

ELECTROCHEMICAL BLEACHING OF YELLOW 4GN AND BLUE 2R DYES WITH Ti/Pt

Sara Andrea Álvarez Alvarado

E Student of the Master's Degree in Chemical
Science and Technology

Faculty of Chemical Sciences of:

``Universidad Autónoma de Coahuila``

Saltillo, Coahuila, Mexico

Judith Amador-Hernández

Professor and Researcher at the Faculty of
Chemical Sciences

Department of Analytical Chemistry of:

``Universidad Autónoma de Coahuila``,

Saltillo, Coahuila, Mexico

<https://orcid.org/0000-0003-1873-024X>

Miguel Velázquez-Manzanares

Professor and Researcher at the Faculty of
Chemical Sciences

Department of Analytical Chemistry of:

``Universidad Autónoma de Coahuila``,

Saltillo, Coahuila, Mexico

<https://orcid.org/0000-0002-5125-1040>

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Abstract: The growing contamination of water by textile dyes encourages the search for methodologies for their treatment, such as advanced oxidation techniques. In this work, the electrochemical behavior of the synthetic dyes yellow 4GN (A4GN) and blue 2R (A2R) used in the dyeing of Saltillo sarapes was studied using cyclic voltammetry (VC), as well as their electrochemical decolorization. For CV, a three-electrode cell was used (Pt working electrode and counter electrode, Ag/AgCl reference), 0.1 M KCl as support electrolyte and 50 mg/L sample solutions. It was observed that the oxidation of the dyes occurs, although its signal is masked by the oxidation of the chloride ion because its concentration is higher than that of the analytes. For decolorization, a sandwich flow cell with 2 Ti/Pt electrodes, 0.1 M KCl as electrolyte and 50 mg/L sample was used. The applied voltage, pH and flow rate were analyzed. Voltage, flow rate and the interaction between them were the most significant factors in the oxidative process for both dyes, while pH was not a relevant factor. The discoloration performances were 95.5% for A4GN and 96.4% for A2R, when applying 3.0 V respectively. This methodology is easy to operate and allows the reuse and/or recirculation of the water used in wool dyeing, an important artisanal activity in the manufacture of textiles.

Keywords: electrocoloration, textile dyes, advanced oxidation, contamination.

INTRODUCTION

Currently, water pollution has increased to alarming levels around the world, representing a great challenge in the search for solutions by the scientific community. This way, the treatment of contaminated water is a task that must be prioritized. Water pollution is caused by various human activities; Among them, the textile industry is one of the largest contributors. In addition to

generating effluents contaminated with high concentrations of synthetic dyes and other compounds, large quantities of water are consumed during the dyeing process [1].

Synthetic dyes present in water affect the balance of ecosystems, interrupt the photosynthetic process of aquatic plants and induce the bioaccumulation of many of these compounds in aquatic species, affecting their metabolism [2, 3]. On the other hand, the absorption of these compounds in humans can trigger carcinogenic and mutagenic effects [4, 5]. Currently, there is a wide variety of synthetic dyes; When classified by their chemical structure, the group of azo dyes is the largest. Such compounds are characterized by their chemical stability and significant molecular weight, which is why they are recalcitrant in their degradation [6]. Therefore, the first step to avoid the imbalance of aquatic ecosystems in which water with dyes is discharged is the elimination of color from these effluents.

Currently there are various physical, chemical and biological methodologies that lead to addressing the problems of both discoloration, as a first step, and degradation, as a next step, of synthetic dyes in effluents, as environmentally friendly strategies in close relationship with the Objectives of Sustainable Development established in the 2030 Agenda by the United Nations in 2018 [7].

The applications of electrochemical degradation are extensive. In the field of dyes, the discoloration of black 5 has been addressed using graphene as electrodes, for which degradation percentages of the order of 95% were achieved [8]. In another work, 98.9% degradation of blue D-SRN was achieved using boron-doped diamond (BDD) as the anode [8]. On the other hand, for bright yellow X6G a degradation of 100% was achieved through BDD [9]. Other textile dyes present in wastewater reached a degradation

of 95.5% with conductive activated carbon fabrics [10].

In particular, it is of great interest to study the treatment of effluents from the dyeing of wool used in the production of Saltillo serapes using advanced oxidation techniques. This seeks to reduce the environmental impact of a craft activity representative of the region. Thus, in this work the electrodecoloration of the synthetic dyes A4GN (from the azo group) and A2R (from the anthraquinone group) was studied, both used especially in wool dyeing [11], whose chemical structures are presented in Figure 1.

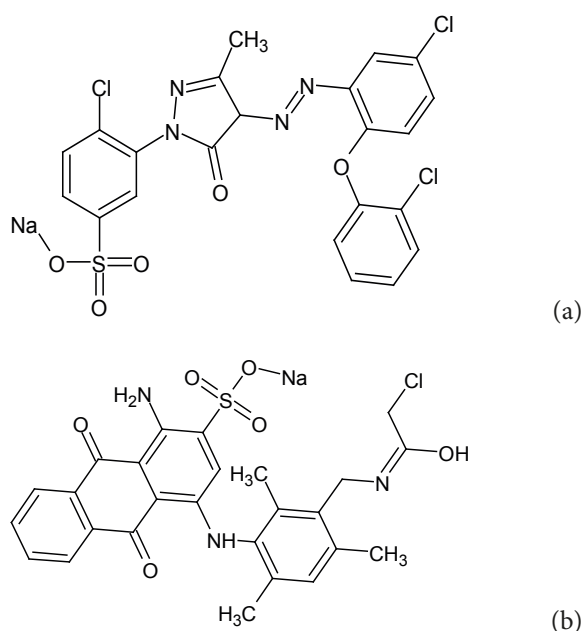


Figure 1. Chemical structure of the dyes studied, (a) A4GN (CAS No.: 72479-28-8), (b) A2R (CAS No.: 70209-96-0) [11].

METHODOLOGY

The dyes under study were Lanaset[®], yellow 4GN (A4GN) and blue 2R (A2R).

Cyclic Voltammetry (CV) was used as an electroanalytical technique, for which polarization was carried out with a potentiostat/galvanostat (Gamry Reference 600), with 0.1 M KCl as a supporting electrolyte. In this case, a three-electrode electrochemical cell was used: a) platinum working electrode,

b) platinum counter electrode, and c) Ag/AgCl reference electrode. The surface of the working electrode was cleaned and polished with 0.1 micron alumina. Afterwards, it was rinsed with tridistilled water and sonicated to eliminate possible impurities present on its surface. Each dye was studied individually, in solutions prepared with tridistilled water at 50 mg/L in 0.1 M KCl. The Gamry Analyst software was used to obtain the corresponding data from the cyclic voltammograms.

To carry out its electrodecoloration in aqueous solution, a sandwich flow cell, designed and manufactured in the laboratory, was used. The voltage was applied using a direct current power source (Wanptek, China). A peristaltic pump was also required for continuous flow of the solution (Chonry, China). The distance between the two plates (Ti/Pt, anode and cathode) was 5.0 mm, which favored the reduction of the ohmic drop. 0.1 M KCl was used as a supporting electrolyte; The dye solutions were prepared at 50 mg/L.

The influence of three variables was studied: the pH of the sample, the applied voltage and the flow rate of the solution. For pH, we worked with solutions at pH 5.0, 7.0 and 9.0. The applied voltages were 1.0, 1.5 and 3.0 V. Regarding the flow rates, 1.16, 3.19, 5.22 and 10.15 mL/min were used. Electrochemical discoloration was monitored through a UV-Visible spectrometer (Jenway 7315, UK) by recording absorbance. The assays were performed in triplicate.

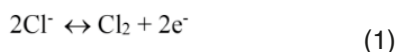
Finally, a Variance Analysis was carried out on the data obtained through the Minitab software, with the purpose of analyzing trends based on statistical trends.

RESULTS AND DISCUSSION

CYCLIC VOLTAMMETRY

For VC, a baseline was initially recorded using only the electrolyte (0.1 M KCl). Figure 2 presents the VC obtained for both dyes (50 mg/L in 0.1 M KCl) at different scanning speeds; The potential window was from -0.8 to 1.5 V. It is known that the platinum electrode is an inert metal and has a considerable polarization range, which allows having a potential window wide enough to study a wide range of electroactive species.

As it can be seen in Figure 2 (a and b), the chloride oxidation peak occurs at 1.4 V and its current is of the order of 7×10^{-4} A. Although the electrode area is small, 0.03 cm^2 , the high concentration of chlorides contributes to the magnitude of the current [12]. This process is represented by the following equilibrium:



In the presence of the dye, the current peaks decrease, as observed in the voltammetric signal. Oxidation occurs in the anodic region, although this is masked by the chloride anion reaction. Even the current of the peak corresponding to the oxidation of the anion decreases in the presence of the colorate. The dye diffuses towards the surface of the electrode, inducing a block, but at the same time its current is decreased, which is to be expected since the concentration of the chloride ion is well above the concentration of the electroactive species.

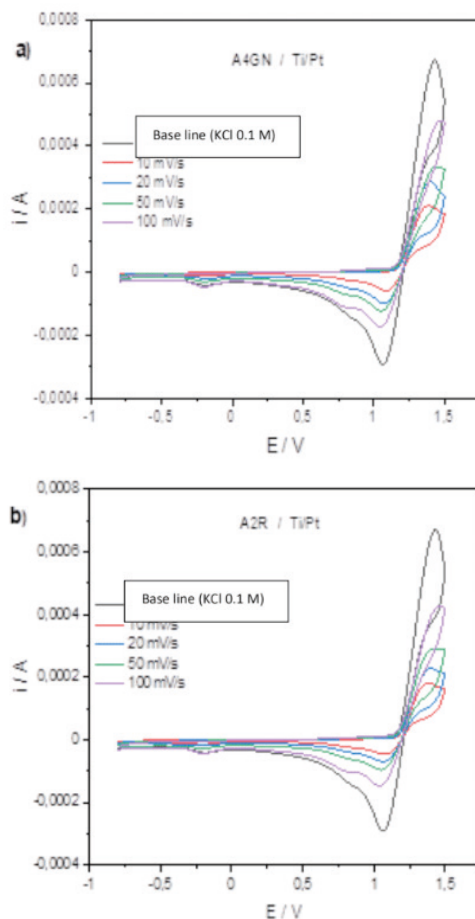


Figure 2: Cyclic voltammograms with Pt as working electrode in 0.1 M KCl, (a) A4GN, (b) A2R.

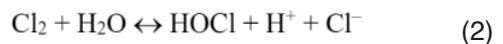
ELECTRODECOLORIZATION

Through a power source, a current flow was induced in the sandwich cell for the electrochemical oxidation of the contaminants until their complete discoloration was observed, either because the organic compounds have been brought to their complete mineralization, or they are transformed into lower molecular weight molecules, which can biodegrade.

In a dye, the elimination of its color is related to the breaking of bonds between the atoms of chromophore and auxochrome groups. In this work, the electrochemically treated samples were monitored spectrophotometrically in the visible region of the electromagnetic spectrum, in the wavelength range of 350 to

650 nm (A4GN) and 400 to 700 nm (A2R), against a reagent blank. As can be seen in Figure 3, the absorption spectra of the dyes of interest present bands with absorption maxima at 410 nm (A4GN), 590 and 630 nm (A2R). These bands present a hypochromic effect as the sample is subjected to treatment under the working conditions proposed in this study, until they disappear and give rise to a colorless solution. Particularly, the use of Ti/Pt electrodes favors the adsorption of hydroxyl radicals, generated from the medium, which participate in an oxidative process of the organic matter [13, 14], making it possible to eliminate color.

The pH can play an important role in the discoloration processes of certain organic acid-base compounds, promoting a more efficient oxidative process in certain conditions. On the other hand, it has been reported that the presence of chlorides improves the oxidation of organic matter when using active anodes, as is the case, which suggests that indirect oxidation may also occur [12]. One of the indirect oxidation mechanisms of the dye focuses on the generation of active chlorine by electrochemical oxidation; This mechanism has been widely discussed by other authors, in which chlorine gas (equation 1), hypochlorite ions and hypochlorous acid are generated, as can be summarized in the following equilibria [12]:



However, the participation of other oxidizing agents from the electrolyte, such as reactive chlorine species, depends largely on the pH of the solution and other factors [15]. In this work, the pH was adjusted to values close to neutrality as is the case of real effluents, as well as seeking safer operating conditions in the future use of the system by artisans.

Table 1 shows the electrodecoloration percentages for both dyes, estimated from concentration calculations using a calibration curve previously recorded in the range of 2 to 50 mg/L. As can be seen in the Table, the process depends largely on the applied voltage. At 1.0 V, low oxidation yields are shown (7.5% A4GN and 11.7% A2R), while at 3.0 V the discoloration reaches 95.5% A4GN and 96.4% A2R; in this case, 3×10^{-3} A/cm² were applied in terms of current flow.

The data obtained suggest that there is an interaction between the effects produced by voltage and flow rate, since when applying 1.5

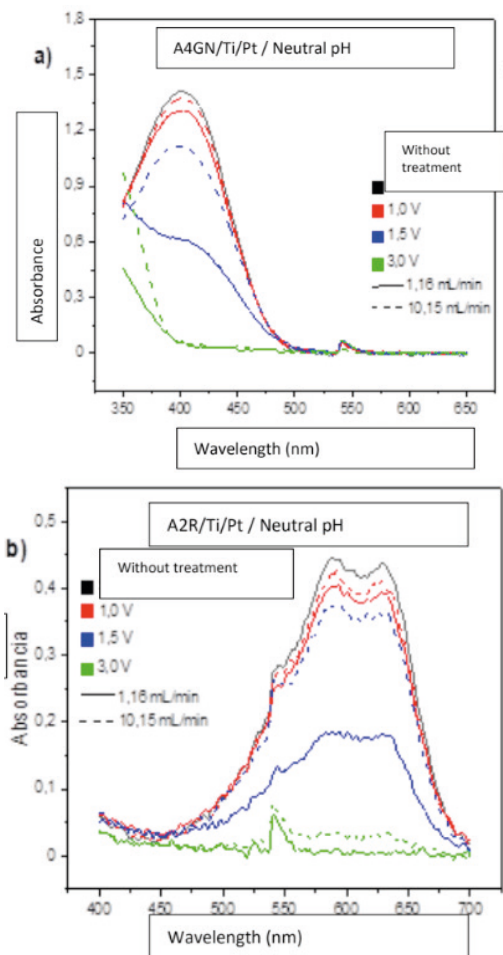


Figure 3. Absorption spectra under different electrodecoloration conditions, (a) A4GN, (b) A2R.

V at short residence times the percentage of discoloration decreases. This is reasonable if one considers that, with a longer residence time (slow flow rate), the dye interacts with the electrode surface for a longer time, increasing performance. This indicates that it is a diffusion process of the analyte towards the electrode.

VARIANCE ANALYSIS

Finally, through an Analysis of Variance (ANOVA) the interactions between the studied parameters were evaluated. This work does not delve deeper into the model, since a predictive model is not sought, only to corroborate trends and help identify the most important factors of the process in the system studied.

Figure 4 shows the effects of the factors analyzed for the electrodecoloration of A4GN, in which it can be seen that voltage is the most relevant factor (as observed previously) followed by flow speed; pH was the factor with the least relevance.

Regarding the effect produced by the dye, Figure 5 (a, b and c) shows the decrease in the absorbance signal at the absorption maximum of A2R is smaller compared to that observed in the A4GN dye. However, this does not mean that electrodecoloration occurs to a lesser extent, since the average obtained with treatments at 3.0 V is more than 95% for both dyes, as seen in Figure 3. The most significant decrease in the signal of the A4GN is due to the fact that its initial absorbance is higher (1.4 AU) than for A2R (0.4 AU).

Likewise, Figure 5d shows the interaction between voltage and flow velocity. It highlights the fact that at 1.0 and 3.0 V, the flow rate does not influence to the same extent as is observed when using 1.5 V. This can be explained based on the kinetics of the reaction that occurred in the system. By using higher potentials, the kinetics will increase. Therefore, applying

3.0 V to the system produces the most discoloration. Under such conditions, the sample flow rate takes a backseat, since the kinetics are high enough for the reaction to occur even at lower residence times. Likewise, it is inferred that when using low voltages (1.0 V) the energy promoting discoloration is insufficient, compared to 1.5 V.

It has been reported that the presence of NaCl improves the kinetics, so it is expected that in the present work this will also occur when using KCl [16]. This increase may be due to the fact that both types of oxidation are possible in the system. While the hydroxyl radicals are adsorbed on the surface of the electrode, the reactive chlorine species act within the solution. Using 1.0 V may not provide the ideal environment for this to occur.

On the other hand, the other interactions between factors did not turn out to be significant for this work, that is, voltage with pH, pH with flow rate or the interaction between the three factors.

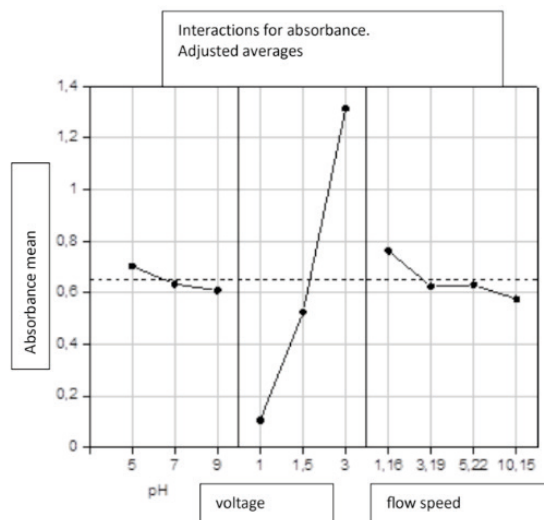


Figure 4. Effect of the factors individually obtained from the ANOVA of the electrodecoloration of A4GN.

Voltage (V)	Flow rate (mL/min)	A4GN discoloration (%)			A2R discoloration (%)		
		pH 5.0	pH 7.0	pH 9.0	pH 5.0	pH 7.0	pH 9.0
1.0	1.16	10.3	10.5	4.2	31.3	23.3	11.8
1.0	3.19	11.9	4.2	9.2	12.8	7.8	12.1
1.0	5.22	11.7	2.8	0.01	2.4	9.8	7.3
1.0	10.15	4.8	4.5	15.4	8.3	8.6	5.2
1.5	1.16	62.7	56.6	71.6	62.9	50.1	38.1
1.5	3.19	37.2	24.3	32.9	16.7	24.5	19.1
1.5	5.22	46.6	30.7	27.7	22.0	17.3	34.8
1.5	10.15	24.4	24.1	19.4	19.5	22.5	21.4
3.0	1.16	96.3	95.0	95.7	100.0	99.0	99.9
3.0	3.19	95.5	95.5	95.9	97.6	100	97.8
3.0	5.22	95.6	95.7	95.3	98.1	96.9	96.4
3.0	10.2	95.2	95.8	95.1	92.4	91.1	88.0

Table 1: Electrocoloration percentages for A4GN and A2R dyes obtained using Ti/Pt electrodes.

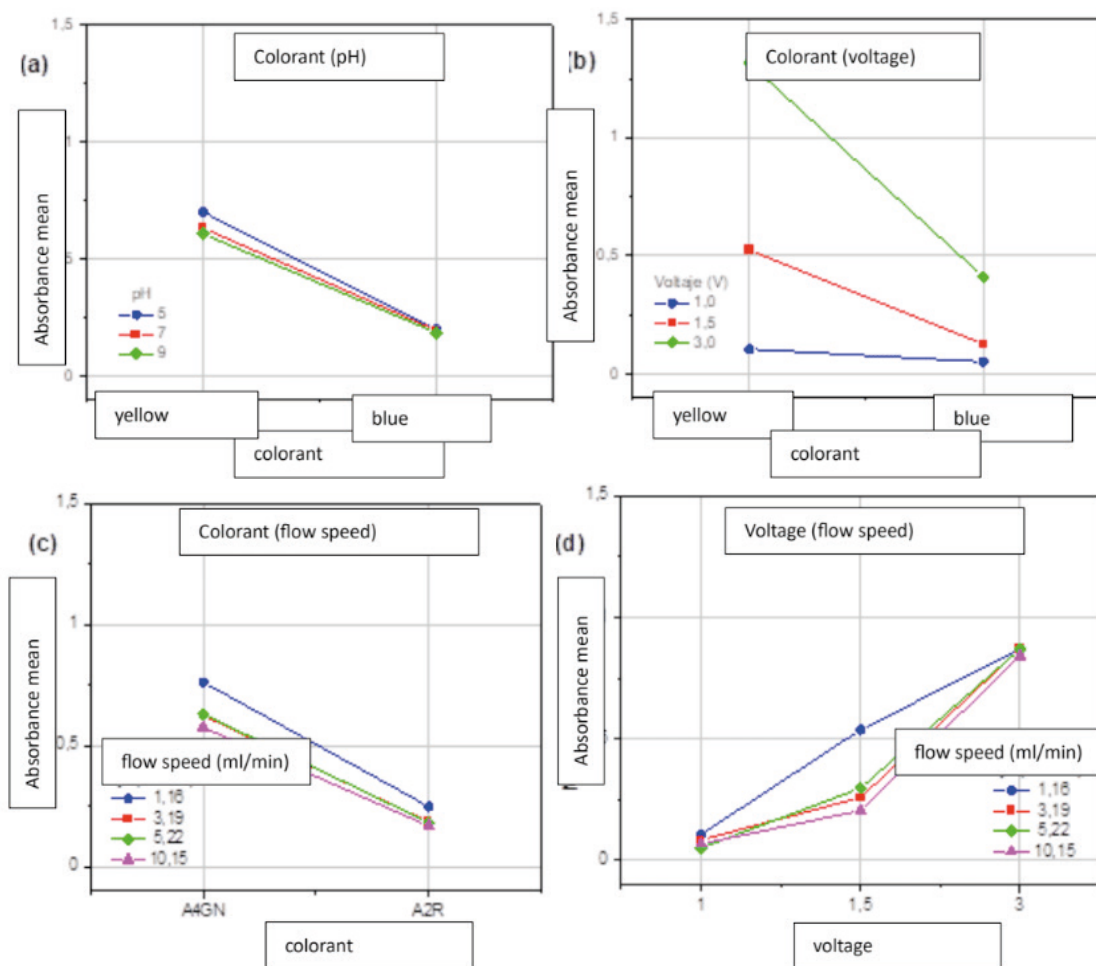


Figure 5. Effect of interactions between factors obtained from the ANOVA of the electrodecoloration of A4GN and A2R, (a) dye*pH, (b) dye*voltage, (c) dye*flow rate, (d) voltage*flow rate.

CONCLUSIONS

In cyclic voltammetry, the magnitude of the dye oxidation current peaks is below the currents attributed to the oxidation of the chloride anion, since the concentration of the electrolyte is higher relative to the analyte.

For the electrodecoloration of the A4GN and A2R dyes, the system used from the cell built with Ti/Pt electrodes was efficient, achieving the degradation of more than 95% of both compounds. The dye itself was a relevant factor in the electrochemical discoloration of this type of products. This is due to the inherent properties of each compound, inferred from its chemical structure.

On the other hand, voltage, flow rate and the interaction between them are the most significant factors in the discoloration of both dyes. The pH showed the least significant effect, so when implementing this process on a larger scale for the treatment of effluents, a sample conditioning step regarding this parameter will not be necessary.

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REFERENCES

1. C. Gallego-Ramírez, E. Chica y A. Rubio-Clemente. (2022). Estudio de los efectos ecotoxicológicos de los colorantes en diferentes organismos acuáticos. *Ciencia Transdisciplinaria en la Nueva Era*, Medellín, Instituto Antioqueño de Investigación. 336-346.
2. F. Yonni, H. Fasoli, M. Giai y H. Álvarez. (2008). Estudio de la biodegradabilidad y ecotoxicidad sobre colorantes textiles. *Higiene y Sanidad Ambiental*. 8, 331-334
3. M. Wawrzkiwicz, E. PolskaAdach y Z. Hubicki. (2019). Application of titania based adsorbent for removal of acid, reactive and direct dyes from textile effluents,» *Adsorption*. 25, 621–630.
4. S. P. Ekambaram, S. S. Perumal y U. Annamalai. (2016). Decolorization and biodegradation of remazol reactive dyes by *Clostridium* species. *Biotech*, 6(20) 1-8.
5. P. E. Zaruma Arias, J. B. Proal Nájera, I. Chaires Hernández y H. I. Salas Ayala. (2018). Los Colorantes Textiles Industriales y Tratamientos Óptimos de dos Efluentes de Agua Residual: Una Breve Revisión. *Revista de la Facultad de Ciencias Químicas*. 19, 38-47.
6. J. Shore, Colorants and auxiliaries. *Organic Chemistry and Application*, Second ed., Manchester: Society of Dyers and Colourists, 2002.
7. Naciones Unidas, *La Agenda 2030 y los Objetivos de Desarrollo Sostenible: una oportunidad para América Latina y el Caribe*, Santiago: Naciones Unidas, 2018.
8. A., Pieczyńska, T., Ossowski, R., Bogdanowicz & E., Siedlecka (2019). Electrochemical degradation of textile dyes in a flow reactor: effect of operating conditions and dyes chemical structure. *Int. J. Environ. Sci. Technol.* 16, 929–942.
9. Z., Isik, B., Ozbey-Unal, A., Karagunduz, B., Keskinler, & N. Dizge. (2020) Electrochemical Treatment of Textile Dye Bath Wastewater Using Activated Carbon Cloth Electrodes. *Avicenna Journal of Environmental Health Engineering*, 7(1), 47-52.
10. Y., Tang, D., He, Y., Guo, W., Qu, J., Shang, L., Zhou, W., Dong. (2020) Electrochemical oxidative degradation of X-6G dye by boron-doped diamond anodes: Effect of operating parameters. *Chemosphere*, 258, 127368, 2020.

11. A. L. Martínez Herrera, E. Colunga Urbina, I. M. de la Garza Rodríguez, M. Velázquez-Manzanares, M. E. Poisot Vázquez y J. Amador-Hernández. (2016). Herramientas analíticas en la búsqueda de la protección comercial del sarape de Saltillo, *APORTACIONES CINÉTICAS EN QUÍMICA ANALÍTICA. XXIX Congreso Nacional de Química Analítica*. 209-215.
12. S. Aoudj, K. Bahloul y A. Khelifa. (2021). Degradation of Dyes by Electrochemical Advanced Oxidation Processes, de *Advanced Removal Techniques for Dye-containing Wastewaters, Sustainable Textiles: Production, Processing, Manufacturing & Chemistry*, Singapur, Springer. 129-174.
13. O. M. Rodríguez-Narváez, A. R. Picos, N. Bravo-Yumi, M. Pacheco-Alvarez, C. A. Martínez-Huitle y J. M. Peralta-Hernández. (2021). Electrochemical oxidation technology to treat textile wastewaters. *Current Opinion in Electrochemistry*, 29:100806.
14. C. A. Martínez-Huitle y S. Ferro. (2006). Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes. *Chemical Society Reviews*. 35(12), 1324–1340.
15. N. G. Yasri y S. Gunasekaran. (2017). Electrochemical Technologies for Environmental Remediation. *Enhancing Cleanup of Environmental Pollutants*, Springer, Cham. 5-73.
16. A. Phetrak, P. Westerhoff y S. Garcia-Segura. (2020). Low energy electrochemical oxidation efficiently oxidizes a common textile dye used in Thailand. *Journal of Electroanalytical Chemistry*. 871, 114301.