CHEMICAL ENGINEERING TRANSACTIONS
VOL. 98, 2023

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Sauro Pierucci, Carlo Pirola
Copyright © 2023, AIDIC Servizi S.r.l.
ISBN 978-88-95608-97-6; **ISSN** 2283-9216

DOI: 10.3303/CET2398012

Kinetic Study of Electrocoagulation of Tannery Wastewater

Lorgio Valdiviezo-Gonzales[a*], Franklin Aguilar Mancco[b], Allison Palomino Cartolin[b], Julio Montoya Molina[b], Rita J. Cabello-Torres[b], Patricia Reynoso Quispe[c]

[a]Universidad Tecnológica del Perú, UTP, campus San Juan de Lurigancho, Lima-Perú
[b]Professional School of Environmental Engineering, Universidad César Vallejo, Campus San Juan de Lurigancho, Lima, Perù
[C]Universisdad de Ingeniería y tecnología, UTEC, Departamento de ciencias, Perù
lvaldiviez@utp.edu.pe

The current research aims to investigate the treatment of real chrome tanning effluent by continuing electrocoagulation (EC) with electrodes of aluminum (anode) and iron (cathode). Also, the kinetic study and the effect of current density and operating time on Cr (VI), turbidity, and chemical oxygen demand (COD) removal efficiency were evaluated. The results show that maximum removal efficiency of 84.7 % for Cr (VI), 88.7 % for turbidity and 81.0 % for COD occurred at a current density of 679.3 A /m^2. The maximum turbidity removal value was reached after 15 minutes of operation, while it took 20 minutes to remove the maximum value of Cr (VI) and COD at pH 3.5. The kinetic data were fitted to the pseudo second order model for COD and the pseudo first order for Cr (VI) showing a higher removal rate of Cr than COD. The estimated operating cost was USD 2.74/m^3 of effluent. This value only included anode material and energy consumption costs.

1. Introduction

Tannery and textile industry effluents are characterized by containing various substances, such as dyes, organic compounds, and chromium, but the oxidation of chromium to Cr (VI) is an important concern since it is considered carcinogenic and toxic (Moussa et al., 2017; Castiblanco et al., 2021; Gonzales Delgado et al., 2022). In addition, there are acids, alkalis, tannins, solvents, sulfides, and auxiliary dyes, these substances are not completely fixed to the skins and remain in the effluent (Lofrano et al., 2013). The tanning process is characterized by using huge quantities of water; approximately 90 % of this water is discharged into the environment (Chowdhury et al. 2013). Electrocoagulation (EC) lies at the intersection of three basic sciences (electrochemistry, flotation, and coagulation), it combines the functions and advantages of conventional coagulation, flotation, and electrochemistry (Koukkanen, 2016). Also, due to the high removal efficiencies and low operating costs achieved by the EC, this technology has attracted much attention from the scientific community (Rehman et al., 2015). If aluminum anodes are used, Al^{3+} ions are generated on their surface and combined with OH^- ions generated at the cathode, this combination gives rise to monomeric species that finally transform into Al $(OH)_{3(s)}$ (Koukkanen, 2016). The Al $(OH)_{3\ (s)}$ formed (sweep flocs) has a large surface area, this characteristic allows rapid capture of colloidal particles, and these flocs are easily eliminated by sedimentation or flotation (Koukkanen, 2016 and Hakizimana et al. 2017). A general scheme of the batch cell of EC is shown in Figure 1.The electrode reactions in the aluminum anode are shown in Eq (1) and (2) (Hakizimana et al. 2017):

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^- \qquad (1)$$

$$Al^{3+}_{(aq)} + nH_2O \rightarrow Al(OH)^{3-n}_n + nH^+ \qquad (2)$$

Paper Received: 9 November 2022; Revised: 17 January 2023; Accepted: 3 April 2023
Please cite this article as: Valdiviezo-Gonzales L., Aguilar Mancco F., Palomino Cartolin A., Montoya Molina J., Cabello Torres R.J., Reynoso Quispe P., 2023, Kinetic Study of Electrocoagulation of Tannery Wastewater, Chemical Engineering Transactions, 98, 69-74 DOI:10.3303/CET2398012

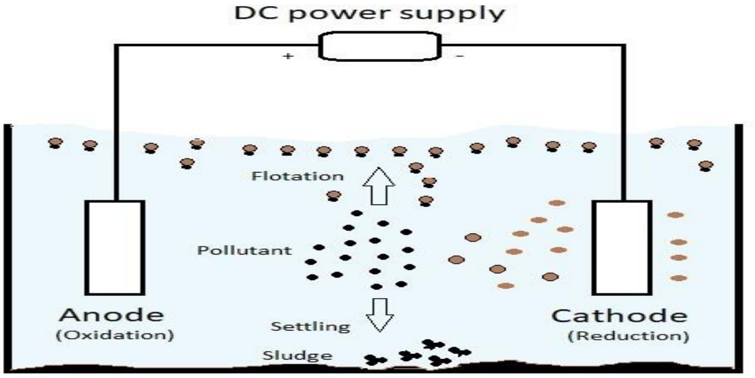

Figure 1 Electrocoagulation Process

Likewise, the generation of oxygen at the anode is possible, Eq(3), at alkaline pH and high anodic potentials conditions (Chen et al. 2016);

$$2OH^- + 2e^- \rightarrow 1/2O_2 + H_2O \qquad (3)$$

In cathode, the generation of hydrogen bubbles and OH^-ions is shown in Eq(4) (Hakizimana et al. 2017).

$$2e^- + 2H_2O \rightarrow H_2 + 2OH^- \qquad (4)$$

In Lima (the capital of Peru), there are about 80 tanneries but only 8 of them are legal and have government permits, the majority of illegal tanneries are small, or poorly run, they also represent a big environmental problem because do not treat their effluents (Ahmad, 2015). Therefore, it studied valued the removal of COD, turbidity, and Cr(VI) by electrocoagulation process, from real chrome tanning wastewater. Additionally, kinetic studies and the operational cost are also investigated.

2. Materials and methods

2.1 Tannery effluent samples, and experimental set-up

The samples were collected directly from storage tanks of the chromium tanning step, in a small tannery in Lima. The wastewater characteristics and all the samples after the EC process was delivered to the ALAB analytic laboratory E.I.R.L for analysis of COD and Cr (VI) according to the standard methods of APHA (APHA, 2005). The pH and conductivity of the treated water were measured using a pH meter, model basic 20, Crison, and a conductivity meter, model HI 8633 Hanna. Samples of 20 L were collected and stored in appropriate conditions. Samples of 2 L were used for each experiment in a continuous system, all experiments were performed in triplicate to minimize experimental error.

An electrochemical reactor was constructed with acrylic (14 cm long, 10 cm wide, and 17 cm height). It contained 5 cathodes (iron) and 5 anodes (aluminum). A pre-treatment to the electrode was performed (active surface 6.9 cm x 9.6 cm). First, it was mechanically polished with abrasive paper, rinsed and dried before operation. The electrodes were connected vertically with a gap distance of 10 mm in monopolar parallel mode to a DC power supply. The electrochemical reactor was fed with a constant flow using a peristaltic pump, at flow rates suitable to maintain nominal residence times of 10 to 30 min.

The effect of the current density (increasing from 377.4 to 754.8 A/m^2, at pH 3.5 and 20 minutes of operating time), on the removal of turbidity, Cr (VI) and COD was evaluated. The Cr, DQO or turbidity removal were evaluated by Eq(5) (Hakizimana, 2017):

$$\%\,removal = \frac{C_0 - C_t}{C_o}\,x\,100 \qquad (5)$$

Where C_0 and C_t are the initial and the final value of turbidity, COD, or chromium (VI). Furthermore, aluminum dissolution (m_{Al}, g) has been defined according to Faraday's law by Eq(6) (Hakizimana, 2017).

$$m_{Al} = \frac{It}{zF}\,M_{Al} \qquad (6)$$

Where, I, t and F are the applied current (A), time (seconds), and Faraday constant, F= 96 486 C/eq) respectively, M_{Al} is the molar weight of aluminum (g /mol) and z the number of electrons transferred during the anodic oxidation of the metal, z = 3 for Aluminum (Hakizimana et al., 2017).

2.2 Kinetic modeling and operation cost

For the kinetic study, the pseudo first and pseudo second order kinetic model were considered, in a batch system. The pollutants removal can be modeled by adsorption phenomena and the calculation of adsorption capacity (qt) of pollutant onto adsorbent at any time, in mg/g, according with Eq(7) (Hakizimana et al., 2017):

$$q_t = \frac{V(C_0 - C_t)}{M} \quad (7)$$

Where V is the volume of the solution in liters, M is the dissolved mass of the anode (oxidation) in grams; C_0 and C_t are the initial concentration and contaminant concentration at any time in mg/L.

The Pseudo first order kinetic model was determined using the Eq(8) (Moussout et al., 2018). Where K_1 is the pseudo first order rate constant in min^{-1}.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

For the second order model the Eq(9) was used (Ouaissa et al., 2014):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

Where K_2 is the second-order rate constant (g/mg. min).

The operation cost of this study included only the anode and energy consumption cost. The dissolved anode material and electricity costs are the main cost components of all processes. It should be noted that it is only rough estimates of the total cost, because the price of materials and energy changes over time (Vepsalainen, 2012), however, it is important information for industrial application.

The amount of electrical energy used was computed by Eq(10) (Hakizimana et al., 2017)

$$E = \frac{UIT}{V} \quad (10)$$

Where E is the specific energy used in kWh/m^3, U is the voltage in volts, I is the current in amperes, T is the time in hours and V is the volume of the treated wastewater in m^3.

3. Results

3.1 Characterization of effluent

The main physicochemical parameters of crude tanning water used in this study are shown in table 1. These parameters were compared with the Peruvian maximum permissible limit values (LMP) (Vivienda, 2009) for wastewater discharged. It is observed that Cr, COD and pH do not comply with national regulations.

Table 1: Physicochemical parameters of raw tannery wastewater used in this study

Parameter	Unit	Average	National Limit *
Cr (VI)	mg/L	3.2± 0.01	0.5
COD	mg/L	3045.1± 10.2	1000
Turbidity	UNT	35.9± 0.5	
conductivity	µS/cm	86007.3± 0.5	
pH		3.5±0.2	6-9

*D.S.Nº 021-2009 (Vivienda 2009)

3.2 Effect of current density

The current density is directly proportional to the coagulant production rate, bubble production, and, consequently, the growth of flocs (Elabbas et al., 2016). So, current density affects the performance of the EC process. Figure 2a shows that an increase in current density improved removal efficiencies of Cr (VI), COD and turbidity. Thus, when the current density value increased from 754.8 to 1358.7 A /m^2, maximum removal was viewed as 84.7 %, 81 % and 88.6 % for Cr (VI), COD and turbidity, respectively. This result could be attributed to the dissolution of the Al anode which generated: high aluminum ions, production of H_2 bubble, and hydroxide ions (OH-) at the cathode by Eq(1) and (4). So, while current density was increasing, conditions became favorable for coagulant production and flocs, consequently improving the removal efficiency of parameters evaluated. Singh and Mishra. (2016) report that Cr (VI) ions are reduced to Cr(III) by reactions around the cathode. Once Cr (III) is formed, it stars precipitating as $Cr(OH)_3$. Similarly, El-Ashtoukhy et al. (2010) achieved higher removal efficiency of Cr(VI) at pH 3.5. However, other authors reported higher removal efficiency under acidic and neutral conditions (Zewail & Yousef., 2014). Also, it was noticed that for higher values that 1358.7 A /m^2, percentage reduction of turbidity, COD and Cr (VI) remain constant. Moussa et al. (2017) attributed this behavior to the existence of a critical value for the current density such that even using a higher value the treated water does not show a significant improvement. At high current density values, a considerable amount of Al^{3+}

ions are available by the anode dissolution, consequently, the molecules formed (Al $(OH)_3$) are entrained to the surface without the presence of contaminants due to the saturation of the sites of adsorption formed by aluminum hydroxide (Benaissa et al. 2014).

In addition, residual energy through the use of high working current values has been associated with the increase in water temperature (Moussa et al. 2017). In this study, a current density value of 1358.7 A/m^2, pH 3.5 and 21 °C were used for evaluation by other parameters.

3.3 Effect of operation time

A shorter electrolysis time, 15 minutes, is required to reach maximum turbidity (79 %) and COD (88.7 %) removal.The effect of contact time on the efficiency of Cr(VI) removal (figure 2b) was different from the other parameters studied. Two stages are observed in the removal of this parameter: First, a slow Cr(VI) removal efficiency in the first 10 minutes and the second stage, a faster removal efficiency between 10 and 20 minutes of operation time. The maximum chrome removal was 84.7 % in 20 min, after this time a fall to efficiency values is observed (51.1 % at 30 min). The high current generates H_2 bubbles rapidly, which inhibits the formation of flocs, results to decrease in the percentage removal of Cr (VI). Varank et al. (2014) reported 82.2 % and 67.4 % of COD removal efficiency, using Al-Al electrodes and Fe-Fe electrodes, at 5 and 45 min; Likewise, Şengila et al. (2009) reported 82 % of COD removal efficiency (Fe-Fe, electrodes) at 10 min (current density of 350 A /m2 and pH 3). Likewise, Espinoza-Quiñones et al. (2009) reported removal of 96 %, 98 % and 50 % of turbidity, Cr and COD respectively in 30-45 min. The same operation time for Cr (VI) removal was reported by Zewail & Yousef (2014). However, Elabbas et al. (2016) indicated that 360 minutes of operation time was necessary by maximum removal efficiency of COD y Chromium by EC from real chrome tanning wastewater.

3.4 Changes of pH and conductivity and operation cost

Changes in pH and conductivity are shown in Figure 2c. According to Barrera-Díaz et al. (2006) at pH lower than 3.5, the main species present in the system is Al^{3+}, however, for $4<pH<9.5$, $Al(OH)_{3(S)}$ is the most predominant species in the system. In this study, values of pH 5.97-6.27 were observed between 15 and 20 minutes of operation, this coincides with the maximum removal values achieved. This increase in pH is related to the production of hydroxide ions (OH^-) which are continuously generated from the cathode by electrolysis of water, as indicated in Eq(4) (Elabbas et al. 2016). So, in this short period, there was a higher HO^- produced by water electrolysis and it was used in hydroxides and/or polyhydroxides production or were bound to the sludge. So, the major presence of $Al(OH)_3$ achieved by high pH values has positively affected the removal of contaminants evaluated. The results are consistent with those reported by Benaissa et al. (2014).The conductivities of samples depended on the concentration of residual aluminum and pH in the system. When the initial pH is acidic, conductivity is naturally high. The lowest conductivity values (61.0 - 57.0 mS/cm) are observed during the first 15 and 20 min. This indicates that ionic substances present in the system contributed quickly to flocs generation in this range of time, consequently increasing removal efficiency values and conductivity decrease. There was no major change in effluent conductivity during the 30 minutes of treatment. This differs from conventional coagulation, which significantly increases the concentration of salts, such as chlorides or sulfates, in water (Vepsalainen, 2012).

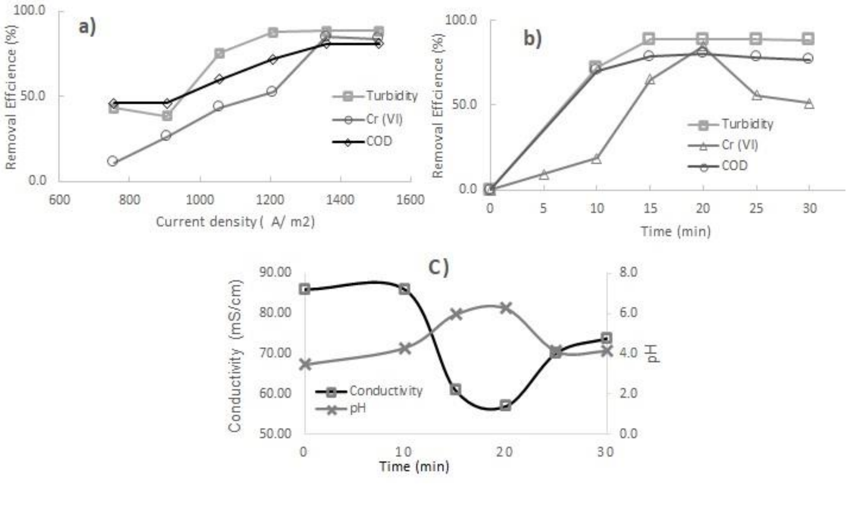

Figure. 2 Effect of a) current density and b) operation time on the removal of chromium, COD, and Turbidity. c) conductivity and pH variations by EC process.

The cost of operation is considered one of the main disadvantages in the EC process and is related to its low application to an industrial scale (Moussa et al., 2017). So, the consumed energy E (kWh/ m^3) was calculated by Eq. 8, at the optimum operation conditions of current density 679.3 A/m^2, operation time 15 min and monopolar parallel connection mode. The consumed energy was 13.5 KWh/ m^3. The current market prices of electricity in Peru in January 2022, were 0.203 US$/KW (Luz del Sur 2022). The current market price of Al was 3.86 US$ /kg Al, (Infomine 2022). The cost of EC was 2.74 $ /m^3 of treated effluent. This cost is higher than 1.7 and 1.089 $ /m^3 reported by Espinoza-Quiñones et al. (2006) and Bingül et al. (2022). However, Ölmez (2009), reported that the total cost of the EC process is about two-folds of the conventional process, because of higher electrical energy demand.

3.5 Kinetics studies

According to the literature, a diffusion-controlled process is better described by a pseudo second order model than a pseudo first order model (Simonin 2016). Figure 3a and 3b, shows values of R^2 = 0.98 for Cr (VI) an R^2 = 0.97 for COD. There is a good agreement between experimental and theoretical data to the pseudo first and second order kinetic model to describe the adsorption of Cr (VI) and COD onto aluminum hydroxide respectively. K_{Cr} was determined from the slope of the line, ($K_{Cr(VI)}$ = 0.083 min^{-1}). Also, KCOD was determined (KCOD = 3.11 x10-5 min^{-1}). The results show a higher removal rate for Cr than for COD. The same way other studies reported the first order kinetic model with good correlation for Cr (Bingül et al., 2021, Singh and Mishra 2016 and Vasudevan et al. 2011) and to COD removal more suited to second order model (Bingül et al., 2022). Other studies reported the pseudo first order model for COD removal from dyebath effluent (Kabdaşlı et al., 2009) and dairy wastewater (Benaissa et al. 2014).

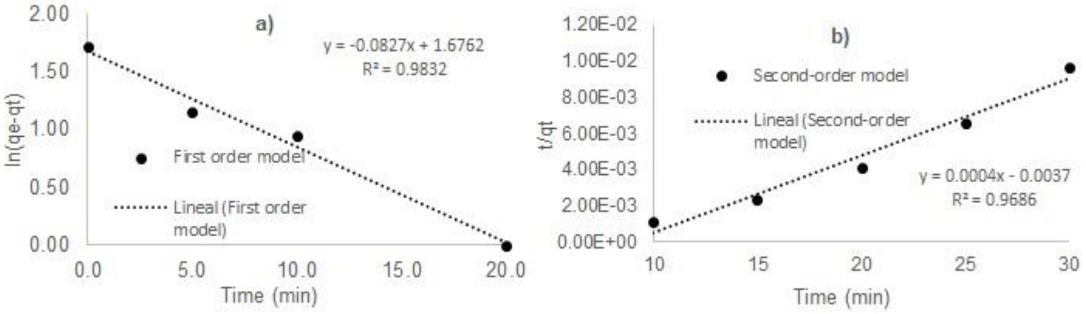

Figure. 3 kinetic model plot for a) Cr (VI)- first-order and b) COD-Second-order

4. Conclusions

According to our results, the maximum removal efficiencies are obtained at a current density of 679.3 A/m^2. The kinetics of Cr (VI) and COD removal is best explained by pseudo first and Pseudo second order kinetic model, with higher R^2 =0.98 and R^2=0.97 respectively. The results showed that the optimized removal efficiency of 84.7 % for Cr (VI), 88.7 % for Turbidity, and 81.0 % for COD occurred at a current density of 679.37 A/m^2 during a contact time of 15 min for turbidity and 20 min for Cr (VI) and COD respectively. The concentrations of Cr (VI) and COD after the EC process were lower than the Peruvian limits for effluent discharge.

References

Ahmad F., 2015. Indian Leather Sector Trade Event in South America Buyer Seller Meet in Lima, Peru – July 23-24, 2015 In Council For Leather Exports (CLE). Ministry of Commerce & Industry, Govt of India. <http://leatherindia.org/wp-content/uploads/2016/03/Aug-BSM-Peru.pdf>. accessed 09.03.2022.

APHA., (21st ed). 2005, American Public Health Association. Standard methods for the examination of water and wastewater, Washington, DC. UE.

Barrera-Díaz, C., Roa-Morales, G., Avila-Córdoba, L., Pavón-Silva, T., & Bilyeu, B., 2006. Electrochemical treatment applied to food-processing industrial wastewater. Industrial & engineering chemistry research, 45(1), 34-38.

Benaissa, F., Kermet-Said, H., & Moulai-Mostefa, N., 2016. Optimization and kinetic modeling of electrocoagulation treatment of dairy wastewater. Desalination and Water Treatment, 57(13), 5988-5994.

Bingül, Z., Irdemez, Ş., Kul, S., Ekmekyapar Torun, F., & Demircioğlu, N., 2021, Investigation of organic and inorganic matters removal from tannery wastewater using iron plate electrode by electrocoagulation process. International Journal of Environmental Analytical Chemistry, 1-14.

Bingül, Z., Irdemez, Ş., & Demircioğlu, N., 2022, Effect of controlled and uncontrolled pH on tannery wastewater treatment by the electrocoagulation process. International Journal of Environmental Analytical Chemistry, 1-16.

Castiblanco, Y., Perilla, A., Arbelaez, O., Velasquez, P., & Santis, A. 2021. Effect of the pH and the catalyst concentration on the removal of hexavalent chromium (Cr (VI)) during photocatalysis of wastewater from plating on plastics industry. Chemical Engineering Transactions, 86, 679-684.

Chen, L., Dong, X., Wang, Y., & Xia, Y., 2016, Separating hydrogen and oxygen evolution in alkaline water electrolysis using nickel hydroxide. Nature communications, 7(1), 1-8.

Chowdhury, M., Mostafa, M. G., Biswas, T. K., & Saha, A. K., 2013, Treatment of leather industrial effluents by filtration and coagulation processes. Water Resources and Industry, 3, 11-22.

Elabbas, S., Ouazzani, N., Mandi, L., Berrekhis, F., Perdicakis, M., Pontvianne, S., ... & Leclerc, J. P., 2016, Treatment of highly concentrated tannery wastewater using electrocoagulation: influence of the quality of aluminum used for the electrode. Journal of Hazardous Materials, 319, 69-77.

El-Ashtoukhy, E. S., Zewail, T. M., & Amin, N. K., 2010, Removal of heavy metal ions from aqueous solution by electrocoagulation using a horizontal expanded Al anode. Desalination and Water Treatment, 20, 72-79.

Espinoza-Quiñones, F. R., Fornari, M. M., Módenes, A. N., Palácio, S. M., da Silva Jr, F. G., Szymanski, N., ... & Trigueros, D. E., 2009, Pollutant removal from tannery effluent by electrocoagulation. Chemical engineering journal, 151(1-3), 59-65.

Gonzalez-Delgado, A., Tejada-Tovar, C., & Villabona-Ortiz, A. 2022. Computer-aided Modeling and Evaluation of a Packed Bed for Chromium (vi) Removal Using Residual Biomass of Theobroma Cacao L. Chemical Engineering Transactions, 92, 517-522.

Hakizimana, J. N., Gourich, B., Chafi, M., Stiriba, Y., Vial, C., Drogui, P., & Naja, J., 2017, Electrocoagulation process in water treatment: A review of electrocoagulation modeling approaches. Desalination, 404, 1-21.

Infomine.,2022, Aluminum Prices and Aluminum Price Charts. InvestmentMine, Mining Markets & Investment. <http://www.infomine.com/investment/metal-prices/aluminum/> accessed 03.03.2022.

Kabdaşlı, I., Vardar, B., Arslan-Alaton, I., & Tünay, O., 2009, Effect of dye auxiliaries on color and COD removal from simulated reactive dyebath effluent by electrocoagulation. Chemical Engineering Journal, 148, 89-96.

Kuokkanen V., 2016, Utilization of electrocoagulation for water and wastewater treatment and nutrient recovery techno-economic studies. PhD Thesis, University of Oulu, Faculty of Technology. Oulu, Finland.

Lofrano, G., Meriç, S., Zengin, G. E., & Orhon, D, 2013, Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: a review. Science of the Total Environment, 461, 265-281.

Luz del Sur., 2022, Luz del Sur, <https://www.luzdelsur.com.pe/media/pdf/tarifas/TARIFAS.pdf> accessed 03//03/ 2022.

Moussa, D. T., El-Naas, M. H., Nasser, M., & Al-Marri, M. J., 2017, A comprehensive review of electrocoagulation for water treatment: Potentials and challenges. Journal of environmental management, 186, 24-41.

Moussout, H., Ahlafi, H., Aazza, M., & Maghat, H. 2018. Critical of linear and nonlinear equations of pseudo-first order and pseudo-second order kinetic models. Karbala International Journal of Modern Science, 4(2), 244-254.

Ölmez, T., 2009, The optimization of Cr (VI) reduction and removal by electrocoagulation using response surface methodology. Journal of Hazardous Materials, 162(2-3), 1371-1378.

Ouaissa, Y. A., Chabani, M., Amrane, A., & Bensmaili, A., 2014, Removal of tetracycline by electrocoagulation: kinetic and isotherm modeling through adsorption. Journal of Environmental Chemical Engineering, 2(1), 177-184.

Rehman, A., Kimb, M., Reverberic, A., & Fabianoa, B. 2015. Operational parameter influence on heavy metal removal from metal plating wastewater by electrocoagulation process. Chemical Engineering Transactions, 43, 2251-2256.

Singh, H., & Mishra, B. K., 2017, Assessment of kinetics behavior of electrocoagulation process for the removal of suspended solids and metals from synthetic water. Environmental Engineering Research, 22(2), 141-148.

Vasudevan, S., Lakshmi, J., & Sozhan, G., 2011, Studies on the Al–Zn–In-alloy as anode material for the removal of chromium from drinking water in electrocoagulation process. Desalination, 275(1-3), 260-268.

Varank, G., Erkan, H., Yazycy, S., Demir, A., & Engin, G., 2014, Electrocoagulation of tannery wastewater using monopolar electrodes: process optimization by response surface methodology, 8, 165-180.

Vepsäläinen M., 2012, Electrocoagulation is the treatment of industrial waters and wastewaters. PhD Thesis, Department of Energy and Environmental Technology, Mikkeli, Finland.154 pp.

Vivienda., 2009, Ministerio de Vivienda, Construcción y Saneamiento. < http://ww3.vivienda.gob.pe/direcciones/Documentos/DS_2009_021.pdf> accessed 2.06.2019.

Zewail, T. M., & Yousef, N. S., 2014, Chromium ions (Cr6+ & Cr3+) removal from synthetic wastewater by electrocoagulation using vertical expanded Fe anode. Journal of Electroanalytical Chemistry, 735, 123-128.