dos dois filtrados. A combinação dos dois filtrados tratados separadamente resultou em remoção de 90% do carbono orgânico dissolvido (COD)

em cinco dias, enquanto, na mistura dos filtrados no estado bruto, no mesmo período, houve remoção de apenas 30% do COD. Para evitar custos adicionais de ajustes de pH, recomenda-se o tratamento apenas do filtrado alcalino, com eletrodo de alumínio (AlF-Al), para em seguida, o seu envio ao tratamento biológico combinado com o filtrado ácido bruto (AcF). Nessa configuração, é necessário apenas o ajuste inicial de pH do filtrado alcalino, antes ao processo de eletrocoagulação, uma vez que, na situação de mistura e envio à estação de tratamento não é necessário o ajuste. Por fim, os custos de operação dos tratamentos dos filtrados ácido e alcalino com eletrodos de alumínio são mais caros do que com eletrodos de ferro, devido, além dos maiores tempos e densidade de corrente aplicados, ao preço comercial do alumínio ser mais caro. Entretanto, os tratamentos com eletrodos de alumínio se mostraram mais vantajosos na remoção de matéria orgânica recalcitrante.

Palavras-chave: Biodegradabilidade. Superfície de Resposta. Toxicidade. Efluentes.

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INTRODUCTION

Brazil is among the world's largest wood pulp producers, with annual production of over 20 million tons of pulp (IBÁ, 2019). Over three quarters of Brazil's production is of bleached eucalypt kraft pulp, mostly for export. Specific water consumption in Brazilian bleached kraft pulp mills (BKPMs) is on the order of 20 – 30 m³ per air dried ton of pulp. The bleaching process is responsible for up to 50% of the water consumption (Amaral et al. 2013; Huber et al. 2014). Bleaching is carried out in sequential acid and alkaline stages, to remove residual lignin, extractives and other impurities from the pulp. Pulp washing between each stage generates acid and alkaline bleaching filtrates that account for up to 80% of the total mill wastewater volume.

BKPM effluents contain a complex mixture of chemical compounds extracted from the pulp. These wastewaters typically present high organic loads with relatively low biodegradability, quantified as the ratio of biochemical to chemical oxygen demand (BOD₅/COD), which can vary from 0.1 to 0.4 (Aghdam et al. 2016), caused by the presence of recalcitrant compounds, such as residual lignin (Eskelinen et al. 2010). Despite this, BKPM effluents are almost always treated using biological processes. Biologically treated effluents are typically highly colored and contain recalcitrant organic matter that present risks to receiving waters. Possible adverse effects in receiving waters include endocrine disruption, mutagenicity and carcinogenicity in fish and other aquatic organisms (Kamali and Khodaparast, 2014; Bajpai, 2018). Therefore, the development of technologies capable of removing recalcitrant pollutants are necessary. One approach to improving overall BKPM effluent treatment would be the inclusion of a pretreatment of the bleaching filtrates to lower their organic loads and improve their biodegradability prior to biological treatment.

Electrochemical processes have proven to be technically and economically viable alternatives for full-scale effluent treatment (Sridhar et al. 2011; Cotillas et al. 2019). Electrocoagulation (EC) was shown to efficiently remove high molecular weight organic matter responsible for COD and color in BKPM effluents (Moussa et al. 2017). Advantages of electrocoagulation for wastewater treatment include i) high particulate removal, ii) compact unit operation, iii) automation possible, iv) low sludge production and treated effluent with lower concentration of total dissolved solids than other physicochemical treatments (Mollah et al. 2001; Chen, 2004; Sridhar et al. 2011; Barrera-Díaz et al. 2018). Disadvantages include i) possible passivation (film

formation) or sludge deposit on the electrodes that can inhibit the electrolytic process, ii) high concentrations of aluminum, iron or another ion, depending on the electrode used treated effluents, requiring post treatment, and iii) the need replace sacrificial anodes, once they are consumed (Yang et al. 2015).

Only a few studies can be found in the literature that report on EC of individual bleaching filtrates, most focus on treatment of combined bleach plant or whole mill effluents. Sridhar et al. (2011) studied EC electrocoagulation with aluminum electrodes to treat bleaching effluents and found high color (94%), COD (90%) and BOD₅ (87%) removal efficiencies under optimal conditions (pH 7, 28 °C, 150 A/m² and 100 rpm).

Eskelinen et al. (2010) studied the removal of recalcitrant extractives from bleach plant effluents by different treatment technologies, including EC. Under optimal conditions (4.8 A/m², 300 rpm, pH 7, 1h) using diamond electrodes in a boron bath, they observed removals of 51% of linoleic acid, 83% of abietic acid and 76% of β -sitosterol from the effluent.

Patel and Suresh (2008) studied the removal of pentachlorophenol (PCB), an organochlorine compound from alkaline bleaching filtrates of bamboo pulp. Iron and graphite were used as cathode and anode, respectively, and PCB was completely removed in less than 10 min, at a current density of 60 A/m². The authors found greater PCB removal under acidic conditions (pH 5.5) than under basic conditions (pH 9.3).

EC operating conditions, including type and arrangement of electrodes, applied voltage, initial effluent pH, electrolysis time and nature and concentration of pollutants significantly affect EC treatment performance (Garcia-Segura et al. 2017; Hakizimana et al. 2017; GilPavas et al. 2018). Response surface methodology (RSM) can be used to study the combined effects of these conditions and thus generate optimized mathematical models capable of describing the effects of selected conditions on the desired response (Varank and Sabuncu, 2015).

The aim of this study was to evaluate the potential of electrocoagulation to increase biological treatability of bleached eucalypt kraft pulp filtrates using RSM. A central composite design (CCD), with pH, current density and electrolysis time as independent factors and the BOD₅/COD index as response, was used to generate models to predict biodegradability of acid and alkaline bleaching filtrates after electrocoagulation with aluminum (Al) and iron (Fe) electrodes.

Electrocoagulation of kraft pulp bleaching filtrates to improve biotreatability

1. Introduction

Brazil is among the world's largest pulp producers, with annual production of over 20 million tons of pulp (IBÁ, 2019). Over three quarters of Brazil's production is of bleached eucalypt kraft pulp. Specific water consumption in Brazilian bleached kraft pulp mills (BKPMs) is on the order of 20 to 30 m³ per air dried ton of pulp. The bleaching process is responsible for up to 50% of the water consumption, mainly used for washing the pulp after each bleaching stage to ensure the removal of oxidized materials in order to achieve high pulp brightness (Huber et al. 2014; Sharma et al. 2020). Pulp washing between each stage generates acid and alkaline bleaching filtrates that account for up to 80% of the total mill wastewater volume (Colodette and Gomes, 2015). Bleaching filtrates contribute to more than half the BOD₅, COD and color of the whole mill effluent (Amaral et al. 2013; Hubbe et al. 2016). Furthermore, raw BKPM effluents contain toxic substances with the potential to cause endocrine disruption in aquatic organisms (Hewitt et al. 2008; Balabanič et al. 2012, Balabanič et al. 2017) and they must be treated before discharge to receiving waters.

Pulp mill wastewater is most commonly treated using biological processes (Camcioglu et al 2017). However, due to the presence of recalcitrant organic material, such as residual lignin, which possesses many unsaturated bonds in its molecular structure (El-Ashtoukhy et al. 2009), the wastewater biodegradability index (BOD₅/COD) typically ranges from 0.1-0.4 (Aghdam et al. 2016), leading to limited biological treatment efficiency (Eskelinen et al. 2010). An approach to improving overall BKPM effluent treatment would be inclusion of a pretreatment of the bleaching filtrates to lower their organic loads and improve their biodegradability prior to biological treatment.

Electrochemical processes have proven technically and economically viable for full-scale effluent treatment (Sridhar et al. 2011; Cotillas et al. 2019). EC has advantages over classical chemical coagulation/flocculation that include lower sludge production and operating cost (Xu et al. 2018) and the capacity to remove colloidal particles because of applied electric field (Uğurlu et al. 2008) and the possibility of other

electrochemical processes occurring simultaneously, such as formation of strong oxidants responsible for mineralization of organic compounds.

EC operating conditions, including type and arrangement of electrodes, applied voltage, initial effluent pH, electrolysis time and pollutant nature and concentration, can significantly affect EC treatment performance (Garcia-Segura et al. 2017; Hakizimana et al. 2017; GilPavas et al. 2018). Response surface methodology (RSM) is a useful tool to predict the combined effects of selected conditions on the desired response (Varank and Sabuncu, 2015).

Electrochemical processes have been studied for treatment of pulp and paper mill sectorial and final effluents (Table 1). Most of these studies focused on color and COD removal, with only two reporting increased biodegradability after EC, but no reports on the effects of EC bleaching filtrate biodegradability were found.

Therefore, the aim of this study was to evaluate the potential of electrocoagulation with iron and aluminum electrodes for increasing biological treatability of bleached eucalypt kraft pulp filtrates using RSM. A central composite rotatable design (CCRD), with pH, current density (CD) and electrolysis time (T) as independent variables, was used to generate models that describe biodegradability (BOD₅/COD index) of acid (AcF) and alkaline (AIF) bleaching filtrates after EC. To the authors' knowledge, this is the first study that reports on EC of individual acid and alkaline filtrates to improve biodegradability and reduce toxicity.

In order to determine the efficiency of electrocoagulation on removal of recalcitrant organic matter, color, acute toxicity and estrogenic activity, experiments were performed under conditions leading to maximum BOD₅/COD indices for each electrode-filtrate combination and the results were compared with respect to operating costs and overall effectiveness of electrocoagulation.

Table 1

Electrochemical treatment of pulp and paper mill wastewaters

Wastewater	Electrode material Cathode/Anode	Optimal conditions	Removal efficiency, %				$\Delta \frac{BOD_5}{COD}$, %	Energy consumption	Reference
			Color	Toxicity	BOD ₅	COD			
Debarking effluents	Fe/Fe	20 mA/cm ² pH 8	–	22.14 ^b	–	–	–	–	Vepsäläinen et al. (2011)
Black liquor	Al/Al Fe/Fe	4.8 mA/cm ² pH 7.5	–	–	Al: 70 Fe: 80	Al: 75 Fe: 55	–	–	Uğurlu et al. (2008)
Black liquor	Pb/Steel	6.6 mA/cm ² 60 min pH 8	53 - 100	–	–	–	–	4 – 29 kWh/m ³	El-Ashtoukhy et al. (2009)
Black liquor	Al/Al	115 A/m ² 75 min pH 7	99.6	–	–	77	–	–	Shankar et al. (2014)
Decker filtrate	Fe/Fe	112.9 A/m ² 6,9 min pH 7.3	87	–	- 88	55	318	1.19 kWh/kgCOD	Soloman et al. (2009)
Bleaching filtrates	Fe/Graphite	6 mA/cm ² 30 min pH 5.5	90	–	–	90	–	0.56 kWh/m ³	Patel and Suresh (2008)
Bleaching filtrates	BDD/MMO ^a	0.48 A/cm ² 60 min pH 6.9	–	–	–	28	–	–	Eskelinen et al. (2010)
Bleaching filtrates	Al/Al	15 mA/m ² 20 min pH 7	94	–	87	90	–	11.05 kWh/m ³	Sridhar et al. (2011)
Primary effluent	Fe/Fe	1.5 mA/cm ² 25 min	95	–	45	60	58	–	Wagle et al. (2020)

Table 1

...continued

Wastewater	Electrode material Cathode/Anode	Optimal conditions	Removal efficiency, %				ΔBOD_5 , % COD	Energy consumption	Reference
			Color	Toxicity	BOD ₅	COD			
Secondary effluent	Steel/Steel	15 A/m ² 120 min pH 7	94	–	–	85	–	–	Sharma et al. (2014)
Secondary effluent	Al/Fe	4.167 A/m ² 60 min pH 5	100	–	–	85	–	8.334 kWh/m ³	Aghdam et al. (2016)
Secondary effluent	Al/Al Fe/Fe	<u>Al</u> 1.2 A 10.8 min pH 5.8 <u>Fe</u> 1.4 A 10.9 min pH 5.4	Al: 100 Fe: 80.9					Al: 8.82 kWh/kg COD Fe: 14.58 kWh/kg COD	Camcioglu et al. (2017)

^a BDD = Boron-doped diamond, MMO = mixed metal oxide.

^b Toxicity to the green alga *R. subcapitata*

2. Material and Methods

2.1. Bleaching filtrates

Acid (AcF) and alkaline (AIF) filtrates were collected at a Brazilian bleached eucalyptus kraft pulp mill that produces ECF (*Elemental Chlorine Free*) pulp using the PreO₂-D_{HT}-(EP)-D₁-P sequence (oxygen delignification - hot chlorine dioxide - alkaline extraction with hydrogen peroxide - chlorine dioxide - hydrogen peroxide). In the mill, equal volumes of AcF and AIF are generated and sent to the wastewater treatment plant, from the D_{HT} stage and EP stage, respectively. The filtrates samples were collected at these stages and transported in plastic drums to the Sanitary and Environmental Engineering Laboratory (LESA) of the Universidade Federal de Viçosa, where they were characterized and stored at 4°C in the dark until used.

2.2 Electrocoagulation

The filtrates underwent electrocoagulation (EC) with iron (Fe) and aluminum (Al) electrodes. Independent experiments were carried out for the four filtrate-electrode combination: AcF-Al (acid filtrate with Al electrodes), AcF-Fe (acid filtrate with Fe electrodes); AIF-Al (alkaline filtrate with Al electrodes) and AIF-Fe (alkaline filtrate with Fe electrodes). For each filtrate-electrode combination, a central composite rotational design (CCRD) with three factors (pH, current density, and electrolysis time) was set up and analyzed using Minitab®. Biodegradability (BOD₅/COD) of dissolved organic matter after EC was used as response variable. Current density (A/m²) and electrolysis time (min) were defined based on previous EC studies of BKPM wastewaters (Table 1), while pH levels were selected based on initial pH of the acid and alkaline bleaching filtrates collected at the pulp mill (Table 2). Each of the four CCRD consisted of 8 factorial points (2³), 6 axial points and 3 repetitions at the central point, totaling 17 experimental runs.

EC was performed in a glass, bench-scale reactor (300 mm x 135 mm x 200 mm, L x W x H) with a 2 L working volume (Supplementary Figure S1), operated in batch mode and equipped with parallel monopolar electric connection to a 32 V, 5 A constant dual current source (DC model MPL-3305M, Brazil), thermostat (ATMAN Termostato AT-50, Brazil) and mechanical mixer (FISATOM 710, Brazil).

Six 1.0 mm thick Al (99 % Al) or 1.5 mm Fe (99.5 % Fe) electrodes, with submerged total surface areas of 381 cm², were vertically positioned in the reactor with an inner gap of 15 mm to ensure circulation between them and guarantee filtrate

homogenization during treatments. Before each treatment, the electrodes were immersed in H₂SO₄ (15 % v/v) for at least 10 min, scoured with sandpaper, washed with tap water and rinsed with deionized water to remove residue and/or oxide layers.

In each EC run, 2 L of filtrate were preheated to 25 °C, followed by adjustment to the desired initial pH. The DC source was then turned on to the appropriate current density under continuous mixing (200 rpm) of the filtrate. After the desired electrolysis time, the DC source and mixer were turned off and the effluent left at rest for 20 minutes (sedimentation/flotation step), after which treated filtrate was siphoned off to measure its pH, temperature, color and dissolved BOD₅ and COD.

Table 2

Low (-1) and high (+1) factor levels, central (0) and axial points (- α , + α) for central composite rotational design used to evaluate electrocoagulation of kraft pulp bleaching filtrates.

Factor	Level				
	$-\alpha = -1.68$	- 1	0	- 1	$\alpha = +1.68$
pH	3.6	5.3	7.7	10.1	11.8
Current density (A/m ²)	50	70	100	130	150
Electrolysis time (min)	10	20	35	50	60

2.3. Model generation and validation

A second-order polynomial hierarchical model was fitted to the CCRD results. Analysis of variance (ANOVA) was performed using the RSM to estimate the model parameters, as well as their predictions at the 5% significance level. Optimization was performed using the *Response Optimizer* function of Minitab® software, with the maximum value of the response function equal to unity (the maximum value attributable to the biodegradability index, BOD₅/COD = 1). Experimental values were compared to predicted values and response surface graphs were generated to visualize effects of pH, electrolysis time and current density on BOD₅/COD. (Nonsignificant variables, except for linear terms, were not included in the hierarchical models).

The models were validated in three independent assays. In the first, optimal values of pH, current density and electrolysis time were used and in the other two, random

values of these variables were used. Experimental and predicted values of BOD₅/COD were compared. The predictive capacity of the models was evaluated based on the significance of the regression models ($p \leq 0.05$), lack of fit ($p > 0.05$), coefficient of determination (R^2) and adjusted coefficient of determination (adj. R^2).

Graphs were prepared using STATISTICA 10.0 (StatSoft, Tulsa, OK, USA), MINITAB® (MINITAB INC., 2016) and Microsoft® Excel spreadsheets (Microsoft, Redmond, WA, USA).

2.4. Analytical methods

Raw and optimally treated filtrates were characterized through physicochemical and molecular weight distribution analyses, estrogenic and acute toxicity assays.

2.4.1. Physicochemical analyses

Standard methods (APHA, 2017) were used to quantify COD (5220D, Hach DR3800 spectrophotometer), BOD₅ (5210B), DOC (5310B, Shimadzu TOC-VCSH analyzer), color (2120C, Hach DR3800 spectrophotometer), total phenols (5530 A, SPEKOL 1300 UV-Vis spectrophotometer), pH (4500-H⁺, Qualxtron QX 1500 Plus pH meter), electrical conductivity (2510B, Tecnopeon mCA-150 conductivity meter), iron (3500-Fe B), aluminum (3500-Al B) and total and volatile suspended solids (2540-B,D). Dissolved BOD₅, COD, iron, aluminum, total phenols and true color were measured after filtering samples through 0.22 µm membranes (Unifil cellulose nitrate). Sample pH was adjusted to 7.6 ± 0.04 with 2 mol/L NaOH or 1 mol/L H₂SO₄ for color measurements

The BOD₅ seed was prepared by adapting domestic sewage to combined raw filtrates. The sewage-filtrate mixture (1:1 v/v) was incubated at room temperature under constant aeration. One-third of this mixture was discarded and replenished daily for one week, and thereafter every third day with increasing proportions of filtrate, up to 80% of the total volume. The adapted seed was kept under aeration until needed for the BOD₅ assay. Aeration was stopped and after one hour at rest, aliquots of 1.5 mL supernatant were used as BOD₅ seed.

2.4.2. UV-Vis spectroscopy

In order to identify specific groups of compounds, absorbances were read at 254 nm (conjugated double-bonds in chromophores, indicative of aromatic compounds) and 280 nm (lignin derivatives). UV-Vis spectra were obtained for samples of raw and

optimally treated filtrates, using a spectrophotometer (SPEKOL 1300, Analytik Jena, Germany) equipped with 10 mm quartz cuvettes.

Samples for absorbance analysis were prefiltered on 0.22 µm membranes (Unifil cellulose nitrate), and diluted 40x (raw filtrates) or 20x (treated filtrates) in 3% H₂SO₄ (v/v) to achieve absorbance values of up to 0.9 cm⁻¹ (Chaparro and Pires, 2011). All absorbance measurements were made at natural filtrate pH or final pH after EC.

Specific ultraviolet absorption at 254 nm (SUVA) and UV₂₅₄/UV₂₈₀ ratios were measured according (Edzwald and Tobiason, 1999) and (Çeçen, 1999), respectively. SUVA₂₅₄ was calculated using Equation 1:

$$\text{SUVA (L/mg.m)} = \frac{\text{UV}_{254}}{\text{DOC}} \cdot \text{D} \cdot 100 \quad (1)$$

in which UV₂₅₄ is the measured absorbance (cm⁻¹), D is the dilution factor, DOC is the dissolved organic carbon (mg/L) and 100 is the correction factor (cm/m).

2.4.3. Molecular weight distribution

The molecular weight distribution of dissolved organic matter in the filtrates was determined using a 500 mL stirred ultrafiltration cell (Amicon, model 8200) equipped with 1 kDa nominal MWCO membrane (Millipore), prepared according to the manufacturer's instructions. Ultrafiltration cell pressure (0.5 MPa) was provided by a steady stream of high purity N₂ (99.99 vol%). Fifty mL filtrate aliquots were filtered until the passage of sample through the membrane was no longer observed or when 25 mL of permeate was collected. The high (HMW) and low (LMW) molecular weight fractions were each reconstituted to the original sample volume (50 mL) with deionized water to quantify their COD.

2.5. Toxicity assays

Acute toxicity was quantified using the *Daphnia similis* immobilization assay (ABNT, 2016) at the Aquatic Ecotoxicology Laboratory (Aquatox /LESA/UFV). The static assay consisted of exposing neonates to dilutions of samples for 48 hours, at 22 ± 2 °C, under a 16 h light (700 lux)/ 8 h dark photoperiod. After 48 hours, the number of immobilized organisms was quantified and compared to the unexposed control group. The dilution that caused 50% immobility of the test organisms (EC₅₀, %) was determined by the *Trimmed Spearman-Kärber* method (USEPA, 2002) using *Comprehensive Environmental Toxicity Information System™* software (Cetis, 2018). The sensitivity of

organisms was periodically checked in the laboratory using sodium chloride (NaCl) as reference material. Assay results were expressed in acute toxicity units, $TUa = 100/EC_{50}$.

Estrogenic activity in the raw and in the optimally treated filtrates was quantified as 17β -estradiol equivalents (E2 eq.) using the yeast estrogen screen (YES), according to Routledge and Sumpter (1996) and Bila et al. (2007). Three hundred mL (raw filtrates) or 400 mL (optimally treated filtrates) sample aliquots were extracted on C18 solid phase extraction cartridges (6 mL x 500 mg, Agela Technologies) and eluted by passing 4x1 mL acetone through the cartridges. The acetone was completely volatilized under a nitrogen gas flow (N_2 99.99 vol%) and the extract reconstituted in 1 mL ethanol (HPLC grade) for testing. The 17β -estradiol standard curve ranged from 26.61 ng/L to 54.48 μ g/L, with an EC_{50} of 14.41 ng/L and limit of detection of 0.03 ng /L E2 eq.

2.6. Aerobic biodegradability assays

Aerobic biodegradability assays (OECD, 1992) were performed using acid and alkaline filtrates with the highest BOD_5/COD indices after EC (Tukey, $\alpha = 0.05$), in order to verify the effect of treatment on filtrate biotreatability. Six assays were performed in which equal volumes of raw or EC-treated acid and alkaline filtrates were combined: 1) AcF + AIF (mixed raw filtrates), 2) AcF + EC-AIF (mixed raw acid and EC-treated alkaline filtrates), 3) EC-AcF + AIF (mixed EC-treated acid and raw alkaline filtrates), 4) EC-AcF + EC-AIF (mixed EC-treated acid and alkaline filtrates), 5) positive control (glucose solution) and 6) blank (deionized water).

One hundred mL of mineral medium and 60 mL of sample or glucose solution, each diluted to approximately 50 mg/L DOC with deionized water, were added to 250 mL Erlenmeyer flasks. Initial pH of all solutions was adjusted to 7.4 ± 0.2 . Forty mL adapted BOD_5 seed were added to establish an initial food/biomass (F/M) ratio of approximately 0.5 g DOC/g volatile suspended solids (VSS) in all flasks. Test solutions were incubated under aerobic conditions in the dark, on an orbital shaker (130 rpm) at 22 ± 2 °C. Aliquots were removed at different intervals and filtered through 0.45 μ m membranes (Unifil 510.047) to measure DOC and calculate its removal using Eq. (2):

$$Dt (\%) = \left[1 - \frac{C_t - C_{Bt}}{C_A - C_B} \right] \times 100 \quad (2)$$

in which, D_t = DOC removal at time t ; C_A = initial sample DOC (mg/L); C_t = sample DOC at time t (mg/L); C_B = initial blank DOC (mg/L); C_{Bt} = blank DOC at time t (mg/L).

2.7. Economic analysis

A simplified operational cost (OC) analysis was undertaken based on electrical energy and electrode consumption (E_{EL}) under optimal operating conditions. Energy consumption (E) per volume of treated filtrates was calculated using Eq. 3:

$$E = \frac{V.I.t}{V_{ol}} \quad (3)$$

in which E = energy consumption per volume of treated filtrate (kWh.m^{-3}); V = average applied voltage (V); I = electrolysis current (Ampere); t = electrolysis time (hour); V_{ol} = volume of treated filtrate (m^3).

Electrode consumption (E_{EL}) per unit volume of treated effluent was calculated using Eq. 4:

$$E_{EL}(\text{kg. m}^{-3}) = \frac{I.t.MW}{Z.F.V_{ol}} \quad (4)$$

in which MW = molecular weight of the used material (g/mol); I = electrolysis current (Ampere, A); t = electrolysis time (s); Z = number of electrons transferred (Al^{3+} , $\text{Fe}^{3+} = 3$); F = Faraday's constant, $96.485 \text{ (C.mol}^{-1}\text{)}$; $V_{ol.}$ = volume of treated filtrate (m^3). The theoretical operating cost (OC) was calculated as the sum of electricity and electrode materials costs (Eq. 5):

$$\text{OC (US \$.m}^{-3}\text{)} = E_P \cdot E + E_{LP} \cdot E_{EL} \quad (5)$$

in which E_P = electrical energy cost (US \$. kWh^{-1}); E = energy consumption per unit volume of treated filtrate (kWh.m^{-3}); E_{LP} = electrode cost (US \$. kg^{-1}); E_{EL} = theoretical electrode consumption per unit volume of treated filtrate (kg.m^{-3}). $E_P \cdot E$ and $E_{LP} \cdot E_{EL}$ represent the costs of energy and theoretical electrode consumption during the treatment process, in US \$/m³. Brazilian market prices in 2019 were adopted for

aluminum (7.24 US \$/kg), iron (1.98 US \$/kg) and electricity (0.15 US \$/kWh) for the calculations.

Experimental electrode consumption (E_{ELP} , $\text{kg}\cdot\text{m}^{-3}$) was also determined by weighing the six electrodes in the reactor before and after the four experiments (AcF-Al, AcF-Fe, AIF-Al and AIF-Fe) performed at the optimal treatment times. In order to avoid material loss during washing, the electrodes were washed only with deionized water and dried in an oven at 50 °C for at least 24 hours for weighing before and after use. The difference in mass (kg) was considered as the experimental electrode consumption (E_{ELP}) used to calculate the practical operating cost (OC_P) (Eq. 6):

$$OC_P (\text{US } \$\cdot\text{m}^{-3}) = E_P \cdot E + E_{LP} \cdot E_{ELP} \quad (6)$$

3. Results and Discussion

3.1. Bleaching filtrate characteristics

Raw bleaching filtrates contained high levels of organic matter (Table 3) with biodegradability indices on the high end (0.4 - 0.5) of the range typically reported in the literature for these effluents (Bajpai, 2018). The high electrical conductivity of the filtrates made them good candidates for electrocoagulation treatment (Boroski et al., 2009).

Differences in physicochemical and ecotoxicological quality of the acid and alkaline filtrates stemmed from the bleaching sequence used at the mill. The higher organic content in the acid filtrate (COD, BOD, DOC) was a result of the inclusion of the chlorine dioxide (D_{HT}) bleaching stage (Zhang et al. 2018), whose main function is delignification rather than whitening (Colodette and Gomes, 2015). The higher AcF SUVA value indicates it contained more aromatic, hydrophobic high molecular weight organic matter (Edzwald and Tobiasson, 1999) than the AIF, which corroborates the efficient removal of organic matter (COD) from the pulp during the D_{HT} stage. On the other hand, the similar levels of UV_{254}/UV_{280} indicate that lignin and its derivatives contribute similarly to aromaticity of the two filtrates (Chaparro and Pires, 2011).

Table 3

Raw acid (AcF) and alkaline (AIF) kraft pulp bleaching filtrate characteristics (means \pm standard deviations^a).

Parameter	AcF	AIF
pH	3.6 \pm 0.1	11.8 \pm 0.1
Conductivity (mS/cm)	4.65 \pm 0.20	3.93 \pm 0.15
Color (mg/L PtCo)	893 \pm 100	629 \pm 13
COD (mg/L)	2118 \pm 190	1622 \pm 92
COD(t) (mg/L)	2714 \pm 105	1843 \pm 29
BOD ₅ (mg/L)	863 \pm 63	739 \pm 26
BOD ₅ (t) (mg/L)	891 \pm 40	750 \pm 31
BOD ₅ /COD	0.41 \pm 0.05	0.46 \pm 0.01
DOC (mg/L)	827 \pm 124	794 \pm 141
TSS (mg/L)	820 \pm 114	107 \pm 20
Al (mg/L)	< 0.006	< 0.006
Fe (mg/L)	0.74 \pm 0.18	0.96 \pm 0.01
Phenols (mg/L)	613.7 \pm 5.2	422.6 \pm 12.7
SUVA ₂₅₄	1.755 \pm 0.019	1.003 \pm 0.028
UV ₂₅₄ /UV ₂₈₀	1.951 \pm 0.009	1.667 \pm 0.330
TUa <i>D. similis</i>	6.3	4.6
Estrogenic Activity (ng/L E2 eq.)	< 0.03	0.55

^an = 2, except COD and BOD₅, n=3.

3.2. Electrocoagulation biodegradability models

3.2.1 BOD₅/COD indices

BOD₅/COD indices were modified after electrocoagulation, but in different manners for Al and Fe electrodes (see Supplementary Table S1 for results of all experimental run). In almost all treatments, filtrate biodegradability increased, however, EC with Al-electrodes was more effective than with Fe-electrodes, producing BOD₅/COD ratios above 0.9, especially for the AIF-Al combination. BOD₅/COD indices greater than 0.8 were produced under medium to high electrolysis time, medium current densities and acid to neutral pH for all four filtrate-electrode combinations.

Treatment at pH 11.8 led to the worst results for all four experiments. Large variations of the applied voltage were observed within the first 3 min at this pH, indicating anode passivation, as confirmed by the formation of a fluffy layer on electrode surfaces after the treatments. Anode passivation is favored at high initial solution pH, caused by microflocs that form and spread across anode surfaces blocking their active sites (Mahesh et al. 2016; Dura and Carmel, 2019).

3.2.2 Biodegradability index models

In general, all three variables (pH, current density and electrolysis time) had significant effects on filtrate biodegradability indices, but in different ways (see Supplementary Table S2 for ANOVA results). The four models predicting BOD₅/COD indices (Eq. 7-10) adjusted well to the data, as demonstrated by the non-significant lack of fit ($p \geq 0.05$) (Bezerra et al. 2008). The high coefficients of determination (R^2 , $R^2_{adj.}$) indicated that the models effectively explained 90% or more of total variation in BOD₅/COD (Barros Neto, 2007). Model response surfaces are presented in Figures 1 and 2.

AcF-Al

$$\text{BOD}_5/\text{COD} = -0.733 + 0.2275\text{pH} + 0.01017\text{CD} + 0.00565\text{T} - 0.02212\text{pH}^2 - 0.000073\text{CD}^2 - 0.000486\text{T}^2 + 0.002494\text{pH.T} + 0.000172\text{CD.T} \quad (R^2 = 96.4; R^2_{adj.} = 92.8) \quad (7)$$

AcF-Fe

$$\text{BOD}_5/\text{COD} = -1.443 + 0.1196\text{pH} + 0.02919\text{CD} + 0.03082\text{T} - 0.01295\text{pH}^2 - 0.000142\text{CD}^2 - 0.000392\text{T}^2 \quad (R^2 = 92.2; R^2_{adj.} = 87.5) \quad (8)$$

AIF-Al

$$\text{BOD}_5/\text{COD} = -0.056 - 0.1116\text{pH} + 0.02931\text{CD} - 0.01829\text{T} + 0.01016\text{pH}^2 - 0.000104\text{CD}^2 + 0.000288\text{T}^2 - 0.000956\text{pH.CD} \quad (R^2 = 94.8; R^2_{adj.} = 90.8) \quad (9)$$

AIF-Fe

$$\text{BOD}_5/\text{COD} = -2.718 + 0.3061\text{pH} + 0.03290\text{CD} + 0.04658\text{T} - 0.01729\text{pH}^2 - 0.000164\text{CD}^2 - 0.000396\text{T}^2 - 0.002175\text{pH.T} \quad (R^2 = 89.8; R^2_{adj.} = 81.9) \quad (10)$$

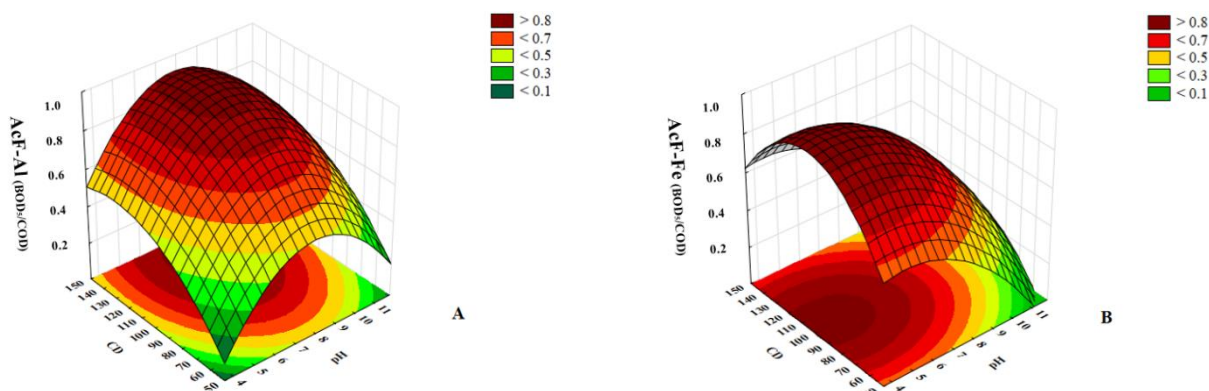


Figure 1. Acid filtrate BOD₅/COD indices after electrocoagulation. A) Effect of current density (CD) and pH at optimum electrolysis time (49 min), using aluminum electrode (AcF-Al). B) Effect of current density (CD) and pH at optimum electrolysis time (40 min), using iron electrode (AcF-Fe).

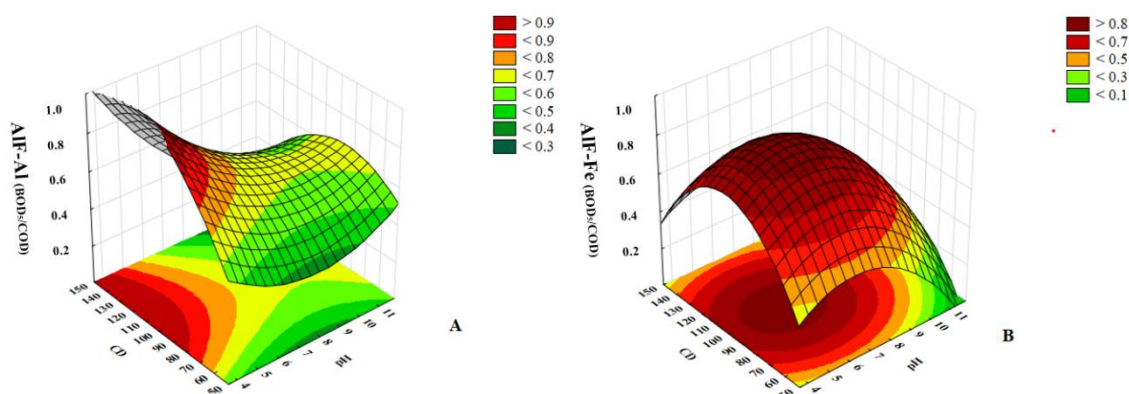


Figure 2. Alkaline filtrate BOD₅/COD indices after electrocoagulation. A) Effect of current density (CD) and pH at optimum electrolysis time (52 min), using aluminum electrode (AIF-Al). B) Effect of current density (CD) and pH at optimum electrolysis time (42 min), using iron electrode (AIF-Fe).

Maximum biodegradability was reached at electrolysis time at or above 40 min and current density greater than 100 A/m² for all filtrate-electrode combinations. Optimal initial pH differed from the original pH values of the two filtrates, with a smaller difference found for treatment with iron electrodes. Optimal pH values were different from ranges reported in the literature for EC with iron (pH 5-9) and aluminum (pH 6-8) electrodes (Lakshmanan et al., 2009; Hakizimana et al., 2017), in which the greatest amounts of amorphous iron hydroxide Fe(OH)_{3(s)} and aluminum Al(OH)_{3(s)} that

contribute to sweeping the pollutants from solution are formed (Garcia-Segura et al. 2017). Initial filtrate pH adjustments before EC treatment may have influenced the optimal pH. During pH adjustments, color changes occurred in the filtrates. Addition of NaOH to AcF caused an increase in color due to nucleation of lignin with sodium ions and formation of soluble salts containing chromophoric groups. Acidification of AIF with H₂SO₄ caused lignin protonation and precipitation, consequently, reducing the filtrate color (Jose et al. 2019). Therefore, changes in pH alter the initial quality of the filtrates prior to electrocoagulation.

Maximum biodegradability indices (> 0.8) for the AcF-Al combination (Fig 1A) were reached at pH 7.9 and medium to high current densities. An increase of one pH unit required a 15-fold increase in current density to achieve a 50% increase in biodegradability. For the AcF-Fe combination (Fig 1B), maximum biodegradability was achieved at more acidic pH and mid-range current density.

Saddle behavior was only observed for the AIF-Al combination surface response (Figure 2A) indicating that optimum EC conditions lay outside the boundary conditions of the experiment. However, BOD₅/COD indices higher than 0.8, could be achieved at a pH range of 5-6 and current density above 100 A/m². For the AIF-Fe combination (Fig 2B), the highest biodegradability indices (BOD/COD > 0.8) were found at more neutral pH and mid-range current density.

3.2.3 Model validation

Observed BOD₅/COD values results were similar to predicted values for all models in the three validation tests (Table 4). The models overestimated the BOD₅/COD indices by 10 to 15% for the validation under optimal EC conditions (test 1), while under random EC operating conditions (tests 2 and 3), the observed BOD₅/COD indices ranged from -11% to 40% higher than the predicted values.

Table 4

Comparison of observed (O) and predicted (P) BOD₅/COD results from regression model validation tests performed under optimal (test 1) and random (tests 2 and 3) operating conditions.^a

Test ^a	AcF-Al			AcF-Fe			AlF-Al			AlF-Fe		
	O	P	O/P	O	P	O/P	O	P	O/P	O	P	O/P
1	0.87	0.94	0.93	0.81	0.94	0.86	0.91	1	0.90	0.77	0.81	0.91
2	0.77	0.86	0.9	0.85	0.84	1.01	0.54	0.57	0.95	0.76	0.82	0.93
3	0.51	0.5	1.02	0.69	0.66	1.05	0.81	0.91	0.89	0.44	0.32	1.38

^a Operating conditions: Test 1 - values reported in Table 5; Test 2 - pH 7.0, 88 A/m², 41 min; Test 3 - pH 4.0, 140 A/m², 25 min

3.3. Quality of bleaching filtrates after electrocoagulation under optimized conditions

3.3.1 Physicochemical and ecotoxicological quality

The optimized EC operating parameters within the experimental boundary conditions (Table 5) produced maximum biodegradability indices (BOD₅/COD). However, for each filtrate-electrode combination, a range of conditions around the optimal point will result in BOD₅/COD greater than 0.8 and adjusting EC operating conditions within these ranges would still improve filtrate biodegradability by close to two-fold or more. COD was generally removed, with maximum removal of about 50%, while BOD₅ was partially removed or even increased, which was responsible for the 1.6 to over 2-fold increase in biodegradability (Table 5). Although up to five-fold BOD₅/COD increases were reported by Soloman et al. (2009) after EC pretreatment of pulp and paper mill effluents, final values did not reach the levels observed in the present study.

Higher dissolved organic matter (COD and BOD) removal in filtrates treated with Al electrodes may be associated with the higher applied current density (Table 5) that resulted in higher coagulant and H₂ production rates that acted to remove pollutants from solution by sedimentation and flotation (Särkkä et al 2015; An et al. 2017). Another possible explanation is the production of metal ions at the cathode (Chellam and Sari 2016) caused by the occurrence of a super faradaic condition, that resulted in greater generation of ions than predicted by Faraday's law (Mechelhoff et al. 2013), and consequently greater availability of coagulating agent. Super faradaic conditions

can occur when the cathode is corroded by OH⁻ ions, which releases metal ions to solution. They are more common in reactors that operate with aluminum electrodes than with iron (Jiménez et al. 2012). Higher COD and BOD removals during AcF/AIF-Al treatments than AcF/AIF-Fe treatments (Table 5) corroborates their occurrence.

Table 5

Optimal operating conditions for electrocoagulation and quality of acid and alkaline filtrates they produced.¹ (Average removal efficiencies in parenthesis).

Parameter	AcF-Al	AcF-Fe	AIF-Al	AIF-Fe
Initial pH	7.9	4.6	3.8	6.3
CD (A/m ²)	128	104	150	101
T (min)	49	40	52	42
COD (mg/L)	692 ± 78 (67%)	875 ± 39 (58.7%)	495 ± 3 (69.5%)	859 ± 61 (47%)
BOD ₅ (mg/L)	597 ± 44 (31%)	710 ± 7 (17.7%)	450 ± 7 (39.1%)	658 ± 14 (10.9%)
BOD ₅ /COD	0.87 ± 0.03	0.81 ± 0.02	0.91 ± 0.01	0.77 ± 0.04
DOC (mg/L)	324 ± 11 (60.7%)	474 ± 10 (42.6%)	278 ± 15 (65.3%)	418 ± 9 (47.3%)
Color (mg/L PtCo)	130 ± 9 (85.4%)	177 ± 43 (80.2%)	21 ± 8 (96.7%)	107 ± 8 (82.9%)
Final pH	10.1 ± 0.2	8.5 ± 0.6	9.0 ± 0.3	10.4 ± 0.2
Al (mg/L)	5.5 ± 0.7	< 0.006	4.0 ± 0.5	< 0.006
Fe (mg/L)	< 0.01	3.4	< 0.01	0.10
E2 eq.(ng/L)	< 0.03	0.28	0.28	0.62
TUa	1.9 (69.8%)	1.4 (77.7%)	1.8 (60.8%)	1.4 (69.6%)

¹ Except for final pH, all values refer to dissolved forms of parameters.

Electrocoagulation removed compounds responsible for SUVA and increased UV₂₅₄/UV₂₈₀ ratios (Figure 3), indicative of a decrease in aromaticity linked to the removal of lignin derivatives in the treated filtrates. High phenols removals are also evidence that residual lignin was efficiently removed.

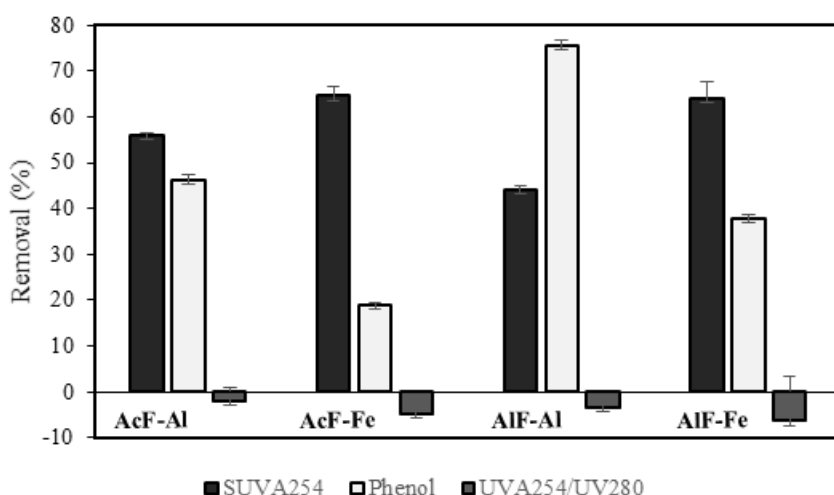


Figure 3. Removal of SUVA, phenols and UV_{254}/UV_{280} from acid (AcF) and alkaline (AlF) bleaching filtrates after electrocoagulation with Al and Fe electrodes under the optimized conditions.

No large differences in the increase in UV_{254}/UV_{280} ratios were found among treatments, but treatment with Fe electrodes greater SUVA reductions, indicating greater destruction of aromatic compounds. However, treatment with Al electrodes resulted in greater removal of phenolic compounds, which accompanied the greater color and COD removal efficiencies (Table 5).

The higher acute toxicity reductions when Fe electrodes were used may be associated with shorter reaction times (Table 5) resulting in greater removal of aromatic compounds (Figure 3), as reported previously by Vepsäläinen et al. (2011) who observed more efficient removal of toxic aromatic compounds present in pulp and paper mill effluents at lower EC reaction time.

However, use of Fe electrodes increased estrogenic activity. The lower dissolved organic matter removal efficiency in the Fe-treated filtrates may explain the greater estrogenic activity. Furthermore, the increase in estrogenicity suggests formation of intermediate compounds of estrogenic nature.

3.3.2 Molecular weight distributions

Low molecular weight (LMW) compounds were responsible for about 60% of the total dissolved COD of the raw filtrates, while the COD remaining in treated filtrates was mainly constituted of high molecular weight (HMW) compounds (Figure 4). Similar

MW distribution of bleaching filtrate COD has been reported previously (Amaral et al. 2013).

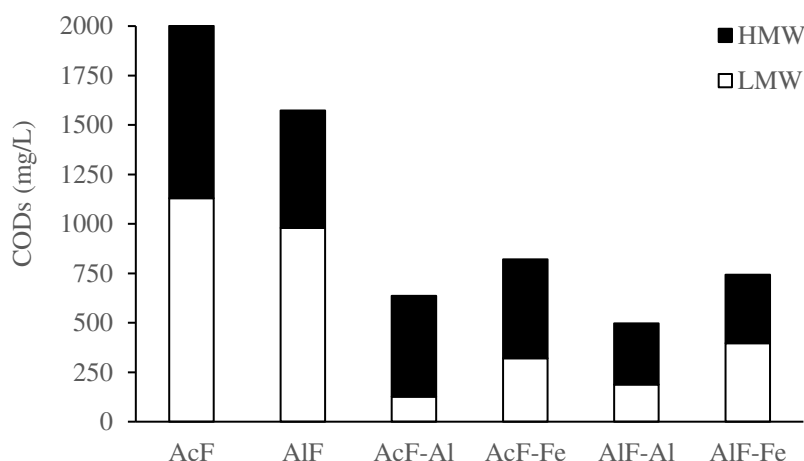


Figure 4. Contributions of high (HMW) and low (LMW) molecular weight fractions to dissolved COD (CODs) of acid and alkaline filtrates before and after electrocoagulation under optimized conditions.

The HMW fractions are considered to contain highly recalcitrant aromatic and hydrophobic compounds (Lindholm-Lehto et al. 2015) and the increase in biodegradability presented by the four treated filtrates contrasts with the higher proportion of HMW COD they contained (Figure 4). However, the HMW fractions may have been oxidized into intermediate compounds of somewhat lower MW (Soloman et al. 2009) and lower aromaticity (Figure 3).

The greater toxicity of the raw filtrates is likely associated with the greater amount of LMW compounds they contain. Components with molecular weight less than 1 kDa have greater toxic potential due to their more hydrophilic nature and greater ability to penetrate biological cells, resulting in greater bioavailability (Pereira et al. 2009).

3.4. Aerobic biodegradability assays

Based on the results of the optimized filtrate treatments (Table 4), the filtrates treated with Al electrodes were chosen to prepare mixtures for the aerobic biodegradability tests, since they resulted in greater COD removals. (See Supplementary Table S3 for details of test solutions). DOC removal was greater than 70% after five days for the mixtures that contained at least one EC-treated filtrate

(Figure 5). The mixture of the two EC-pretreated filtrates exhibited the highest and most rapid biodegradability, reaching 88% DOC removal after five days, while DOC removal in the combined raw filtrates reached only 27%. Pre-treatment of one bleaching filtrate by electrocoagulation (AcF + AIF-AI and AcF-AI + AIF) improved aerobic biodegradability in a similar manner (DOC removals of 70-72%).

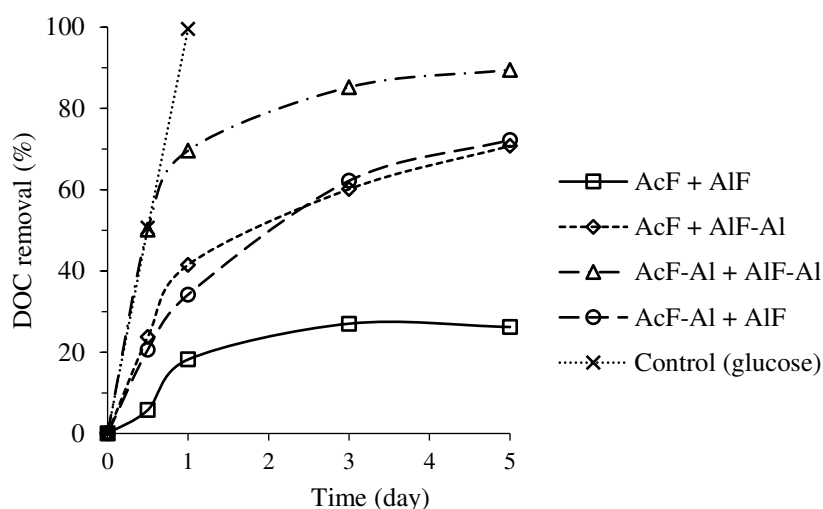


Figure 5. DOC removal over time during aerobic biodegradability tests.

The results confirmed the potential of electrocoagulation to produce high filtrate biodegradabilities without formation of substances, such as dissolved aluminum, that would be toxic to aerobic microorganisms. Furthermore, pre-treatment of at least one bleaching filtrate by electrocoagulation will improve aerobic biological treatment of combined bleaching effluents. However, the choice of which filtrate to pretreat must also consider costs of pH adjustment to the optimal EC pH values, and, potentially for further pH adjustment prior to biological treatment.

Two pH adjustments would be necessary for pretreatment of AcF with raw or treated AIF, the first to adjust AcF to pH 7.9 pH before EC and the second to neutralize the mixed filtrates before biological treatment, since both would have pH > 9 (Table 4). If raw AcF (pH 3.6) is combined with pretreated AIF, the only pH adjustment necessary would be to acidify the AIF to pH 3.8 prior to coagulation, since the mixture of AcF with alkaline EC-AIF would have pH in the neutral range. Thus, if only one filtrate is to be pretreated it is recommended that it be the alkaline filtrate. Pretreatment of the alkaline

filtrate only would lower EC sludge production compared to pretreatment of both filtrates. Even though acid filtrate contained more organic matter (Table 4), similar biotreatabilities were observed for the AcF + AIF-Al and AcF-Al + AIF mixtures (Figure 5). Furthermore, it is expected that the lower organic load entering the biological treatment plant would result in lower aeration energy demand, lower biological sludge production and greater overall treatment efficiency.

3.5. Electrocoagulation operating costs

The operating costs of treating the filtrates with Al electrodes were higher than with Fe electrodes (Figure 6), because of the need for longer electrolysis times and applied current densities using the former. In addition, the difference between practical (OC_P) and theoretical (OC) operating costs for Al-electrodes was much greater than for Fe electrodes. This indicates possibly the occurrence of super-faradaic conditions when Al electrodes were used, that led to corrosion not only of the anodes but of the cathodes, that led to greater electrode materials loss.

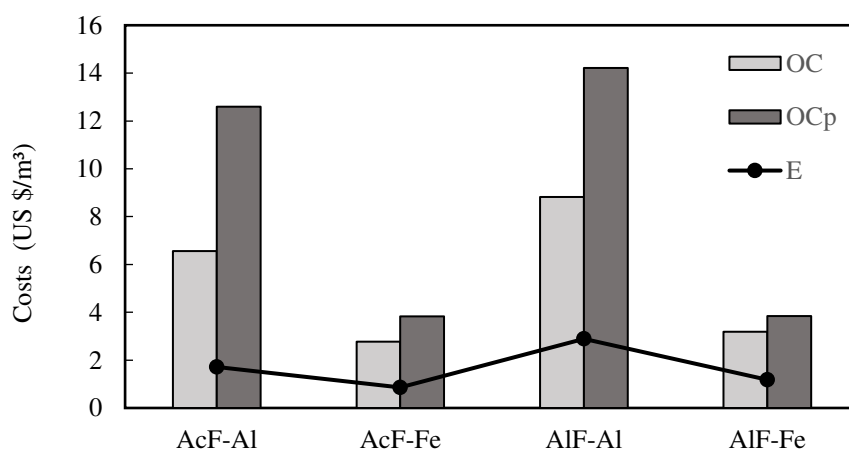


Figure 6. Theoretical (OC) and practical (OC_P) operating costs, including electrical energy (E) costs of EC under optimal conditions for the four filtrate-electrode combinations.

The highest energy and operating costs were found for alkaline filtrate treated with Al electrodes. Energy cost for Al electrodes was more than double the cost for Fe electrodes (2.89 vs. 1.18 US\$.m⁻³), while theoretical operating cost was 2.7 times higher (8.82 vs. 3.19 US\$.m⁻³). In addition, practical operating cost using Al electrodes was about 60% higher than the theoretical operating cost (14.21 vs. 8.82 US\$.m⁻³),

whereas, practical cost using Fe electrodes was only about 20% higher than the theoretical cost (3.84 vs. 3.19 US\$.m⁻³).

Electric energy cost of treatment of acid filtrate (1.72 US\$.m⁻³) with Al electrodes was about twice that of treatment with Fe electrodes (0.86 US\$.m⁻³). Practical operating cost was almost double the theoretical operating cost for Al electrodes (12.59 vs. 6.56 US\$.m⁻³), whereas for the Fe electrodes, the practical cost was only 38% higher than the theoretical cost (3.83 vs. 2.77 US\$.m⁻³).

Although EC with Al electrodes proved more efficient in improving filtrate quality, operating costs were more than two to three times more compared to EC with Fe electrodes. The large cost difference arose both from the need for longer reaction times and higher current densities to reach maximum BOD₅/COD and the higher cost of electrode material, with Al more than 3.5 times more expensive than Fe on the Brazilian market.

4. Conclusions

Electrocoagulation with Al and Fe electrodes efficiently removed recalcitrant dissolved organic matter from acid and alkaline kraft pulp bleaching filtrates and improved filtrate biodegradability (BOD₅/COD).

Current density, pH and electrolysis time significantly influenced biodegradability with positive and negative effects of their interactions on removal of recalcitrant organic matter.

Optimal operating conditions for electrocoagulation of acid filtrate were pH 7.9, 128 A/m² and 49 min with Al electrodes (AcF-Al) and pH 4.6, 104 A/m² and 40 min with Fe electrodes (AcF-Fe). For the alkaline filtrate, optimal conditions were pH 3.8, 150 A/m² and 52 min with Al electrodes (AlF-Al) and pH 6.3, 101 A/m² and 42 min with Fe electrodes (AlF-Fe).

The mathematical models generated to predict BOD/COD ratios adjusted well to the data and can be used within their boundary conditions.

For all four filtrate-electrode combinations, the biodegradable fraction corresponded to more than 75% of the total dissolved organic matter after electrocoagulation. Electrocoagulation with Al electrodes proved to be more efficient in removing true color and estrogenic activity, while treatment with Fe electrodes resulted in lower toxicity to *Daphnia similis*.

Pretreatment of at least one filtrate by electrocoagulation improved aerobic biodegradability of the combined filtrates. Pretreatment of both filtrates resulted in removal of 88% of DOC in a five-day aerobic biodegradability test, while only 27% of DOC was removed from raw combined filtrates in the same test. Electrocoagulation cost and sludge production can be reduced by treating only one filtrate, with treatment of alkaline filtrate with Al electrodes recommended to minimize the need for pH adjustment before and after EC treatment.

Electrocoagulation with Al electrodes presented higher operating costs than with Fe because of both the longer electrolysis time and current density needed to maximize biodegradability and the greater Al electrode consumption and the higher market price of this metal.

Pretreatment of bleaching filtrates by electrocoagulation should benefit the pulp mill's biological treatment plant because the lower organic load will reduce aeration requirements, biological sludge production and improve overall treatment efficiency. Future studies to quantify these benefits are recommended, as well as are studies on electrocoagulation sludge management.

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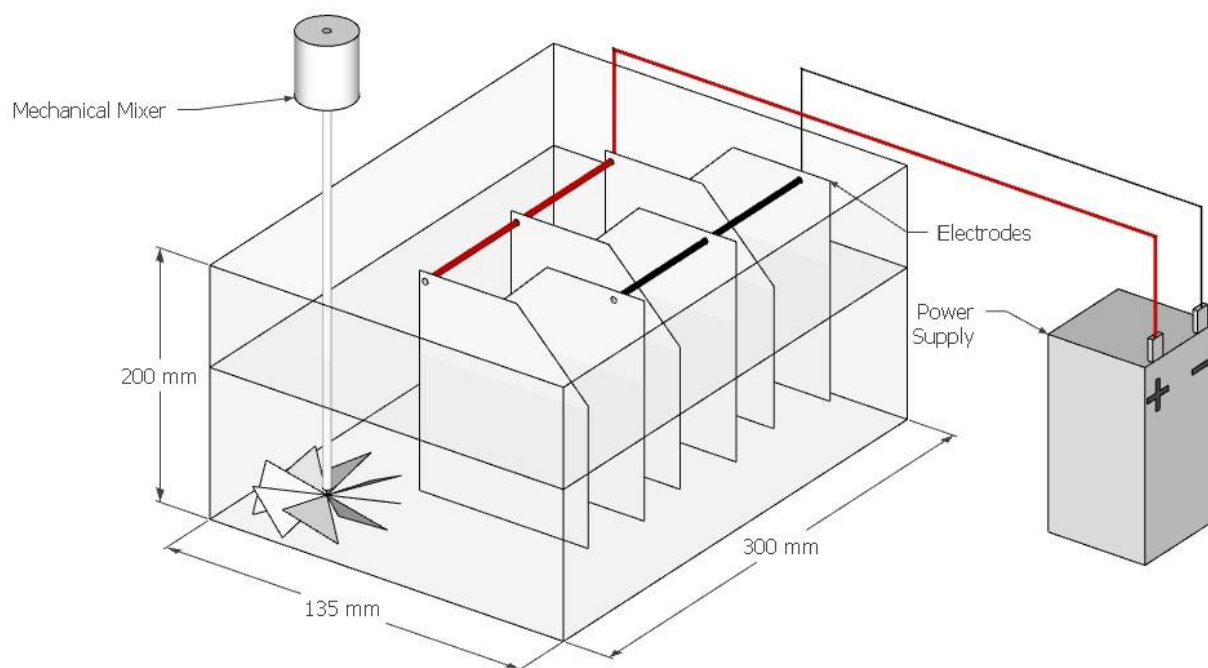
APPENDIX A – Supplementary information

Figure S1. Schematic representation of the bench-scale electrocoagulation reactor.

Table S1

BOD₅/COD indices and COD and BOD₅ removal efficiencies (E_{COD} , E_{BOD_5} , %) in the 17 experimental runs of the central composite rotatable design for each filtrate-electrode combination.

Run	pH	CD ^a (A/m ²)	T(min)	AcF-Al			AcF-Fe			AIF-Al			AIF-Fe		
				BOD ₅ /COD	E_{COD}	E_{BOD_5}	BOD ₅ /COD	E_{COD}	E_{BOD_5}	BOD ₅ /COD	E_{COD}	E_{BOD_5}	BOD ₅ /COD	E_{COD}	E_{BOD_5}
1	5.3	70	20	0.70	52.60	18.91	0.62	45.99	17.27	0.57	27.73	9.65	0.41	13.56	22.33
2	10.1	70	20	0.35	10.81	22.94	0.35	16.38	28.27	0.50	25.18	17.40	0.39	8.82	21.92
3	5.3	130	20	0.57	46.46	25.48	0.71	45.66	5.56	0.87	36.05	-22.71	0.53	10.97	-3.52
4	10.1	130	20	0.35	12.84	25.14	0.39	39.38	41.93	0.36	35.82	49.94	0.55	39.03	26.72
5	5.3	70	50	0.54	36.45	15.76	0.82	47.09	-6.26	0.65	56.17	37.03	0.61	49.01	31.53
6	10.1	70	50	0.61	52.27	28.51	0.33	11.95	29.55	0.48	38.13	34.44	0.40	14.18	24.76
7	5.3	130	50	0.77	42.68	-8.11	0.79	54.01	11.01	0.84	35.14	-18.94	0.74	33.05	-8.80
8	10.1	130	50	0.86	56.70	8.69	0.26	5.52	38.59	0.56	15.54	-4.19	0.32	12.70	38.57
9	3.6	100	35	0.61	54.19	31.11	0.83	50.57	-0.20	0.91	17.93	-33.17	0.69	26.39	-12.04
10	11.8	100	35	0.34	0.14	16.69	0.27	6.14	38.93	0.51	23.98	14.34	0.35	2.16	24.76
11	7.7	50	35	0.56	47.73	27.58	0.35	12.61	25.61	0.26	14.09	51.86	0.49	33.23	28.42
12	7.7	150	35	0.77	45.37	-3.13	0.54	45.99	28.97	0.30	27.27	51.55	0.32	38.31	57.12
13	7.7	100	10	0.30	11.33	34.76	0.38	15.30	20.38	0.67	34.90	3.65	0.49	38.92	33.73
14	7.7	100	60	0.79	47.69	-1.27	0.72	58.73	27.29	0.76	58.48	30.48	0.64	53.31	34.80
15	7.7	100	35	0.91	50.85	-9.39	0.82	46.55	-7.07	0.58	53.85	41.57	0.78	38.66	-4.60
16	7.7	100	35	0.88	50.00	-8.00	0.78	43.63	-8.57	0.54	45.76	35.71	0.85	42.17	-7.85
17	7.7	100	35	0.85	47.26	-10.2	0.84	48.68	-5.56	0.56	46.69	33.95	0.84	44.27	-3.11

^a CD: Current density.

Table S2ANOVA results of models of BOD₅/COD index as a function of electrocoagulation operating conditions (pH, CD and T) for each filtrate-electrode combination

Factor	AcF-Al					AcF-Fe				
	DF	SS	MS	Fcal	p	DF	SS	MS	Fcal	p
Model	8	0.6505	0.0813	26.8	<0.05	6	0.7794	0.1299	19.70	<0.05
pH	1	0.0541	0.0541	17.9	<0.05	1	0.5179	0.5179	78.55	<0.05
CD	1	0.0348	0.0348	11.52	<0.05	1	0.0091	0.0091	1.37	0.268
T	1	0.1956	0.1956	64.69	<0.05	1	0.0347	0.0347	5.27	<0.05
pH ²	1	0.1948	0.1948	64.42	<0.05	1	0.0668	0.0668	10.13	<0.05
CD ²	1	0.0463	0.0463	15.31	<0.05	1	0.1766	0.1766	26.79	<0.05
T ²	1	0.1301	0.1301	43.03	<0.05	1	0.0845	0.0845	12.82	<0.05
pH*T	1	0.0653	0.0653	21.61	<0.05	-	-	-	-	-
pH*CD	-	-	-	-	-	-	-	-	-	-
CD*T	1	0.0464	0.0464	15.35	<0.05	-	-	-	-	-
Residual	8	0.0241	0.0033			10	0.0659	0.00659		
Lack of fit	6	0.0226	0.0037	4.91	0.179	8	0.0644	0.00806	11.22	0.084
Pure error	2	0.0015	0.0007	-	-	2	0.0014	0.0008	-	-
TSS	16	0.6747	-	-	-	16	0.8454	-	-	-

DF: degrees of freedom; SS: sum of squares; MS: mean square; Fcal: calculated F; TSS: total sum of squares.
 AcF-Al: Ftab = 3.438 (model), 19.33 (Lack of fit); AcF-Fe: Ftab = 3.217 (model), 19.37 (Lack of fit).

Table S2.

...cont.

Factor	AIF-AI					AIF-Fe				
	DF	SS	MS	Fcal	p	DF	SS	MS	Fcal	p
Model	7	0.5304	0.0757	23.48	<0.05	7	0.4647	0.0664	11.37	<0.05
pH	1	0.2089	0.2089	64.75	<0.05	1	0.1073	0.1073	18.38	<0.05
CD	1	0.0182	0.0182	5.64	<0.05	1	0.0001	0.0001	0.02	0.894
T	1	0.0107	0.0107	3.3	0.103	1	0.0138	0.0138	2.36	0.159
pH ²	1	0.0411	0.0411	12.73	<0.05	1	0.1191	0.1191	20.39	<0.05
CD ²	1	0.0945	0.0945	29.29	<0.05	1	0.2368	0.2368	40.76	<0.05
T ²	1	0.0457	0.0457	14.16	<0.05	1	0.0862	0.0862	14.76	<0.05
pH*T	-	-	-	-	-	1	0.0497	0.0497	8.51	<0.05
pH*CD	1	0.0384	0.0384	11.89	<0.05	-	-	-	-	-
CD*T	-	-	-	-	-	-	-	-	-	-
Residual	9	0.02905	0.0032			9	0.0525	0.0058		
Lack of fit	7	0.0028	0.0041	11.52	0.082	7	0.0493	0.0070	4.36	0.199
Pure error	2	0.0007	0.00035	-	-	2	0.0032	0.0016	-	-
TSS	16	0.5595	-	-	-	16	0.5172	-	-	-

DF: degrees of freedom; SS: sum of squares; MS: mean square; Fcal: calculated F; TSS: total sum of squares.
 AIF-AI: Ftab = 3.293(model), 19.35 (Lack of fit); AIF-Fe: Ftab = 3.293 (model), 19.35 (Lack of fit)

Table S3Initial characteristics of filtrate mixtures used in aerobic biodegradability tests.^a

Sample	DOC (mg/L)	Initial pH
AcF + AIF	692	7.3
AcF + AIF-AI	526	7.4
AcF-AI + AIF	549	7.3
AcF-AI + AIF-AI	364	7.2
Glucose (control)	220	7.0
Mineral medium	0	7.1
Inoculum (adapted sludge) ²	70	6.8

^aF/M = 0.5 g DOC/g VSS. ²670 mg TSS/L; 80% active biomass

APPENDIX B – Ancillary data

Table B1. Final pH, temperature and true color^a after EC for the four filtrate-electrode combinations.

Run	EC operating conditions			AcF-Al			AcF-Fe			AIF-Al			AIF-Fe		
	pH	CD (A/m ²)	T (min)	pH _f	Color (mg/L PtCo)	T _f (°C)	pH _f	Color (mg/L PtCo)	T _f (°C)	pH _f	Color (mg/L PtCo)	T _f (°C)	pH _f	Color (mg/L PtCo)	T _f (°C)
1	5.3	70	20	8.6	852	25.7	8.4	492	25.5	7.3	152	27.2	7.4	390	25.5
2	10.1	70	20	9.4	909	25.8	11.0	1591	23.5	9.8	945	25.7	11.1	872	25.3
3	5.3	130	20	9.3	663	27.9	8.8	3068	25.5	9.1	68	29.2	7.9	375	28.0
4	10.1	130	20	9.8	534	28.0	11.0	568	26.2	9.9	125	28.3	11.3	736	28.6
5	5.3	70	50	9.5	424	26.5	9.6b	689	25.6	9.6	55	26.3	7.9	131	26.0
6	10.1	70	50	9.8	1330	27.9	10.9	1155	25.5	10.1	174	27.3	11.7	697	25.1
7	5.3	130	50	9.8	148	33.0	11.8	473	29.5	9.5	39	33.9	10.3	164	31.3
8	10.1	130	50	10.1	128	32.7	12.3	1061	27.8	10.1	64	35.3	11.8	507	31.1
9	3.6	100	35	6.1	144	28.7	6.6	227	27.1	5.9	41	27.8	6.6	216	26.5
10	11.8	100	35	10.6	1241	28.1	12.1	1345	26.3	11.0	1886	28.4	11.9	1284	29.1
11	7.7	50	35	9.5	871	25.6	10.5	1856	26.6	9.4	227	25.1	9.9	398	24.7
12	7.7	150	35	9.8	345	30.2	11.8	2443	27.8	9.9	77	34.7	10.7	140	30.2
13	7.7	100	10	9.1	887	27.4	9.0	2784	25.2	9.5	299	25.5	9.7	136	25.2
14	7.7	100	60	9.9	133	28.8	11.8	183	27.9	9.9	95	30.9	11.3	117	27.7
15	7.7	100	35	9.6	404	29.0	11.1	316	26.2	9.7	95	29.1	10.7	210	27.4
16	7.7	100	35	9.6	348	27.3	10.9	318	26.4	9.8	49	29.4	10.9	218	27.9
17	7.7	100	35	9.9	371	29.2	10.6	382	26.2	9.7	83	27.9	10.8	214	27.4

^a Color (mg/L PtCo) of raw filtrates: AcF = 893, AIF = 629. Color measured at pH 7.6.

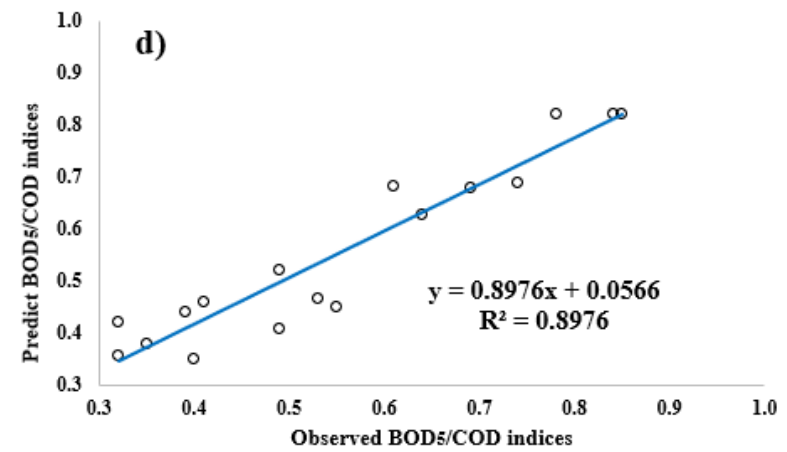
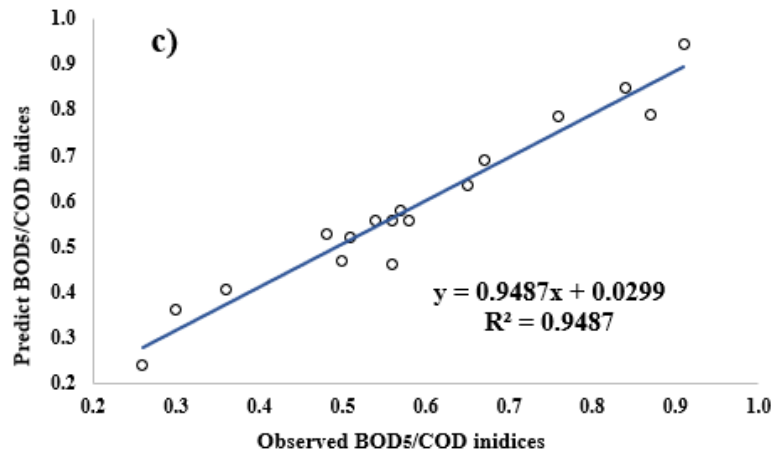
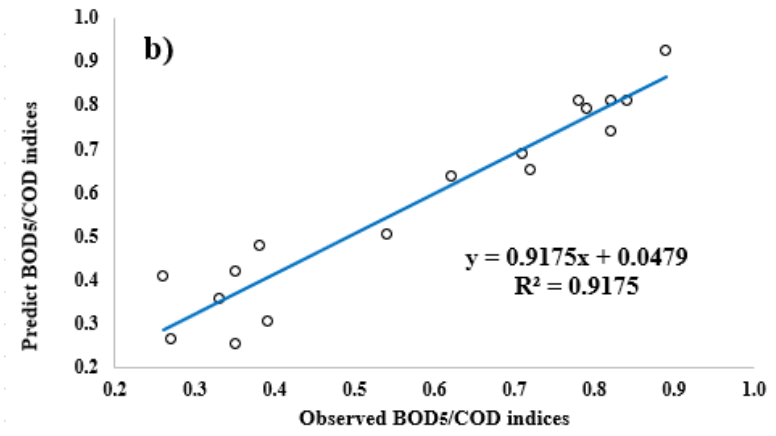
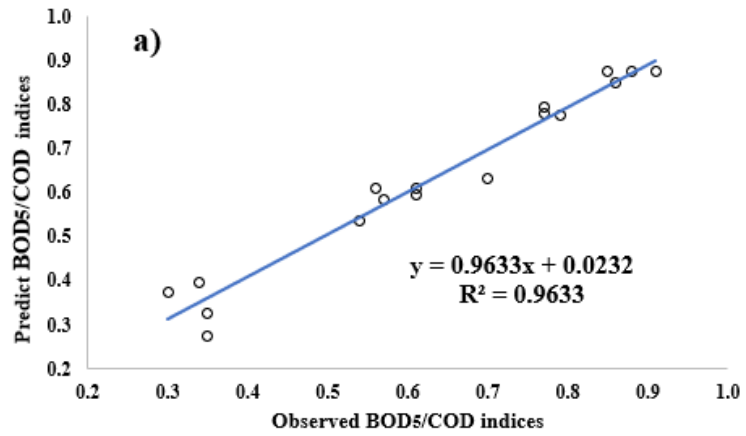


Figure B1. Observed versus predicted BOD₅/COD indices for: (a)AcF-Al, (b) AcF-Fe, (c) AIF-Al and (d) AIF-Fe.

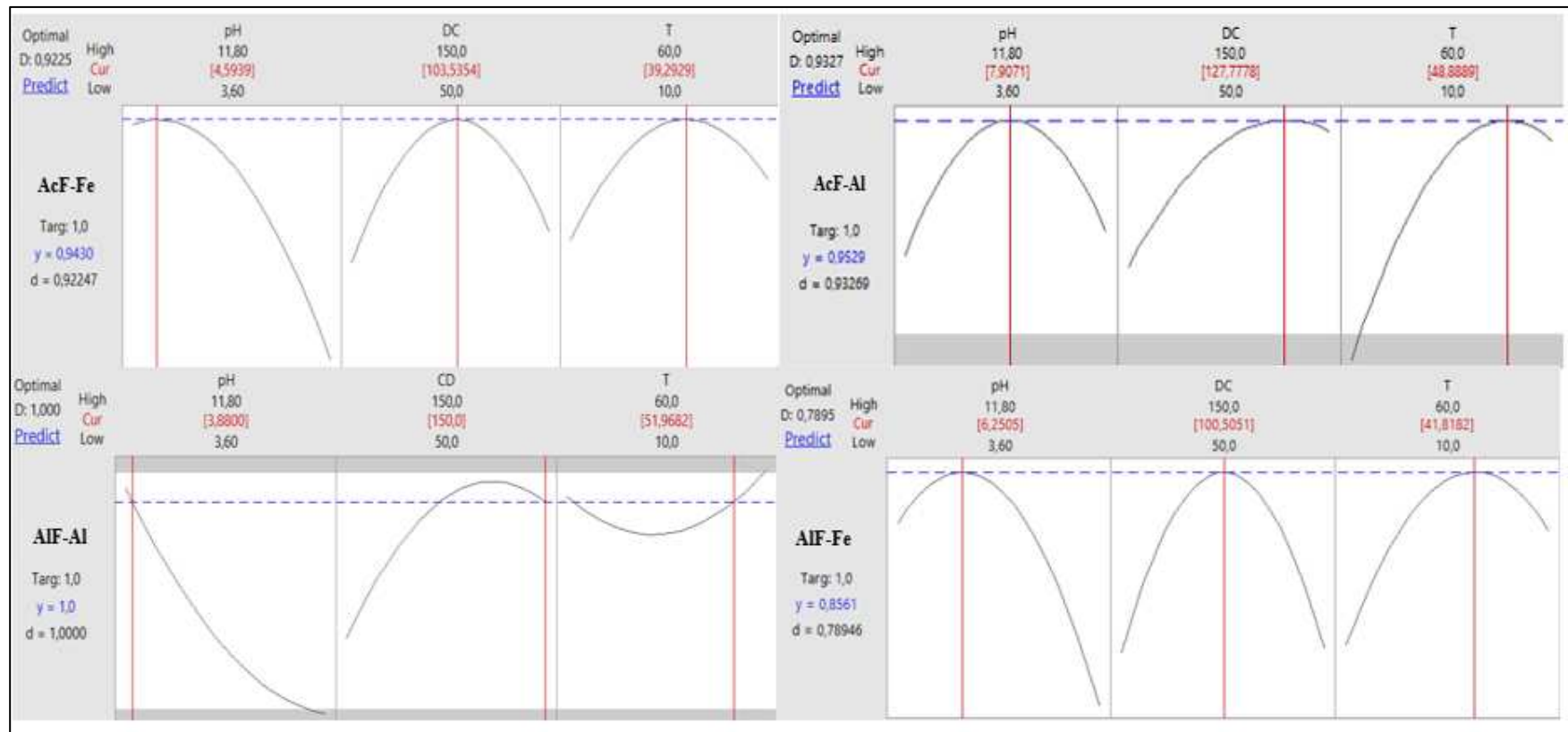
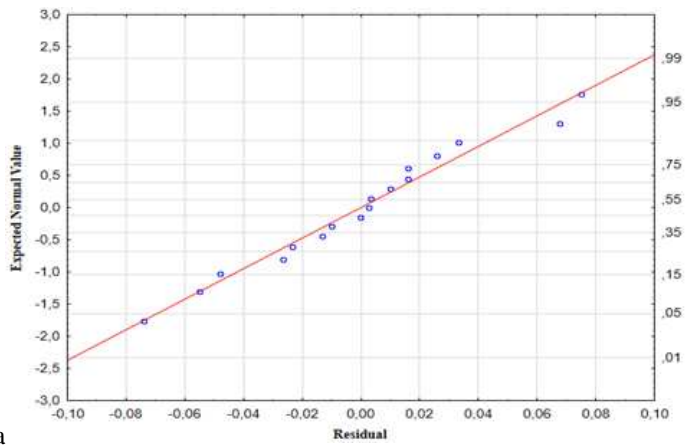
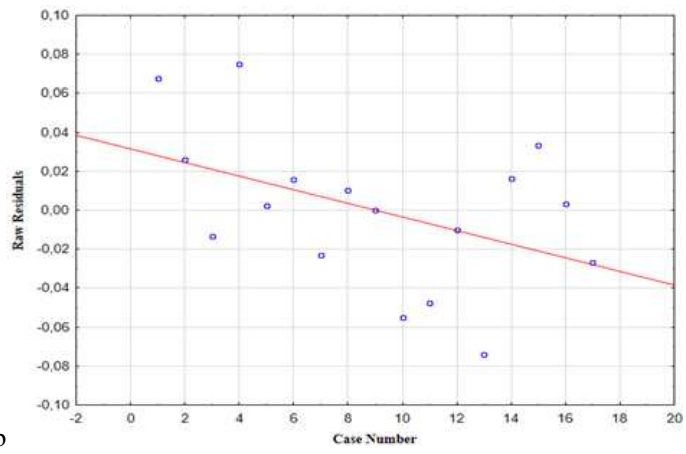


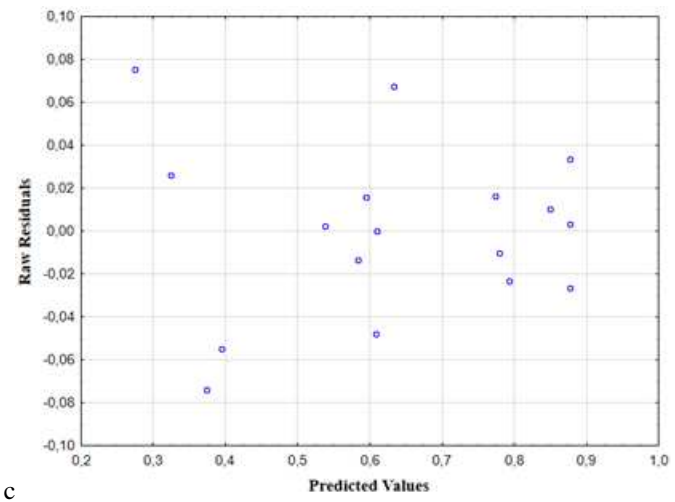
Figure B2. Optimized values of pH, current density and electrolysis time, for the four filtrate-electrode combinations, obtained by the Minitab® response optimizer function.



a



b



c

Figure B3: Residuals plots for AcF-AI model (Eq 7): a) normality b) independence c) homoscedasticity.

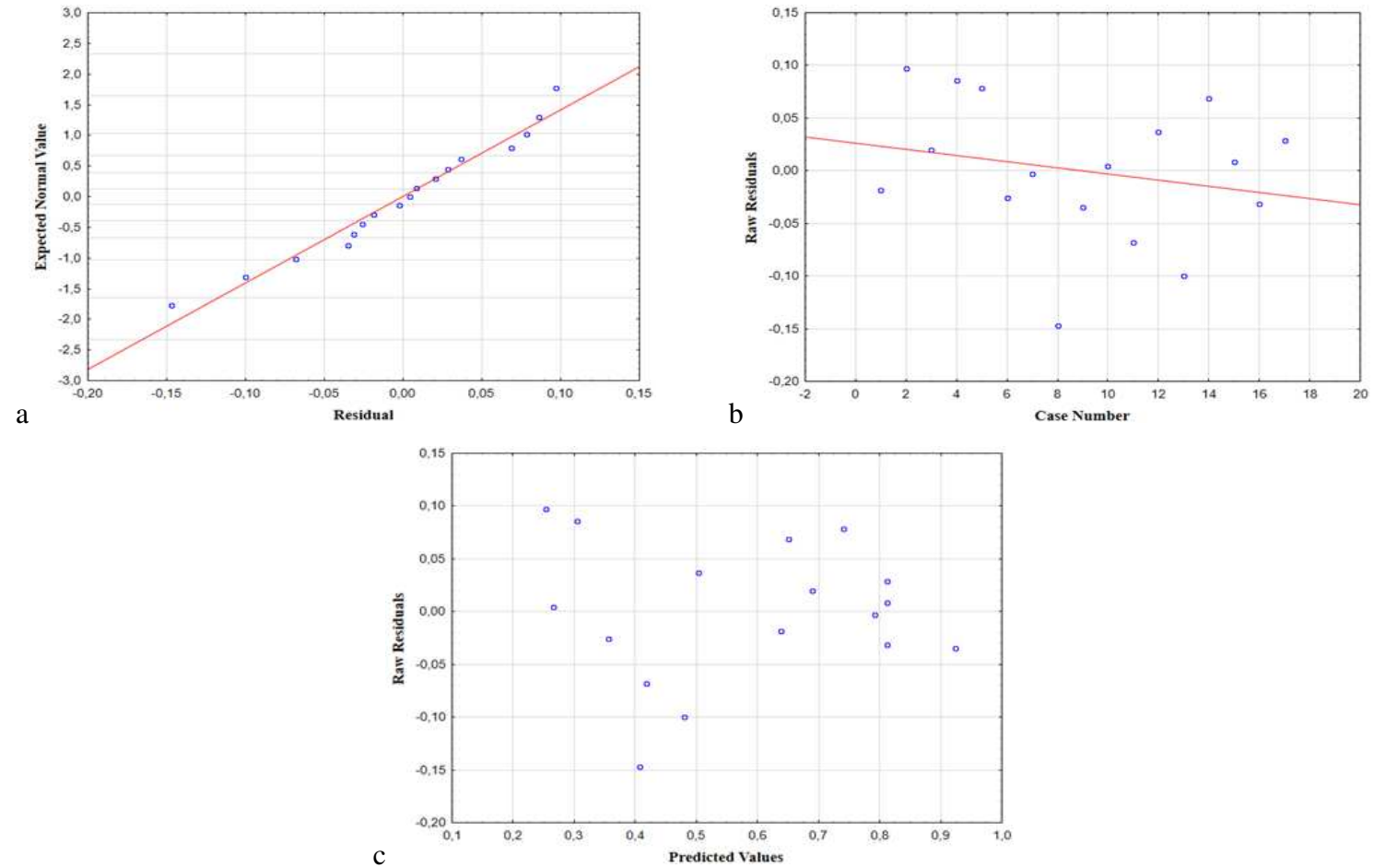


Figure B3: Residuals plots for AcF-Fel model (Eq 8): a) normality b) independence c) homoscedasticity.

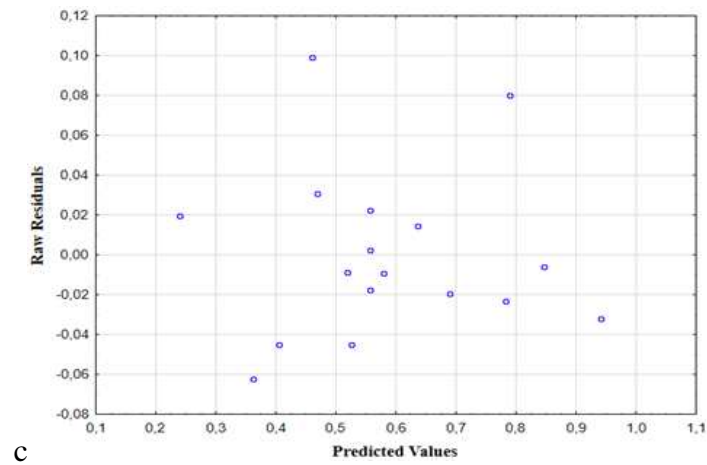
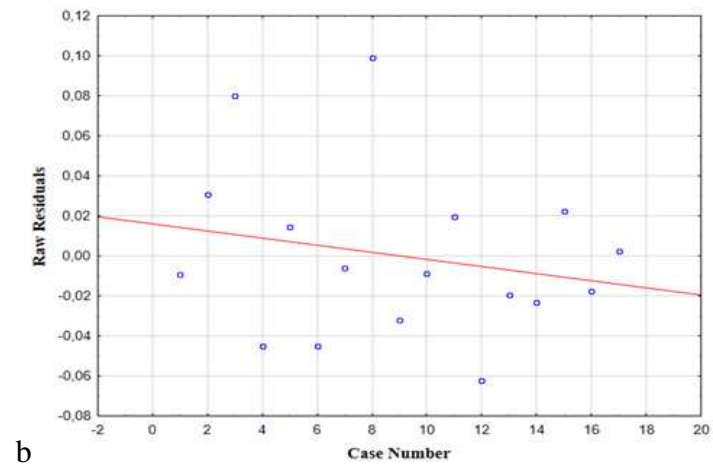
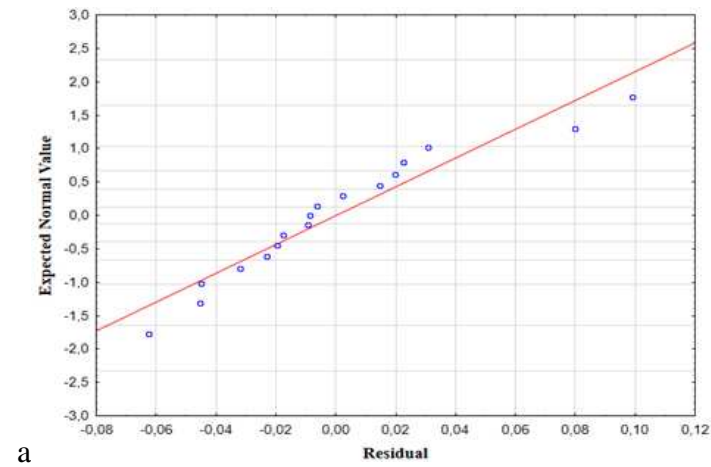


Figure B4: Residuals plots for AIF-AI model (Eq 9): a) normality b) independence c) homoscedasticity.

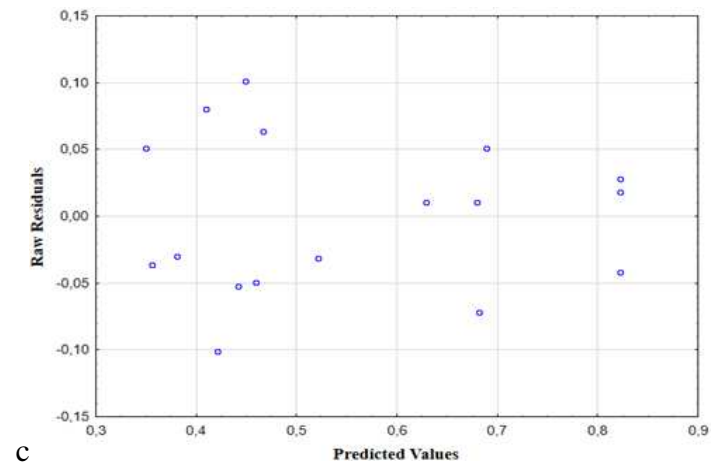
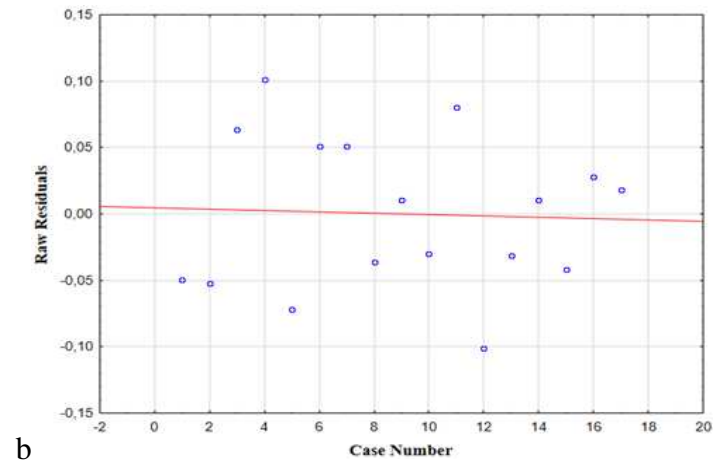
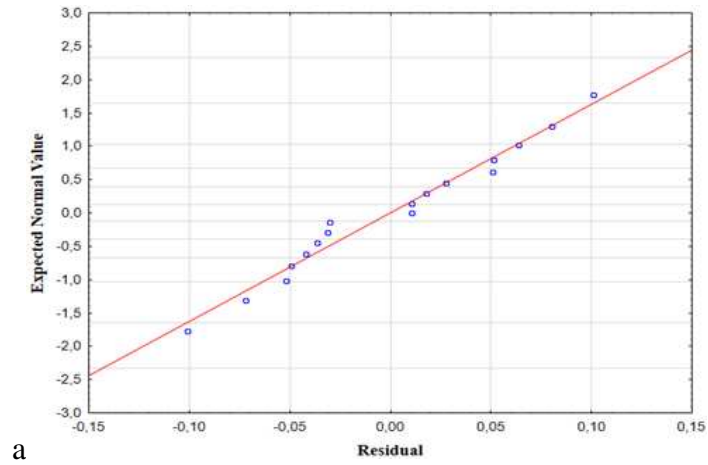


Figure B4: Residuals plots for AIF-Fe model (Eq 10): a) normality b) independence c) homoscedasticity.

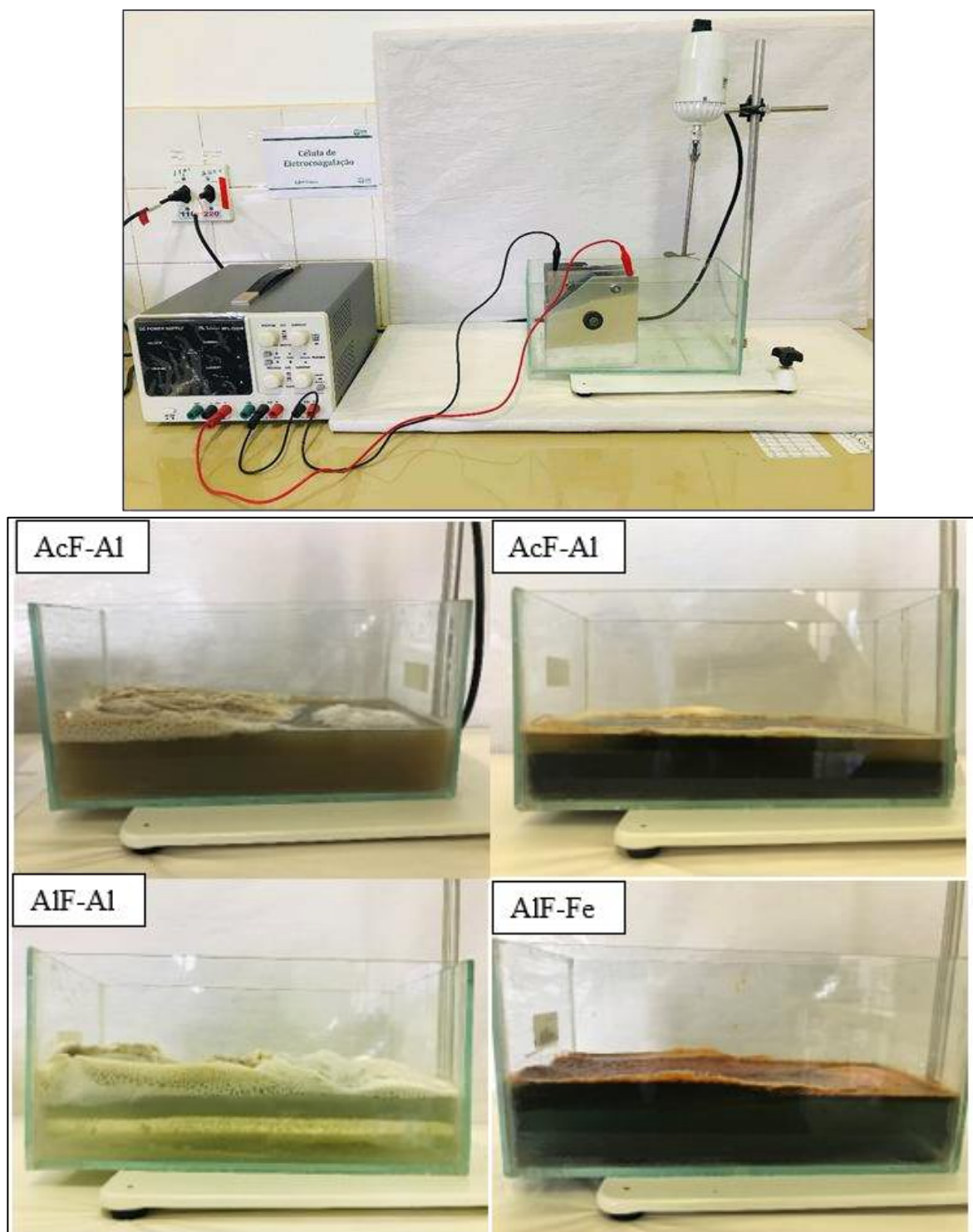
APPENDIX C – Electrocoagulation cell images

Figure C1. Bench scale electrocoagulation reactor and filtrates after treatment under optimized conditions.