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Electrolytic Cell Applied for the Breakdown of Endocrine Disrupting Drugs in Aqueous Tributaries

*Jorge Alberto Mendoza Pérez,
Abril Gardenia Martínez Castillo,
Jorge Octaviano Gomez Castrejon
and Juan Carlos Gómez Buendía*

Abstract

In this chapter, we report previous results about advances of an electrolysis process developed for breakdown of endocrine disrupting drugs in aqueous media. The objective is to achieve the breakdown of two drugs: trimethoprim and a mixture of clavulanic acid-amoxicillin (1:7) with an electrolytic cell by means of oxidization-reduction reactions. The evaluation of the process was carried out using spectrometry techniques UV-Vis, thin layer chromatography (TLC), chemical oxygen demand (COD), and total organic carbon (TOC). Handcrafted mineral carbon electrodes doped with titanium dioxide were designed, platinum and copper wires were placed, and a potassium hydroxide solution was used as electrolyte. The electrolyte, being an alkaline salt, allows the transport of charges from one side to the other, and electrode doped with titanium dioxide is used in order to help the electronic transfer, and the mineral carbon, having a strong affinity for organic and non-polar compounds, performs an adsorption process. Results from several performed assays showed that after 1 hour of treatment, it can be seen the breakdown of the drugs present in a synthetic wastewater solution.

Keywords: electrolysis, oxidation, reduction, drug, depuration, breakdown, absorbance, concentration, electrode

1. Introduction

Unregulated emerging pollutants enter aquatic systems through wastewater treatment plants after consumption and use by humans and animals [1].

This poses a significant risk to aquatic organisms and to public health. Among the main effects described to date are the appearance of changes in fish reproduction due to the presence of hormones and inhibition of photosynthesis in algae

by the presence of these [2]. We know that the presence of antibiotics in the environment can make bacteria in wastewater relatively more resistant to them and resistant microorganisms develop.

To make clear how these molecules act as endocrine disruptors, we must indicate that they interfere with the body's homeostasis, usually by mimicking the natural hormones that lead to the activation or blocking of their receptors [3].

Trimethoprim in Mexico is one of the most used drugs for treating urinary tract infections, and it is commonly used in the foreign tourism for attending the traveler's diarrhea [4]. Trimethoprim is incompletely metabolized by humans during the therapeutic process and approximately 80% is excreted in the pharmacologically active form, which can promote the development of bacterial resistance to this compound's form promoting it as an emerging contaminant [5].

Clavulanic acid-amoxicillin is a mixture of two drugs in typical commercial compositions of 185/125 and 500/125 mg and commercially known in México as Augmentin and Clamoxin or Gimaclav, respectively. It is indicated for the treatment of acute and chronic infections of the upper and lower respiratory tracts, meningitis and genitourinary, skin, soft tissue, gastrointestinal and biliary infections, and in general for the treatment of infections caused by pathogens sensitive to this mixture of drugs [6].

Both drugs have been studied by our research group as emerging pollutants with an effect of endocrine disruptors due to their high presence in wastewater of domestic and hospital effluents in México (work in process of being published) and their consequent impact on all types of aquifers, which could act as final receiving bodies. However, in our research group, different advanced oxidation processes have been used and improved for the removal of these kinds of contaminants, these processes include cavitation, photo-catalytic oxidation, or Fenton chemistry, but they have high costs. New expectations were found when it has been applied an electrochemical process.

Electrochemical oxidation is based on the application of an electric current or a potential difference between two electrodes (anode and cathode), wherewith hydroxyl radicals or other oxidizing species can be generated, depending on the anode material used and the type of electrolyte support used [7].

In this chapter, the use of electrolysis for the removal of pharmaceutical-type pollutants is based on the chemical reactions that are carried out between the electrodes submerged in electrolytic solutions by effect of the passage of the electric current, being the function of the electrolyte to serve as a means of transporting electrical loads and provoke the reactions of oxidation-reduction for the degradation of compounds in order to transform them into less hazardous compounds for the environment. The electrolyte being of the family of salts allows the anions to carry negative loads toward the anode and the cations transport the positive loads to the cathode [8]; the effectiveness of several visible light-activated TiO_2 photocatalysts has been proven for the treatment of emerging contaminants. Doping or co-doping of titanium dioxide using nitrogen, nitrogen-silver, sulfur, carbon, and copper and incorporating graphene nano-leaves increases its effectiveness. The use of titanium dioxide is to improve photocatalytic activity [9]. Considering all the above backgrounds, the experiments reported hereby were performed in order to establish if the proposed system could breakdown or transform the pollutants (drugs) into simpler molecules.

Based on different references, it is known that the trimethoprim can be determined with an absorbance at 237.6 nm [10] or that it can be displayed at a

wavelength of 283–350 nm [11], and it is mentioned that in visible light, it is still observed at a wavelength between 400 and 600 nm [12]. In the case of amoxicillin-clavulanic acid mixture, the spectra recorded are in a wavelength range of 200–380 nm [13]. Therefore, the results on the UV-Vis spectrum were analyzed within these intervals.

2. Methodology and materials

2.1 Preparing the model pollutant

For the preparation of synthetic wastewater (SWW) contaminated by trimethoprim and clavulanic acid-amoxicillin, three samples with 500 mL of clean water (0.1 mS/cm) were added with different drug concentrations (trimethoprim 0.1%, trimethoprim 0.2%, and clavulanic acid-amoxicillin 0.2%). Type curves for each drug were prepared with 2 g/L (0.2%) as the highest concentration and 0.1 g/L (0.01%) as the lowest concentration.

The drugs supplied by Merck | Sigma-Aldrich were white powders, and the solutions prepared were kept in refrigeration (6°C) until needed.

2.2 Electrode construction

For the construction of the electrodes, two glass tubes were used, each one of 6.1 cm length and 0.7 cm width, containing the following elements: an electrode connected to the negative pole (cathode) was handcrafted with mineral carbon introducing a copper wire (0.3 mm Ø) and the electrode connected to the positive pole (anode) was also handcrafted with mineral carbon doped with TiO_2 and it was used a platinum wire (0.1 mm Ø). In the cathode, the reduction processes take place and oxidation occurs in the anode, where both are connected to a power supply with a 5 V electrical potential (**Figure 1**).

Platinum is an inert metal that does not participate in the redox reaction but only exchanges electrons [14] since it has a low reactivity with oxygen and with water [15]. Copper is a metal with great ductility and high electrical conductivity [16], which leads to the conclusion that both metal wires are good conductors and will show little corrosion. Furthermore, platinum has catalytic activity and low reactivity. Due to these characteristics, the platinum and copper wires were selected for the electrodes. Doping carbon with TiO_2 aids a better oxidation process at the anode, in addition to having photocatalytic properties that can improve the dissociation reaction in the electrolytic cell.

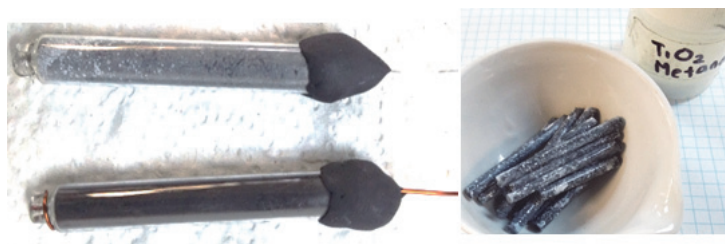


Figure 1.
 TiO_2 -doped electrodes and coal.

2.2.1 Obtaining mineral coal

The mineral coal was obtained from zinc-carbon battery carbon cylinders free of cadmium (0% Cd) and (0% Mg) magnesium, confirmed by atomic absorption; so, the mineral coal is free of these elements. Extracted amounts were obtained from different brands of batteries (MARKS rocket, explosive, Panasonic super hyper, King Kong, Sony-new ultra, and Kodak extra heavy-duty, among others). The cylinders were washed by immersion overnight (almost 8 hours) and rinsed with deionized water type I. The zinc and manganese content were also analyzed by atomic absorption of all the carbon cylinders obtained; determination of ammonium chloride was also performed but in the remaining rinse water used to clean the cylinders (the chlorides were quantified by the Mohr method and ammonia by the selective electrode method). Curiously after washing and rinsing the carbon cylinders, the concentrations of zinc and ammonium chloride were not detectable and there is only less than 0.1% impregnation of manganese, which was considered negligible for the experiment.

The coal cylinders were divided into two portions, one was ground directly and the other portion was doped with TiO_2 and ground.

2.2.2 TiO_2 -doped coal

The mineral carbon was added into a TiO_2 solution at 3.46 g/L (3.46%) and after that it was introduced to a stove at 100°C for approximately 2 hours. Finally, the mineral carbon doped with TiO_2 was crushed, until a homogenous fine powder (0.65–1 μm) was obtained.

2.2.3 Coal electrodes

Having prepared both coals (doped and not doped), the glass cylinders were filled separately with them and the copper and platinum wires were placed along leaving 7.5 cm of free wire.

2.3 Installation of the electrolytic cell

To assemble the electrochemical cell, it was designed with an acrylic cell, a power supply (5 V DC) from STEREN, a porous rectangle glass membrane (length 8.5 cm, height 3.8 cm, and width 7.0 mm), and the handcrafted electrodes. For the proper functioning of the electrolyte cell, moving of charges from the anode to the cathode and to balance the aqueous solution, a KOH electrolyte (0.01 M) from Merck | Sigma-Aldrich was used. The experiments were performed using 50 mL of the mentioned electrolyte solution and about 200–240 mL of SWW, inside the cell. All the experiments were performed in triplicate.

2.4 Experimental sampling

Twenty milliliters of samples of treated synthetic wastewater (TSWW) were taken every half an hour for an experimentation time period between 1.5 and 2 hours, and at time 0, intermediate and final time samples were collected for each experiment. Parameters such as pH, conductivity, and temperature for each sample were measured. A Hach brand Pro HR pocket conductivity tester was used; the temperature is given in $^\circ\text{C}$ and the conductivity in mS/cm .

Determination of total organic carbon (TOC) was performed for all the samples using a Thermo Scientific HiperTOC using the US standard US EPA 415.3.

Another analytical method performed also for all the samples was the chemical oxygen demand (COD) under the Mexican Standard NMX-AA-030/2-SCFI-2011. Both methods were carried out by an IPN reference laboratory, which is certified by the Mexican Accreditation Entity (MAE). Also, each sample was taken for analyzing with thin layer chromatography (TLC) and UV-Vis spectrometry analysis at different wavelengths.

2.5 Analytical method of UV-Vis spectrometry

A visible ultraviolet spectrometer BECKMAN brand model DU 7500i was used for the UV-Vis spectrometry technique. First, an absorbance sweep was performed with the SWW samples at different concentrations, in order to find the highest absorbance wavelength to perform their type curves for both drugs. Subsequently, each of the TSWW samples was also measured at a wavelength ranging from 200 to 350 nm (UV absorbance) and 400 to 800 nm (Vis absorbance) in order to observe the degree of degradation or breakage that was achieved.

In order to validate the analytical methodology, the technical guide on traceability and uncertainty is used with those analytical measurements performed with an ultraviolet-visible spectrophotometry technique, which supports the application of the NMX-17025-IMNC-2006 standard, the foregoing established by the National Metrology Center (NMC) and the Mexican Accreditation Entity (MAE) [17].

2.6 TLC analytical method

For thin-layer chromatography, a 2.5 cm by 4 cm thin gel plate was used as a stationary phase; also, both drug standards from Merck | Sigma-Aldrich, two glass chromatographic cameras, and a 254 nm wavelength UV frame were needed. Polar and non-polar (intermediate) solutions were used as mobile phases (eluent). The polar and non-polar (intermediate) eluent solutions were prepared with different concentrations of hexane and ethyl acetate, both from chromatographic grade (Merck | Sigma-Aldrich). The non-polar (intermediate) contained a 4:6 ratio of ethyl acetate and hexane. The polar eluent does a 6:4 ratio of ethyl acetate and hexane. The TSWW samples were mixed with ethyl acetate in a 4:3 ratio inside a test tube and agitated for 30 seconds.

From the test tube, an aliquot of the TSWW samples was taken with a capillary. For each experiment, the TSWW samples were taken at the start, intermediate, and final times, the aliquots were placed subsequently on the thin plate, and the plate was introduced to the chromatographic chambers each with a different eluent (polar and non-polar). After taken out from the camera, plates were revealed under the 254 nm ultraviolet light. The running fronts for standards and sample components were calculated. The intention to use this method is because it is applied in the pharmaceutical industry as a compound purity determination. Therefore, with this technique, it has been able to see qualitatively whether there is a decrease or breaking of the contaminants in the TSWW sample compared against a SWW sample.

3. Results and discussions

The model designed and constructed for the electrolytic cell used in the breakdown of the trimethoprim and acid clavulanic-amoxicillin is described in **Figure 2**.

The type curves for both drugs that were obtained and are showed in **Figures 3 and 4** with their corresponding equations and linear coefficient.

$$Y = 0.1959x + 1.4541 \tag{1}$$

$$R^2 = 0.9782 \tag{2}$$

Eq. (1) shows the linearity, for the trimethoprim.

$$Y = 0.3535x + 0.004 \tag{3}$$

$$R^2 = 0.9612 \tag{4}$$

Equation (3) shows the linearity for the acid clavulanic.

The results obtained from the UV-Vis spectrometry technique at 350 nm is shown in **Figure 5** and results with a 400 nm wavelength is shown in **Figure 6**, where the absorbance units were plotted with respect to the treatment time. When

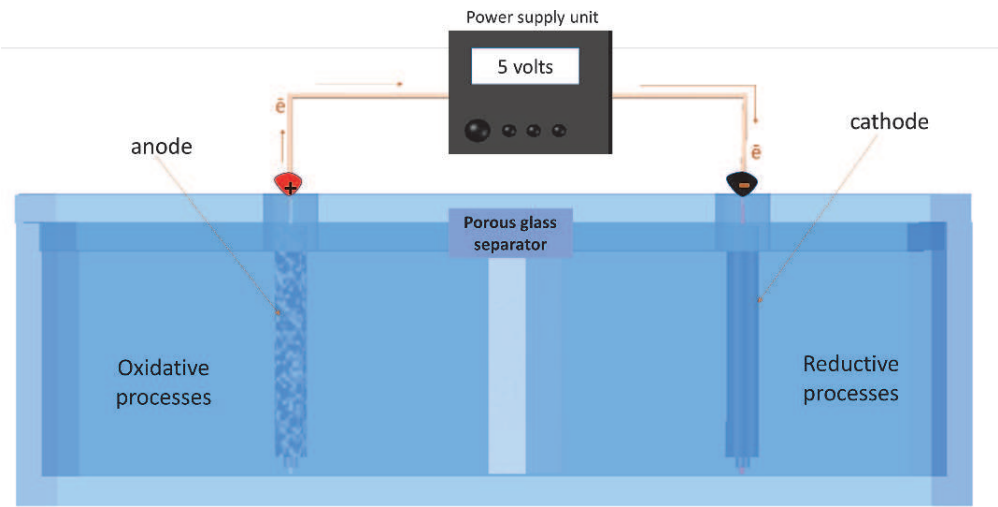


Figure 2.
Main components of an electrolytic cell.

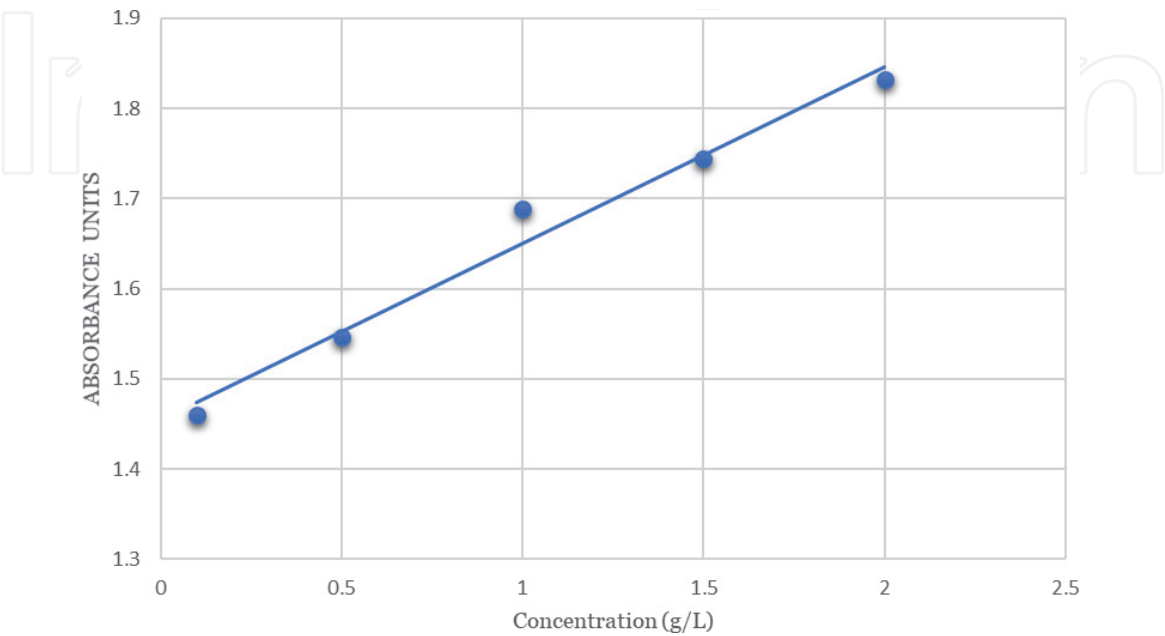


Figure 3.
Type curve of trimethoprim at a wavelength of 300 nm.

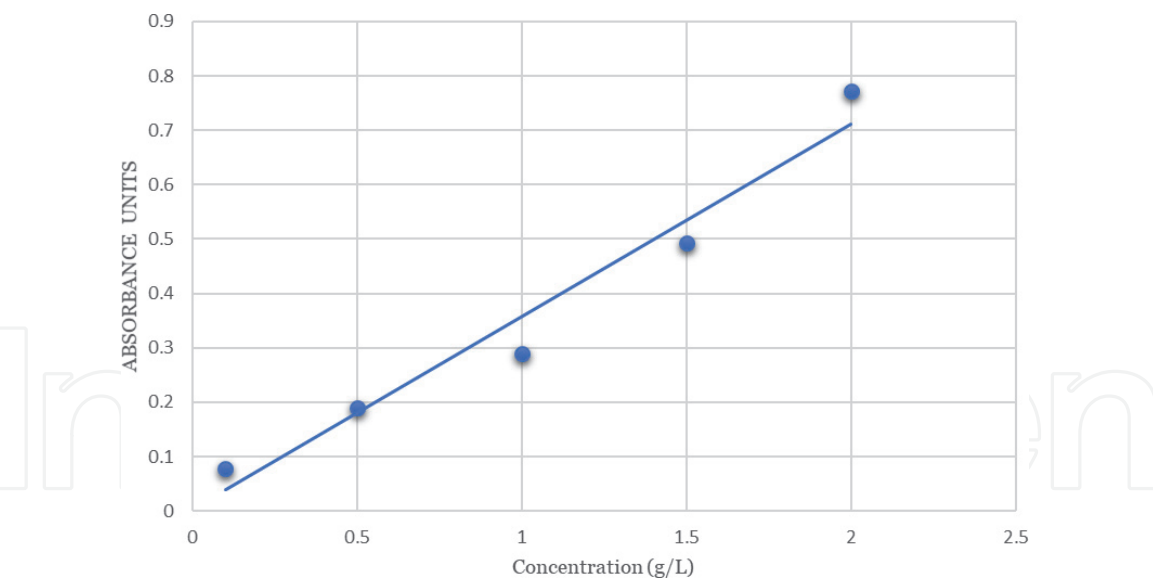


Figure 4.
Clavulanic acid-amoxicillin type curve with a wavelength of 300 nm.

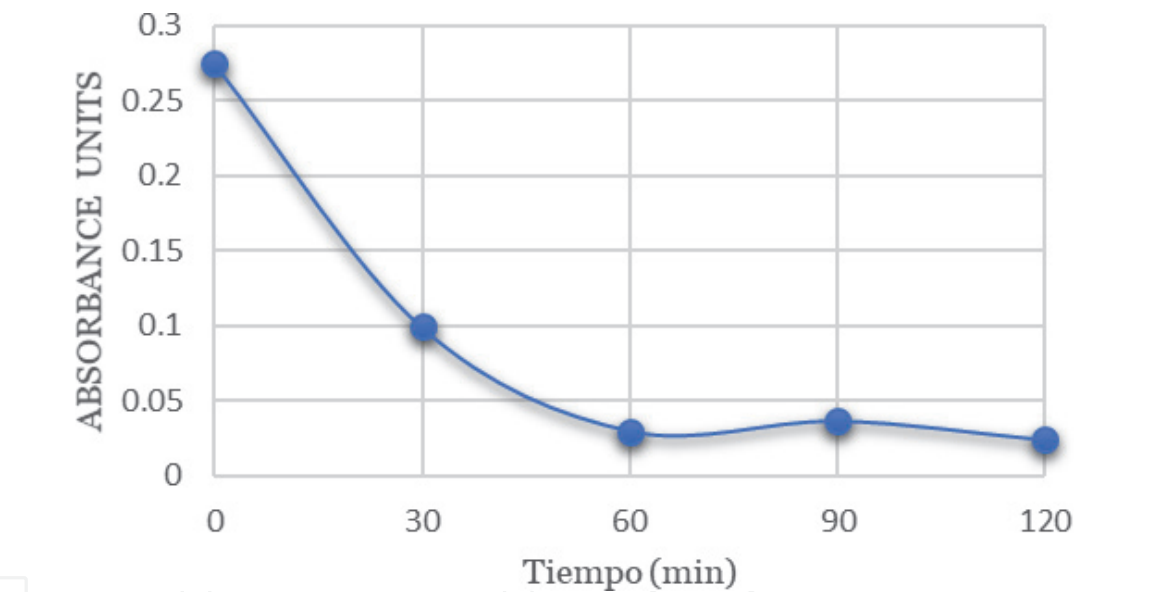


Figure 5.
Mean absorbance decreasing of trimethoprim at different treatment times, at a wavelength of 350 nm.

handling a compound that has rings and double bonds in its molecular structure, it is able to absorb ultraviolet light, and according to the Lambert-Beer law, the absorbance of a substance is proportional to the concentration of the compound.

From the graphs above, we can observe a decay of the absorbance in the trimethoprim at 90 minutes and an increase in the clavulanic acid-amoxicillin mixture experiment after 30 minutes of treatment. These results indicate that there is surely a breakdown in both molecules, but the structure of the molar fragments for trimethoprim differs with respect to the clavulanic acid-amoxicillin mixture. In the first one, the absorbance decreases, but in the second, it increases. It is known that the molecules whose absorbance decays in an electrochemical process present a process of chemical reduction (electron gain), while the compounds whose absorbance increases are understood to undergo chemical oxidation processes (loss of electrons).

For the clavulanic acid-amoxicillin mixture, the increase in absorbance may be due to structural changes in the molecule, so the chemical structure was modified

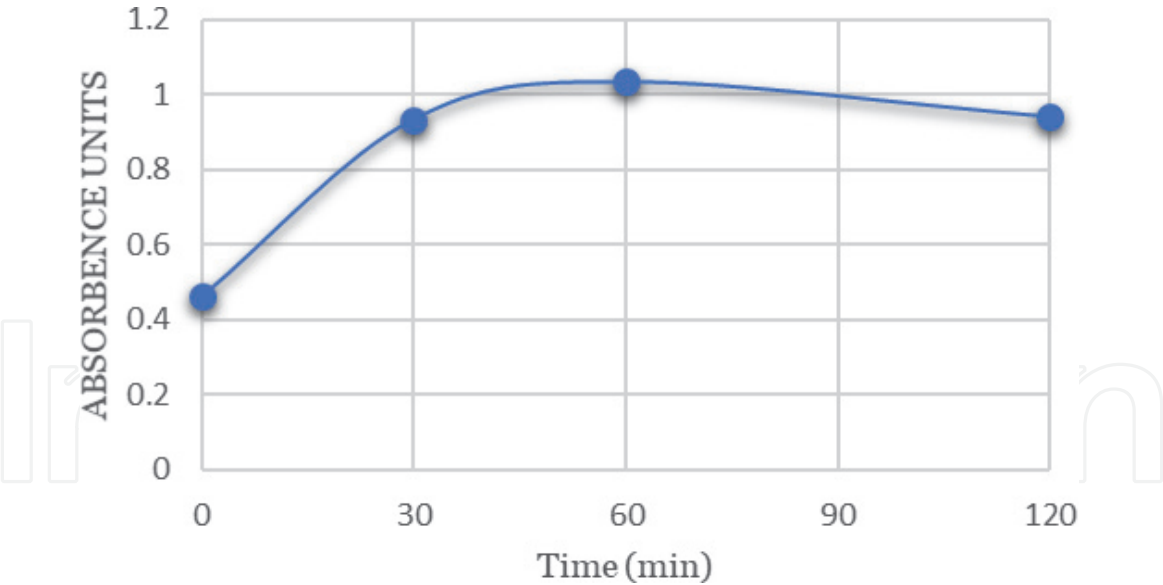


Figure 6.
Absorbance units of the clavulanic acid-amoxicillin mixture at different treatment times, at a wavelength of 400 nm.

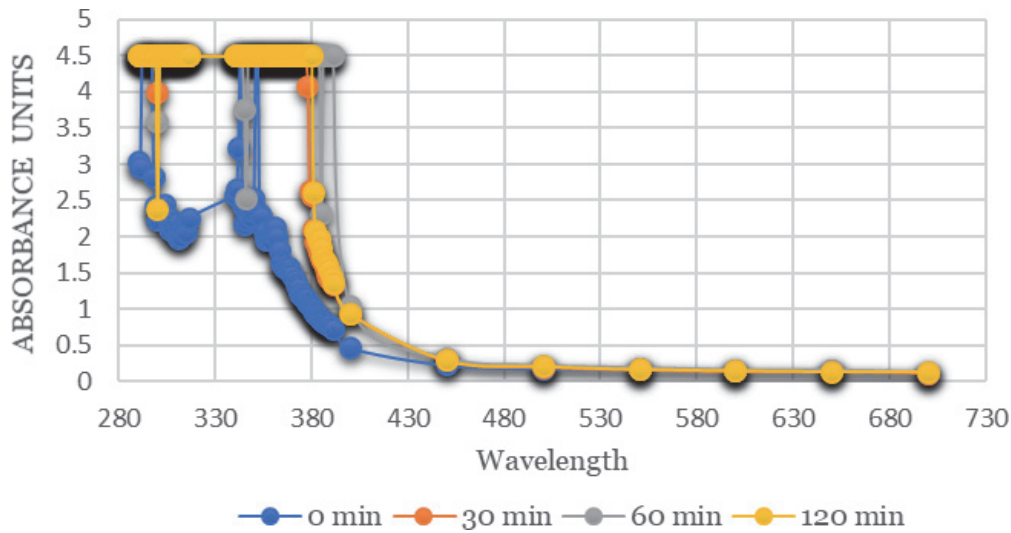


Figure 7.
Full scan of the UV-Vis spectrometer for samples at different treatment times of the clavulanic acid-amoxicillin mixture.

during the reaction, generating resonance systems that will show higher absorbances. Furthermore, this increase in absorbance may be due to the formation of other compounds in the electrolysis reaction, such as hydrogen near the cathode and oxygen near the anode. In the disintegration of water, both ozone and hydrogen peroxide are formed in small quantities [18]; it is known that ozone strongly absorbs radiation in the infrared, visible, and ultraviolet regions [19]. The maximum absorption occurs at a wavelength of 253.7 nm [19], which can be observed in the scanning of the spectrophotometer in **Figure 7**. For these experiments, the wavelength was taken at 400 nm because the sample presented a light yellow hue coloration, which may be due to the fact that the spectral properties of organic molecules depend on the type of valence electrons, on their quantum possibilities of absorption of UV-Vis radiation, and on the presence of chromophoric groups in their structures [20]; therefore, the sigma (σ) electrons make up the single saturated bonds or molecular bonding orbitals of the sigma type, while the pi (π) electrons make up the multiple unsaturated bonds or pi orbitals. These unsaturated

groups are called chromophoric groups [21]. The appearance of color in some organic substances is related to the presence of one or more chromophoric groups whose pi electrons are easily excited by the absorption of radiation from the near and visible ultraviolet region (200–800 nm), of corresponding energy (specific length) to the quantum possibilities for the electronic transition [21]. Therefore, it is not certain that in the case of the clavulanic acid-amoxicillin mixture, there is an adequate decomposition, but for the trimethoprim component, this degradation is observed.

The electrical conductivity is in correlation of the amount of ionizable molecules or radicals present in the water as shown in **Figures 8 and 9**; as time passes, conductivity increases, meaning that the drug molecules are being broken and more ionizable fragments are generated.

The COD graph that was obtained from the Trimethoprim TSWW samples showed a tendency to decrease according to the time elapsed. The initial COD at time 0 for the first experiment (trimethoprim 0.2%) had a concentration of

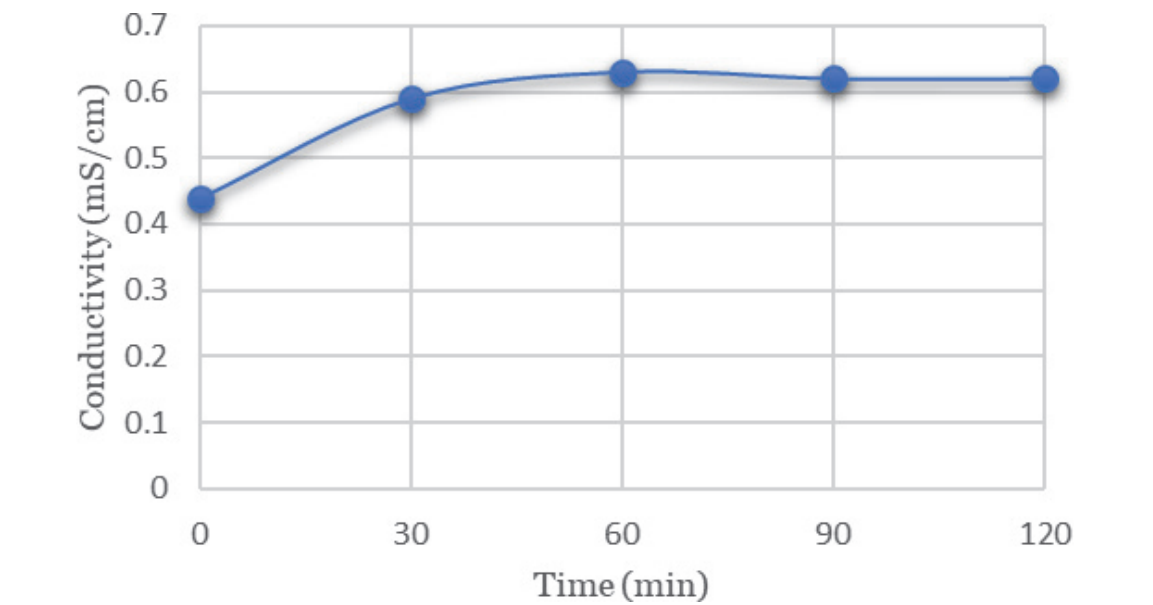


Figure 8.
Conductivity against time for experiments with trimethoprim.

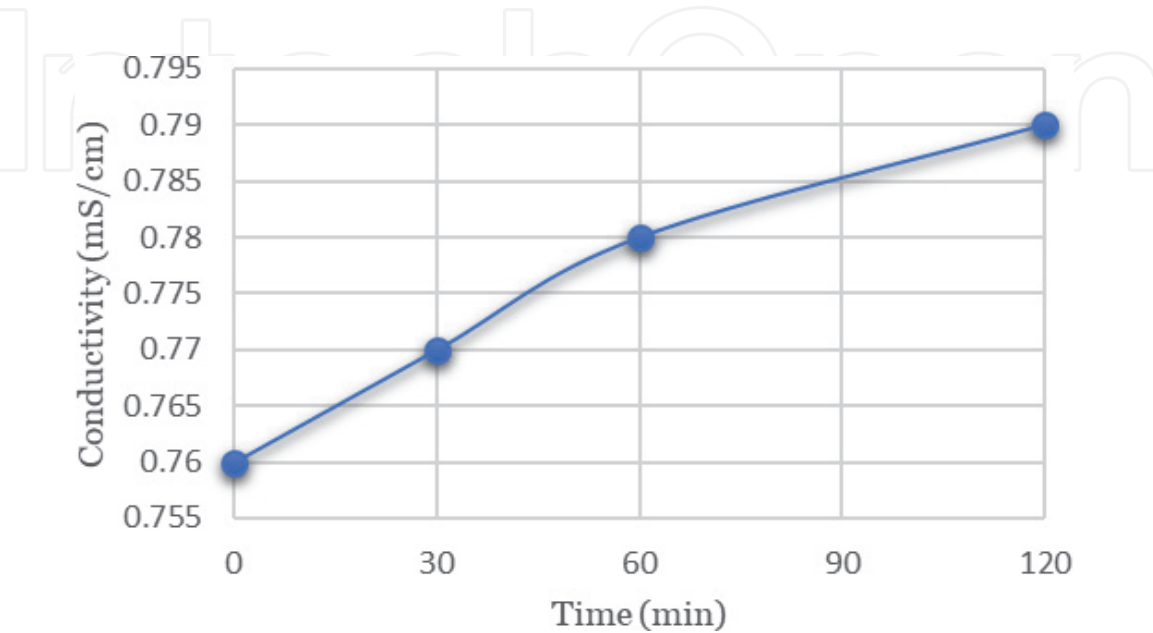


Figure 9.
Conductivity against time for experiments with the clavulanic acid-amoxicillin mixture.

199.1 mg/L and the second experiment (trimethoprim 0.1%) had the lowest drug concentration of 90.3 mg/L of COD; you can see that in 1 hour, the COD concentration of the first trimethoprim 0.2% experiment dropped to 142.8 mg/L, and in the second experiment, it dropped to a concentration of 88.5 mg/L. This shows that the degree of contamination of the water by organic compounds (TSWW) decreases, that is, the organic matter (drug) decreases, and therefore there is a break in the contaminant.

It is also observed that in the second experiment (trimethoprim 0.1%), there is a slightly lower concentration of drug and that when passing through the electrolysis treatment it presents a greater removal efficiency, since the COD decreases more as time passes, compared to the trimethoprim 0.2%, which has a slight increase and decay (**Figure 10**).

The results of total organic carbon can be seen in **Figure 11**. It is observed in the graph that there is a tendency to decrease the concentration of carbon as time goes by.

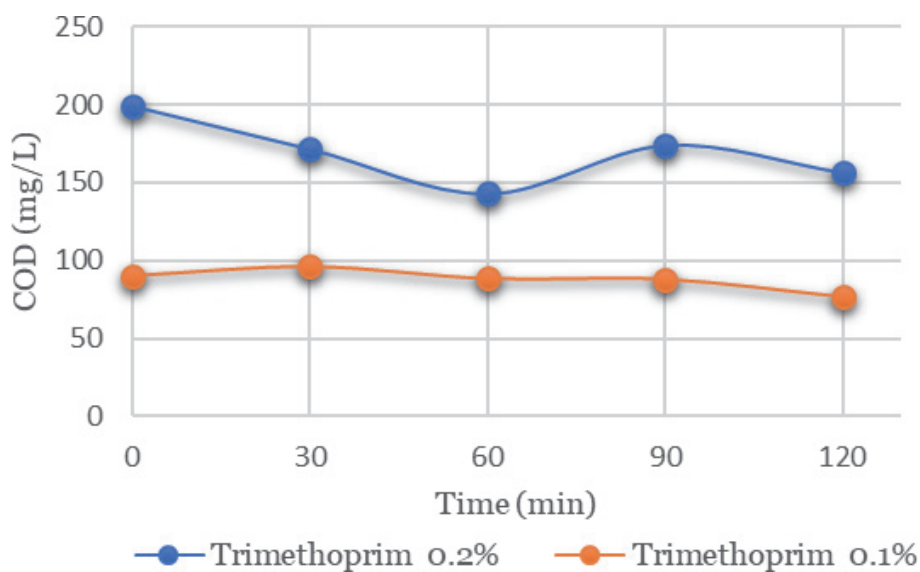


Figure 10.
Chemical oxygen demand with respect to time.

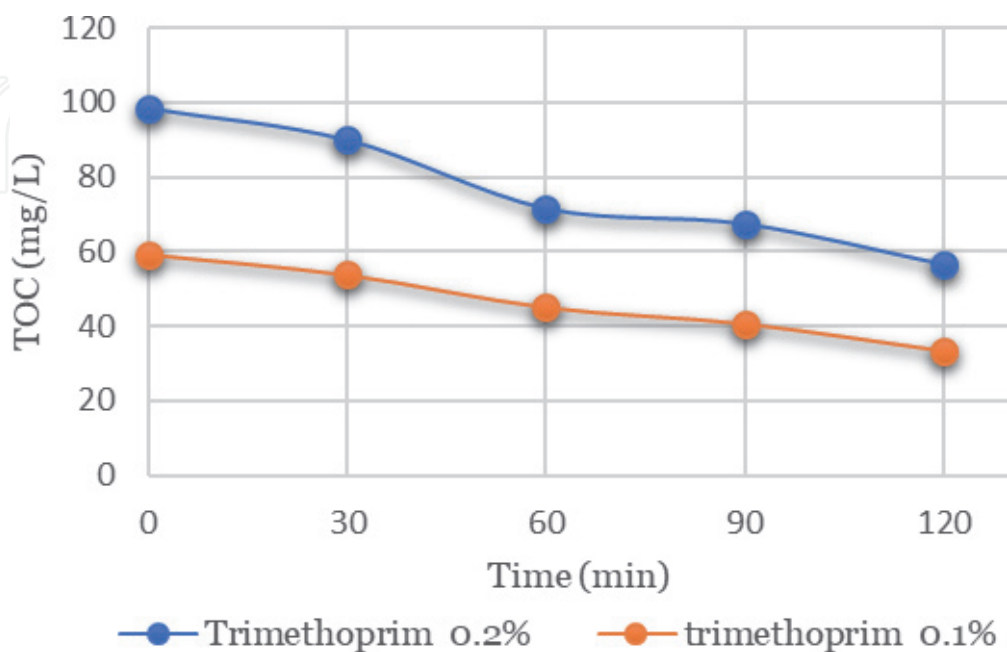


Figure 11.
Total organic carbon with respect to time.

TOC (mg/L)	
Trimethoprim 0.2%	Trimethoprim 0.1%
98.5	59.4
90	53.9
71.6	45.2
67.4	40.8
56.5	33.5

Table 1.
Total organic carbon results from experiments 1 and 2 with trimethoprim.

%Degradation according to TOC	
The first experiment (trimethoprim 0.2%)	The second experiment (trimethoprim 0.1%)
91.3706	90.7407

Table 2.
Maximum percentages of degradation obtained from TSWW samples with electrolysis treatment.

The initial TOC of the first experiment had a concentration of 98.5 mg/L and the second experiment had an initial concentration of 59.4 mg/L. In both cases, from the 30th minute on, it is observed that trimethoprim 0.2% decreases to a concentration of 56.5 mg/L and trimethoprim 0.1% to a concentration of 33.5 mg/L. The above proves that the electrolytic system is an alternative for trimethoprim decomposition.

Table 1 shows that during the electrolytic breakdown, carbon portions are mineralized but some fragments must have been ionized in different forms that affects the UV-Vis absorbance.

Finally, **Table 2** shows the maximum percentage of degradation that was obtained from the synthetic wastewater when it was treated with the electrolytic cell, for the first and second experiments with trimethoprim.

In the case of the clavulanic acid-amoxicillin TSWW mixture, the COD had an oscillating behavior because at 1 minute it began to decrease and at 60 minutes it abruptly increased and then it decreased again. The initial COD at time 0 for the clavulanic acid-amoxicillin TSWW sample (0.2%) has a concentration of

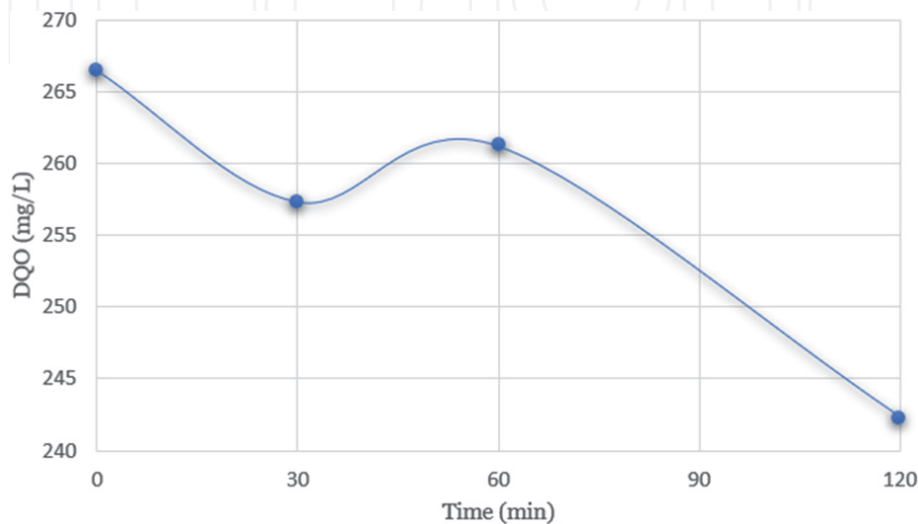


Figure 12.
Chemical oxygen demand against to time.

266.5 mg/L, after 30 minutes, there is a concentration of 257.3 mg/L, but it is observed that at 60 minutes, the COD concentration abruptly increased to 261.2 mg/L. This experiment ended his treatment with a concentration of 242.3 mg/L. According to the bibliography analyzed, the phenomenon obtained in **Figure 12** by the clavulanic acid-amoxicillin (TSWW) mixture could be due to the fact that when the sample is subjected to radiation, the molecule fragments and groups with free electron pairs are exposed and they absorb more radiation, generating increase in the values obtained. These formed fragments absorb a greater amount of energy after 60 minutes and as they continue to degrade and lose this capability.

The total organic carbon (TOC) results for clavulanic acid-amoxicillin TSWW can be seen in **Figure 13**; there is a tendency to decrease the carbon concentration as time passes. The initial TOC of the clavulanic acid-amoxicillin TSWW mixture had a concentration of 182.8 mg/L and drops to a concentration of 164.6 mg/L. The above indicates the decrease in the sample of organic compounds due to the breakdown of the organic molecules to molecules with simpler structures.

The results from the clavulanic acid-amoxicillin mixture experiments presented for the UV-Vis spectrophotometric studies give negative absorbance values, which is observed in **Figure 6**, probably due to the effects of the breakage of the molecule by chemical changes suffered in its structure, which generated ions or fragments with higher absorbances. This is because UV-Vis spectrophotometry excites the free electrons of oxygen, nitrogen, and sulfur that are present in both molecules, just as the molecule contains double bonds in its structure. In the pi bond, the electrons are excited and migrate to a higher energy level, modifying the structure. Therefore, the TOC was not used because negative values were being given in the absorbance.

The results of the clavulanic acid-amoxicillin mixture experiments presented for UV-Vis spectrophotometric studies in **Figure 6** give high absorbance values, probably due to the effects of the breakdown of the molecule due to the electrochemical changes suffered in its structure, whereby ions or fragments with higher absorbances are generated. The modification of its structure is due to the fact that UV-Vis spectrophotometry excites the oxygen, nitrogen, and sulfur free electrons that are present in both molecules, as well as the pi electrons of the conjugated double bonds in its structure. In the pi bond, the electrons are excited but they can be delocalized by resonance effects, modifying the energy absorbed by the structure.

During the reaction, the formation of free radicals like HO^\bullet could occur, which are species with high reactivity, which allows them to attack organic molecules. It is

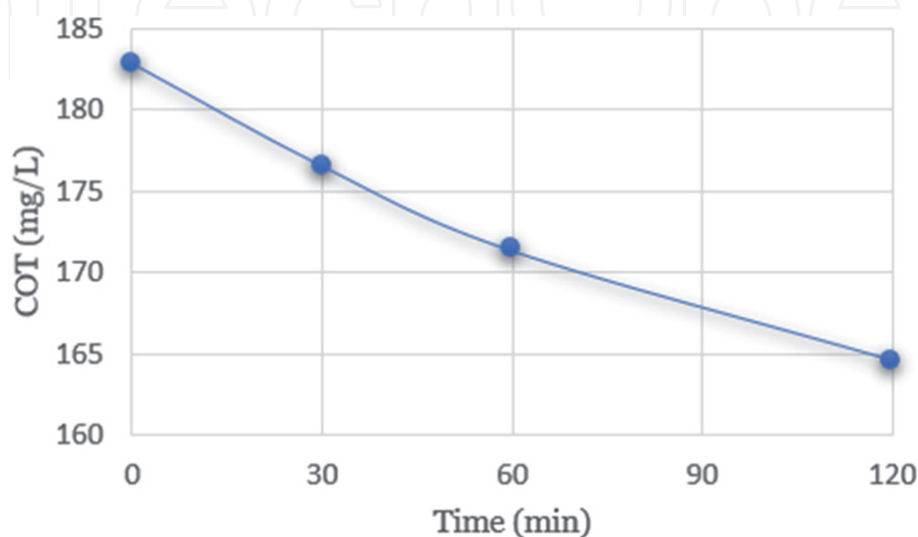


Figure 13.
Total organic carbon over time.

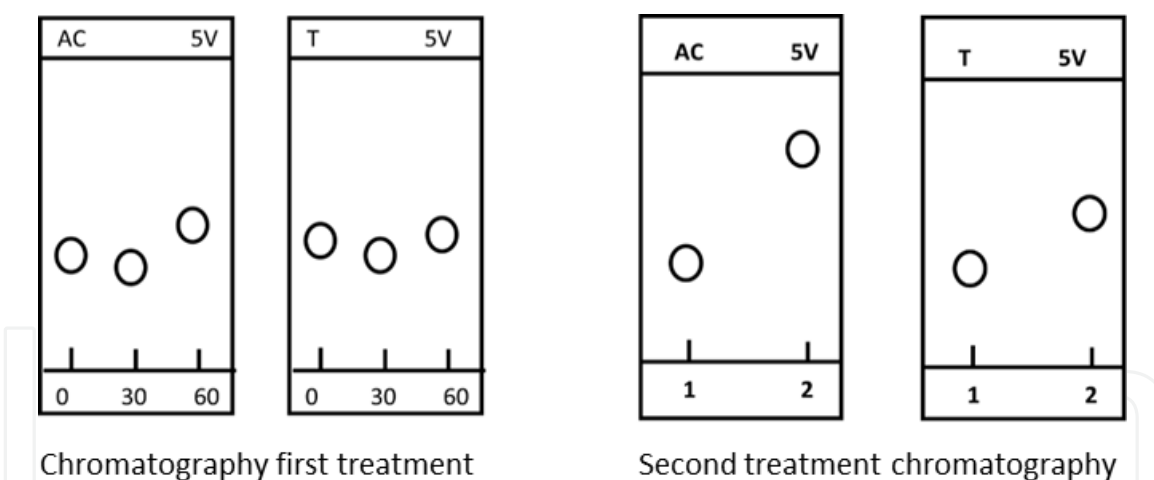


Figure 14.
 Results of the thin layer chromatography demonstrating the rupture or breakdown of trimethoprim as also in the clavulanic acid-amoxicillin mixture, in which a great modification is observed, being less polar the product obtained with the treatment.

worth mentioning that the photochemical process is not developing in the electrolytic cell, despite the fact that TiO_2 reacts with light.

For the thin layer chromatography (see **Figure 14**), it is observed that there is a change of displacement between the 0 time and 60 minutes of the experiment. That is, the RF pattern for both drugs is not observed in comparison with the standards of trimethoprim and clavulanic acid-amoxicillin mixture; this indicates that the molecules at 60 minutes do not present the same structure. This is an expected result because in an electrolytic cell when an electric potential is applied, it generates an electric current passage, which is a flow of electrons between the electrodes creating a circuit of ionic and electric charges transport, besides getting the help of the electrolyte that maintains a balance of charges, which improves the transport of the charges between electrodes, causing the oxidation of fragments of the molecule in the surface of the anode and a reaction of reduction of other fragments of the molecule in the cathode.

In addition, the electrode that is doped with titanium dioxide generates a greater oxidative effect, debt to its catalytic properties and the mineral carbon, has a porous structure and a large contact surface, and allows an adsorption process to take place between the organic compounds and the mineral carbon. Another advantage of using charcoal is that the problem of forming products that may be toxic does not arise, due to its high absorption capacity as mentioned before, although its efficiency may depend on the amount of material organic present in the solution.

The electrolyte cell demonstrated based on the results that it has the feasibility of breaking or/and debugging emerging endocrine disrupting contaminants like trimethoprim. The work developed by Sirés et al. in 2005 on the electrochemical degradation of water acetaminophen by catalytic action of Fe^{2+} , Cu^{2+} , and light showed that the acidic aqueous solutions of the drug acetaminophen were degraded by anodic oxidation in an undivided electrolytic cell with a Pt anode and an O_2 supply [22], proving that the electrolysis process is functional. However, the materials and reagents to be used in this project are cheaper, and for a process tested in a single drug, there is no certainty how it will work in others.

Hirose et al. applied electrolysis for degradation of epirubicin, bleomycin, and mitomycin C with Pt/Ir electrodes and a NaCl solution as electrolyte. The results obtained were a partial degradation of the antibiotics but their cytotoxic and mutagenic activity was absolutely eliminated [23].

This research establishes that an elimination or rupture of different drugs can be carried out with an electrolytic cell, based on the work performed by Giraldo

Aguirre et al. in 2016 on the electrochemical treatment of waters containing β -lactam antibiotics, where by means of electrolysis, the degradation of the drugs oxacillin (OXA), cloxacillin (CLX), and dicloxacillin (DCX) was achieved. Those drugs are also used as antibiotics [7] like trimethoprim and the clavulanic acid-amoxicillin mixture and can affect aquatic systems and health due to the fact that antibiotics are among the most consumed and released drugs to the environment [24]. This release is also due to the unwarranted prescription with antibiotics, its inadequate dispensing, and the laxity in the regulation on the sale of medicines that allows self-medication with antibiotics, which are some of the factors that have been related to this high consumption [24] because it is a chemically defined substance capable of modifying the biochemical and physiological activity in an organism and therefore can produce a biological, beneficial, or toxic effect depending on the dose delivered [25]. Another problem is based on worldwide studies that have evidenced the presence of pharmaceutical compounds in effluents from fully operational treatment plants and with their respective control parameters, apparently operating with a high wastewater purification efficiency [26]; so, it is now known that with conventional wastewater treatments, it is not possible to eliminate this type of compounds in an efficient level [26], having as a consequence the proliferation of bacteria resistant to antibiotics, which will cause major problems in aspects of public health. In the research of Giraldo Aguirre et al. [7], a Ti/IrO₂ electrode was used which led to the oxidation process being better, which is due to the characteristics already mentioned for titanium and oxygen; also, the electrolyte that used sodium chloride helped them in the inhibition of microbial activity. This is because during the electrolysis reaction, chlorine gas is released from the electrolyte, but in our case, potassium hydroxide was used with the intention that the system can be incorporated to a wastewater treatment plant, since this technology usually uses biological reactors; therefore, only the breakdown of the molecule was sought without affecting the bio-catalytic bacteria during the subsequent processes. However, Giraldo Aguirre et al. conclude that electrochemical oxidation induces structural changes in antibiotic molecules and their results also indicate that electrochemical treatment is an effective technique for reducing the antibiotic potential that these compounds present, reducing the environmental risk due to the proliferation of bacteria resistant to antibiotics [7]. The aforementioned was also demonstrated within our experimentation when observed the graph of total organic carbon for the two experiments with trimethoprim and the thin layer chromatography for results with the clavulanic acid-amoxicillin mixture. This helps us show that the systems that use electrolysis break these compounds down into compounds that are less harmful to organisms and the environment. This experiment ends up being an important contribution to science in drug treatment and for a later use of electrolytic cells at higher levels, in addition to being highly versatile and to some extent economical oxidation processes.

4. Conclusion

The electrolytic cell modifies the structures of both molecules through different mechanisms, but in functional aspects, the electrolytic cell achieves the efficient degradation of trimethoprim unlike the clavulanic acid-amoxicillin mixture. It is established that the electrolytic cell can degrade some molecules more easily than others; so, we can establish that those compounds with a structure similar to trimethoprim could be degraded efficiently. However, it is also shown that to achieve the degradation of other compounds, it is necessary that the conditions of the electrolytic cell are adjusted again.

Addressing the problem of emerging pollutants that are endocrine disruptors is something really important and urgent, due to the impact they have not only on the environment but also on the health of living beings; so, it is important to transform them into less dangerous compounds for environment. Unfortunately, the methods of removing these contaminants are now expensive. That is why the implementation of the electrolytic cell is intended to create an economical option for the possible removal of these compounds, as it was shown to have a good degradation rate of trimethoprim. However, in the case of the clavulanic acid-amoxicillin mixture, it is necessary to modify its operating conditions.

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Conflict of interest

The authors declare no conflict of interest.

Abbreviations

nm	nanometer
ml	milliliter
µm	micrometric
L	liter
g	gram
min	minute
Abs	absorbance
ECED	emerging contaminants endocrine disruptors
TOC	total organic carbon
COD	chemical oxygen demand
Redox	reduction-oxidation reaction
V	volts
SWW	untreated synthetic waste water
STWW	synthetic wastewater with treatment
TLC	thin-layer chromatography
mS	millisiemens

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Author details

Jorge Alberto Mendoza Pérez^{1*}, Abril Gardenia Martínez Castillo¹,
Jorge Octaviano Gomez Castrejon² and Juan Carlos Gómez Buendía³

¹ Department of Environmental Systems Engineering, Escuela Nacional De Ciencias Biológicas From Instituto Politécnico Nacional, Mexico City, Mexico

² Escuela Nacional De Ciencias Biológicas From Instituto Politécnico Nacional, Mexico City, Mexico

³ Department of Organic Chemistry, Escuela Nacional De Ciencias Biológicas From Instituto Politécnico Nacional, Mexico City, Mexico

*Address all correspondence to: jorgemendozaperez@yahoo.com

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