

Wastewater Containing 1,2-Dihydro-2,2,4-Trimethylquinoleyn Treated by Electrolysis and Respirometric Method

Thelma Helena Inazaki¹, Peterson Bueno de Moraes², Gisela Regis¹, Paulo Renato Matos Lopes¹, Renato Nallin Montagnolli¹, Antonio Carlos Simões Piao³ and Ederio Dino Bidoia^{1*}

¹Department of Biochemistry and Microbiology, IB, UNESP – Univ Estadual Paulista, Rio Claro, Brazil

²Department of Technology in Environmental Management – DTSA, FT/UNICAMP, Limeira, Brazil

³DEMAC, IGCE, UNESP – Univ Estadual Paulista, Rio Claro, Brazil

Abstract

The electrolytic treatment of a real industrial effluent and simulated wastewater containing the 1,2-dihydro-2,2,4-trimethylquinoleyn compound (Naugard Q[®]) had been investigated in order to improve the wastewater biodegradability. The electrolysis was carried out in a batch electrolytic cell using 70TiO₂/30RuO₂ electrodes (DSA[®] anode). After electrochemical treatment, wastewaters were evaluated in terms of Naugard Q[®] concentration, UV-visible spectrophotometry and biodegradation. Further analyses were conducted in simulated wastewater by gas chromatography and the biodegradation process was monitored using respirometric flasks. Both real effluent and simulated wastewater presented a decrease in Naugard Q[®] concentration. The simulated wastewater electrolytic treatment provided concentration reduction of Naugard Q[®] about 52.04% after 60 min, whereas real effluent concentration was reduced by 62.60% after 40 minutes. Furthermore, UV-visible spectra and gas chromatograms presented significant alterations in molecular structure of the compound. After 30 min electrolysis, an increase in simulated wastewater biodegradation was observed. In real effluent, the biodegradation response was faster, as more CO₂ was produced in assays that underwent 10 and 25 minutes of electrolytic treatment. This result is probably related to modifications in Naugard Q[®] molecular structure. It was concluded that the electrolytic treatment followed by bioremediation could be an alternate treatment to degrade this compound.

Keywords: Naugard Q[®]; industrial effluent; DSA electrodes; biodegradation; water treatment

Introduction

The Naugard Q[®] compound (1,2-dihydro-2,2,4-trimethylquinoleyn) is an aromatic amine which can be found in toxic effluents from rubber antioxidant and antiozonant chemical industry located in Rio Claro (Sao Paulo, Brazil). This compound was chosen mainly because it is one of the most important persistent compounds present in effluents from Brazilian chemical industries [1]. Moreover, many aromatic amines have been reported to be powerful carcinogens and mutagens [2-3], causing treatment of industrial wastewaters containing these chemicals to become a very important way to minimize environmental threatening.

Biological treatments are considered the most efficient and low cost methods in environmental impact reducing of several industrial effluents containing organic pollutants [4]. However, wastewater containing aromatic compounds is both recalcitrant and toxic towards microorganisms during conventional biological treatment. In this context, electrochemical treatment can be a powerful tool in environmental complex matrixes degradation [5-8].

In electrolytic processes, organic and toxic pollutants are usually destroyed by direct anodic process or by indirect anodic oxidation via oxidants generation such as hydroxyl radical, ozone, etc [9]. The electrochemical technology has attracted a huge deal of attention due to its versatility, amenability to automation and environmental compatibility. In fact, the main reagent is the electron, which is considered a “clean reagent” [10]. Besides, biodegradability of wastewaters can usually be improved after electrolytic treatment. Presently it is recognized that the simple modification of the molecular structure of a compound can reduce dramatically its toxicity and increase its biodegradability [11]. Generally, a persistent molecule has aromatic rings and its oxidation results in more biodegradable or biocompatible molecules.

The purpose of this study was to test 70%TiO₂/30%RuO₂ electrodes in two electrochemical treatments in a batch electrolytic cell: (a) real effluent of a rubber antioxidant and antiozonant chemical industry and (b) simulated wastewater containing the Naugard Q[®] compound. After electrolysis, wastewater characteristics were monitored such as concentration, biodegradation and analysis of UV-visible spectrophotometry and gas chromatography.

Material and Methods

Real effluent

It was used a real effluent from a rubber antioxidant and antiozonant chemical industry located in Rio Claro (Sao Paulo, Brazil). This sample was collected at the industry directly before the biological treatment owing to obtain the raw effluent.

Thereafter, the solution was filtered and stored in amber glass flask at 4°C in order to avoid photodegradation. The Naugard Q[®] concentration obtained in the real effluent was 14.93 mg L⁻¹ measured by quantitative analysis using UV-visible absorbance.

According to real effluent, concentrations of organic compound

***Corresponding author:** Ederio Dino Bidoia, Department of Biochemistry and Microbiology, IB, UNESP – Univ Estadual Paulista, Avenida 24 A, 1515 – Bela Vista; CEP: 13506-900; Rio Claro-SP, Brazil, Tel: (55) 19-35264191; Fax: (55) 19-35264176; E-mail: ederio@rc.unesp.br

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present in it was used to prepare a simulated wastewater focusing in 1,2-dihydro-2,2,4-trimethylquinoleyn, which is an aromatic amine with trade name Naugard Q®.

Moreover, a very good model to predict the real effluent treatment is simulation a wastewater with related concentration of the compound analyzed. Therefore, it was done a comparison between real effluent and simulated wastewater containing Naugard Q®.

Simulated wastewater

The simulated wastewater was prepared at laboratory using Naugard Q® solution. This compound is sold for to act as polymerization precursor and in the experimental runs was used without any further purification. Furthermore, Naugard Q® has tablet form and for this reason it was ground using a porcelain mortar and pestle.

Hence, 1.00 g of compound after ground it was dissolved in 5.0 mL of ethyl alcohol (Merck P.A.) and the volume was completed to 1,000 mL with deionized water (Millipore® Milli-Q system). As a supporting electrolyte it was used sodium sulphate 0.15 M (Merck PA).

At the same way of the real effluent, the solution was filtered and stored in low temperature and without light incidence. Naugard Q® concentration in the simulated wastewater was 134.06 mg L⁻¹.

Apparatus

The batch experiments were conducted in a 250 mL reactor, i.e., an electrolytic cell as described in previous work by Inazaki et al. [11]. A DC power supply (Dawer, FCC-3005D) with current-voltage controls and displays was employed to provide the electric power and a magnetic stirrer was used during electrolysis experiments. The DSA electrodes (area = 60.16 cm²) were prepared as according to an expired patent [12], and then have been placed vertically apart 3 mm in the electrolytic cell. The system was operated at constant current density (j) of 25.0 mA cm⁻² with electrolysis duration of 5, 15, 30, 45 and 60 min.

Analyses: Spectrophotometer Shimadzu® model 2401 PC was used to provide rapid indication of alteration and degradation of the Naugard Q® compound. Gas chromatography was performed by using a model HPI 5890 series 2, stationary phase 100% dymethylpolythilozane, volume sample of 0.5 to 1.0 µL, column length of 30 m, column internal diameter of 0.53 mm, film thickness of 0.88 µm, injector temperature of 250°C, detector temperature of 350°C, not polar column, detector flame ionization and a flow of Helium gas.

Biodegradation experiment

Soil source: The soil samples for the laboratory experiments were collected from a site located in the city of Rio Claro (Sao Paulo, Brazil) and thereafter the soil was dried at room temperature, sifted in sieve of mesh 0.2 mm and stored in polyethylene flask. The soil was classified as sandy, sandy fine sub-class by Instituto Campineiro de Análise de Solo e Adubo de Campinas, Brazil. The soil had 30% thick sand, 55.5% fine sand, 12.3% silt and 2.2% clay, and pH 5.0 in water.

Since the microbial respiration rate is correlated with the level moisture content of the soil [13-15], in this work the soil moisture was kept at 60% of the soil's moisture-holding capacity.

Bacterial source: The degrading microorganisms used in respirometric test were collected from the soil of the chemical industry and from the wastewater treatment plant. In laboratory, that

material containing the microorganisms has been exposed to Naugard Q® compound to obtain a better adaptation. The microorganisms were acclimated to grow on a test medium by using the Naugard Q® compound as unique carbon source. The test medium was described by Aaronson [16] and the following alterations were made: 1.00 g of K₂HPO₄; 0.20 g of MgSO₄.7H₂O; 0.10 g of NaCl; 0.10 g of CaCl₂; 0.02 g of FeCl₂; 1.00 g of (NH₄)₂SO₄; 1000 mL of H₂O; 0.60 g of Naugard Q® compound; pH of 7.2 to 7.5.

Afterward, nutrient agar plate-counting technique was used for obtaining the degrading microorganisms by using Plate Count Agar medium (PCA, Difco® Laboratories). The microorganisms obtained were resuspended in liquid PCA medium, and it was standardized with absorbance about 0.40 a.u. at λ = 540 nm, consisting in the inoculum for the biological treatment.

Biodegradation conditions: During the respirometric test, carbon dioxide evolution rates were monitored by using respirometric flasks according to Bartha and Pramer's respirometry [17]. Carbon dioxide which was evolved during the microbial respiration process was trapped in 10.0 mL of aqueous solution of KOH 0.20 M located in the side arm attached to the Bartha respirometric flask. After 1.0 mL of BaCl₂ 0.05 M was added to KOH solution in order to precipitate the carbonate ions, the amount of carbon dioxide was then measured by titration of the residual KOH with a standard solution of HCl 0.10 M. The calculations of CO₂ evolution, biodegraded carbon and biodegradation effectiveness were accomplished in agreement with Technical Standard L6.350 [18].

For the simulated wastewater, each Bartha respirometric flask contained 50.0 g of soil, 1.50 mL of inoculum with microorganisms previously acclimated to Naugard Q® compound and 5.00 mL of simulated wastewater containing Naugard Q®, which was treated during 5, 30 and 60 min by electrolysis. Two blank controls were maintained: only soil (S) and inoculum added to the soil (IS).

Biodegradation was also evaluated for the real effluent. Four systems were done according to different times of electrolytic treatment: 0 minutes (control), 10 minutes, 25 minutes and 50 minutes. Each respirometric flask was composed by 100 mL of the effluent and 1.00 mL of microorganisms' inoculum. The respirometry assays were done in duplicates for all samples and incubated at 28° C.

Results and Discussion

Electrolytic treatment

Simulated wastewater: Analysis of the simulated wastewater after the electrolytic treatment showed that pH values gradually decreased from 5.7 to 3.8 along electrolysis time increase, probably due to solvent breakdown and alterations on Naugard Q® compound molecular structure, resulting in H⁺ production. Conductivity has increased slightly from 17.4 to 19.3 mS cm⁻¹ with the increasing of electrolysis time, evidencing that there was small increment in total ionic concentration during the treatment.

Electrolysis time (min)	Absorbance at 230 nm	Naugard Q® concentration (mg L ⁻¹)
0	2.2994	134.06
5	1.9801	115.53
15	1.7125	100.00
30	1.4793	86.46
45	1.2537	73.37
60	1.1028	64.61

Table 1: Naugard Q® concentration according to UV-Vis absorbance for simulated wastewater (Abs = -0,01048 + 0,01723 . [Naugard Q®]; R² = 0,99334).



Detection at the maximum wavelength was used to follow the dependence of the concentration reduction on time. Table 1 shows concentration reduction from 134.06 mg L⁻¹ to 64.61 mg L⁻¹, i.e., concentration reduction by 52.04% in 60 min of electrolysis (Table 1).

UV-visible spectra of simulated wastewater had been acquired in each electrolysis time to establish their maximum absorbance wavelength (Figure 1). After electrolytic treatment, the peaks on the spectra were shifted to higher wavelengths and there was reduction in the absorption intensity. The untreated wastewater presented maximum absorbance at 229.5 nm. After 60 min of electrolysis the peak was shifted to 234.5 nm.

Therefore, it is possible to conclude that with the increasing of electrolysis time the substances present on the Naugard Q[®] tablet showed a greater chemical transformation. According to Régis and Bidoia [1], the electrolytic process allows modification in aromatic chemicals most probably by opening the aromatic ring.

In (Figure 2) is shown a chromatogram of the untreated wastewater containing the Naugard Q[®] compound. Here, there are five peaks with following retention times: 9.108, 10.051, 10.310, 10.897 and 18.835 min. The peak with larger area (71%), whose

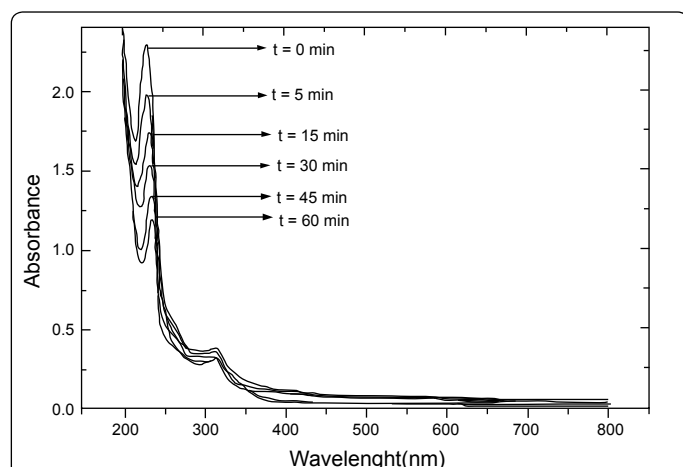


Figure 1: UV-visible spectra of simulated wastewater during electrolysis. J = 25.0 mA cm⁻², 25°C.

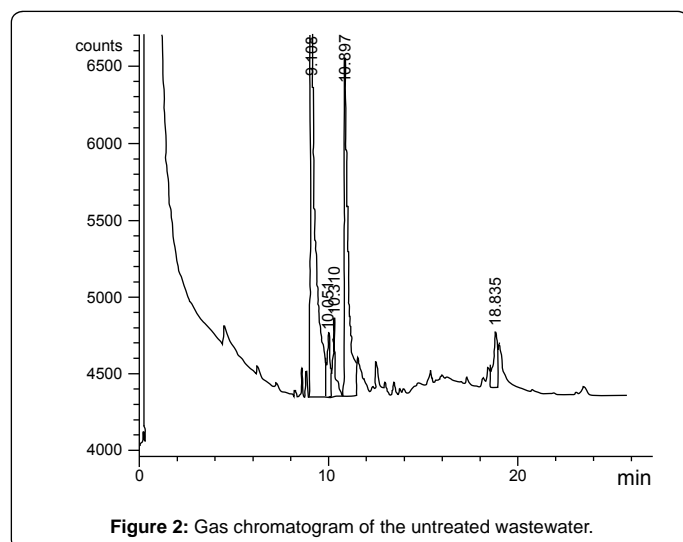


Figure 2: Gas chromatogram of the untreated wastewater.

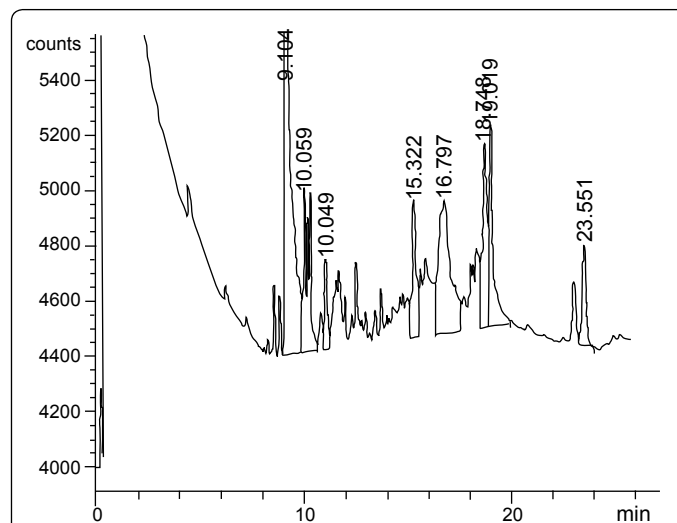


Figure 3: Gas chromatogram of the simulated wastewater in 30 min of electrolysis (J = 25.0 mA cm⁻², 25°C).

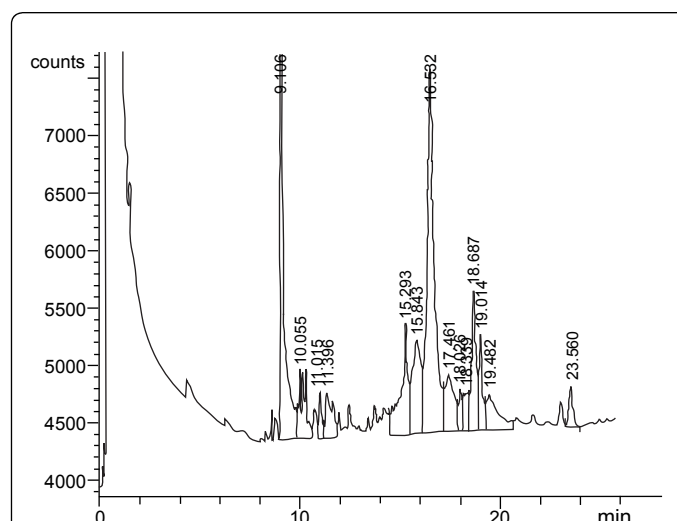


Figure 4: Gas chromatogram of the simulated wastewater in 60 min of electrolysis (J = 25.0 mA cm⁻², 25°C).

retention time is 9.108 min, probably corresponds to the Naugard Q[®] compound. The other peaks in gas chromatogram correspond to impurities present in compound tablet, since the same was used without any further purification. (Figure 3) demonstrates a gas chromatogram obtained from the wastewater treated during 30 min of electrolysis. The number of peaks is higher than gas chromatogram of untreated wastewater. Probably after 30 min of electrolysis, the initial compounds presented in Naugard Q[®] tablet originated new byproducts, which were more biodegradable or biocompatible for microbial consortium in respirometric test.

A gas chromatogram obtained from the wastewater treated during 60 min by electrolytic treatment was presented in (Figure 4). There are several peaks with different retention times from that ones present in the gas chromatogram of untreated wastewater and wastewater treated during 30 min of electrolysis. That result suggests that 60 min of electrooxidation induced new molecules formation in solution. Still, those new molecules were less biodegradable than initial compounds present in untreated wastewater, since the new

molecules showed low biodegradation effectiveness by microbial consortium during respirometric test.

Real effluent: Real effluent pH changed from 5.62 to 6.41 after 50 minutes electrolytic treatment. It was observed that pH values gradually decreased along electrolysis time increase, due to solvent breakdown and alterations on Naugard Q[®] compound molecular structure, resulting in H⁺ production. Also, real effluent conductivity reached higher values after prolonged electrolytic treatment time. Conductivity in real effluent has increased slightly by 6.07 mS cm⁻¹ after 30 minutes with the increasing of electrolysis time, evidencing that there was small increment in total ionic concentration during the treatment.

During both real effluent and simulated wastewater electrolytic treatment analysis, a slight temperature increase by 3.6°C was observed. This occurred due to fluid electrical resistance during electrolysis, however such heating did not cause changes in effluent chemical properties nor affected microorganisms viability.

UV-visible absorbance was determined after 10, 20, 30 and 40 minutes of real effluent electrolytic treatment using different electrodes. After 20 minutes, it was noticeable a decrease in various substances concentration originally present in real effluent, including Naugard Q[®]. As seen in (Figure 5), an analysis onto peak heights in spectra from different time periods treatments confirmed such fact, and also demonstrated changes in Naugard Q[®] maximum absorbance wavelength.

According to (Figure 5), the absorbance values at 230 nm were determined as Naugard Q[®] concentration for different times of electrolytic treatment for real effluent (Table 2).

Biodegradation

Simulated wastewater: A microbial consortium had been

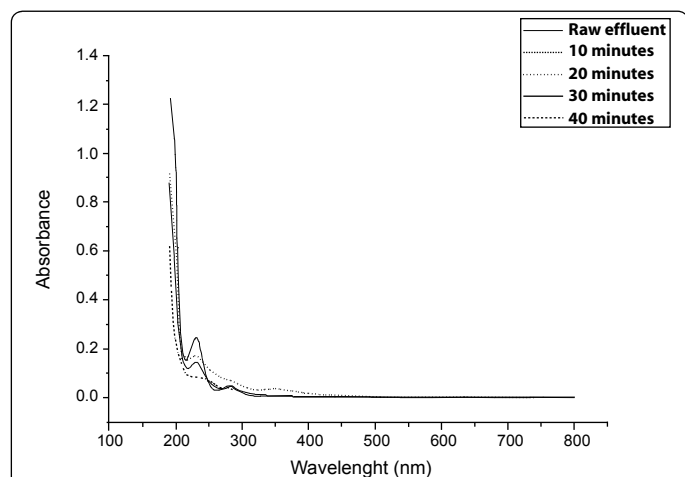


Figure 5: UV-visible spectra of real effluent during electrolysis. J = 25.0 mA cm⁻², 25°C.

Electrolysis time (min)	Absorbance at 230 nm	Naugard Q [®] concentration (mg L ⁻¹)
0	0.2468	14.93
10	0.1741	10.71
20	0.1714	10.56
30	0.1459	9.08
40	0.0856	5.58

Table 2: Naugard Q[®] concentration according to UV-Vis absorbance for real effluent (Abs = -0,01048 + 0,01723. [Naugard Q[®]]; R² = 0,99334).

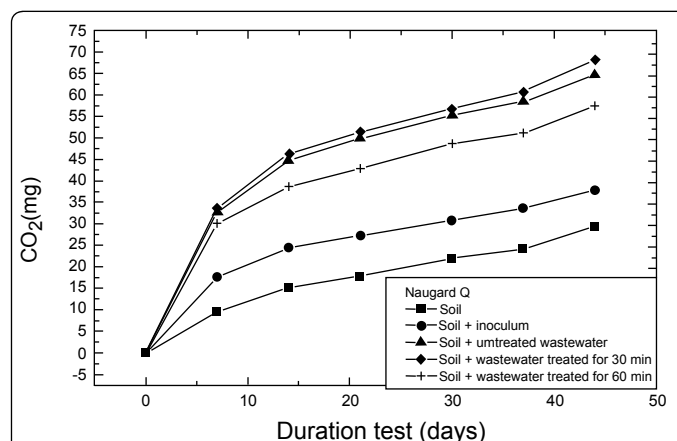


Figure 6: Accumulated CO₂ from biodegradation of the simulated wastewater using Bartha and Pramer's respirometric method.

used to degrade the Naugard Q[®] compound present in untreated wastewater and the one treated by the electrochemical process. The biodegradation experiments in soil were performed by using Bartha and Pramer's respirometric method [17-18]. In (Figure 6) is shown the accumulated evolution of CO₂ results from biodegradation of simulated wastewater containing Naugard Q[®] compound.

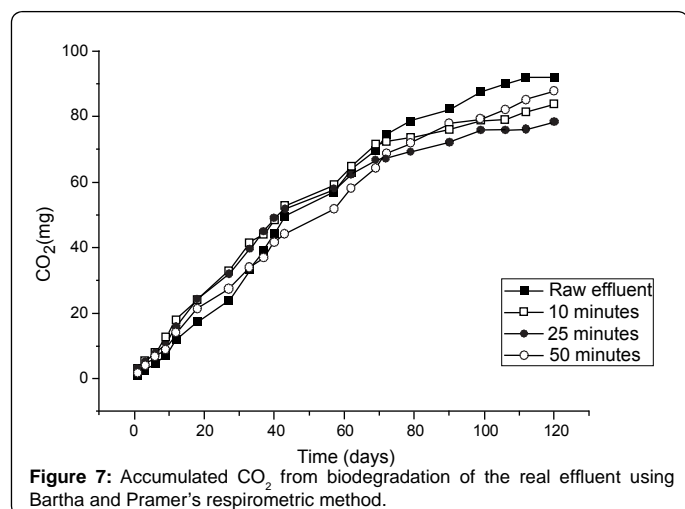
During first week of experiment the largest rates of CO₂ evolution were found: 1.37 mgCO₂ day⁻¹ (soil), 2.51 mgCO₂ day⁻¹ (soil and inoculum), 4.68 mgCO₂ day⁻¹ (soil, inoculum and untreated wastewater), 4.79 mgCO₂ day⁻¹ (soil, inoculum and wastewater treated for 30 min) and 4.30 mgCO₂ day⁻¹ (soil, inoculum and wastewater treated for 60 min). During the remaining days, the CO₂ evolution decreased and the following rates have been obtained: 0.55 mgCO₂ day⁻¹ (soil), 0.56 mgCO₂ day⁻¹ (soil and inoculum), 0.87 mgCO₂ day⁻¹ (soil, inoculum and untreated wastewater), 0.95 mgCO₂ day⁻¹ (soil, inoculum and wastewater treated for 30 min) and 0.74 mgCO₂ day⁻¹ (soil, inoculum and wastewater treated for 60 min).

All samples of simulated wastewater disposed in soil containing the inoculum showed CO₂ evolution by microbial consortium. In opposition, Bartha respirometric flasks containing the simulated wastewater treated during 30 min of electrolysis showed more CO₂ evolution than other treated samples. After 30 min of electrochemical treatment the simulated wastewater became more biocompatible to microorganisms due to the alteration of the initial compounds present in Naugard Q[®] tablet. Also, the formation of more biodegradable byproducts in the solution was observed as well.

The electrolysis time plays an important role in byproducts formation, seeing as in 30 min of electrolysis there were less oxidized products compared to 60 min. Thus, the wastewater treated by electrolysis above 30 min presented byproducts that were more difficult to degrade by microorganisms in respirometric test.

Furthermore, it was observed that there was not an initial lag phase by microbial consortium probably because microorganisms were previously acclimated to the Naugard Q[®] compound. All samples showed higher CO₂ evolution rates at 7th day of experiment followed by a decreasing of CO₂ evolution. It suggests that the microorganisms degraded more biodegradable substances and then the persistent compounds remained. These persistent compounds were slowly degraded towards the end of experiment.

Real effluent: Real effluent biodegradation processes can successfully be evaluated by CO₂ quantification, in either raw or



electrolyzed samples by respirometric methods (Figure 7). During the 20 first biodegradation days, electrolyzed effluents had a higher CO₂ production compared to raw effluent sample. A better biodegradation performance was observed in assays containing electrolyzed effluents. Amongst electrolyzed effluents, the most biodegraded were the ones that underwent 10 minutes (24.2mgCO₂) and 25 minutes (24.5mgCO₂) treatment. CO₂ production in raw effluent surpassed electrolyzed effluent after 25 days.

Biodegradation occurred on every assay, including control assays due to favorable conditions to microorganisms' growth. Thus, all electrolytic treatments showed CO₂ production. Also, the 10 minute treated sample accumulated more CO₂ after 70 days of biodegradation (71.5mgCO₂), meaning a faster biodegradation response. However, after the 70th day, control assays accumulated more CO₂ (83.9mgCO₂).

Regarding biodegradation within electrolyzed effluents, the 25 minutes sample presented a CO₂ accumulation much similar to the 10 minutes sample up to 62nd day, producing 59.2 and 57.8 respectively. Moreover, the 50 minutes has a less efficient biodegradation during the first 80 days, but exceeded the other ones after that, increasing from 71.9 mgCO₂ to 87.8mgCO₂.

A minor biodegradation occurred during the first 40 days in control assay when compared to electrolyzed effluents. Still, after 70 days, this was the assay which presented the highest CO₂ accumulation, reaching values of 92.1 mgCO₂ produced.

As for the electrolyzed effluents, the fastest CO₂ production was in 10 minutes treatment sample. Electrolytic treatments transform persistent substances into more biodegradable ones. This is favorable to microorganisms' metabolism, which makes them able to perform an increased assimilation and ease during biodegradation processes. This treatment leads to an accelerated biodegradation by lowering adaptation and latency periods. Hence electrolytic treatments are improvement to real effluents biodegradation.

Conclusions

Naugard Q[®] concentration decreased after electrolytic treatments in both simulated wastewater and real effluent. Electrolytic treatment of simulated wastewater containing 1,2-dihydro-2,2,4-trimethylquinoleyn (Naugard Q[®]) using DSA electrodes at 25.0 mA cm⁻² during 60 min reduced concentration of Naugard Q[®] by 52.04%, whereas after 40 minutes real effluent Naugard Q[®] concentration was more reduced, as a 62.6% reduction was observed. UV-

visible spectrophotometry and gas chromatography demonstrated significant alterations in the molecular structure of the compound Naugard Q[®]. After 30 min of electrolysis, byproducts have been produced and they were more biocompatible to microorganisms. However, the simulated wastewater treated for 60 min of electrolysis presented lower biodegradation effectiveness than other samples of treated wastewater. Probably, after 60 min of electrochemical treatment the initial compounds present in the Naugard Q tablet were transformed in new and more persistent substances. It is possible to conclude that 30 min of electrolysis is enough to improve simulated wastewater biodegradability. Furthermore, real effluents biodegradation response was equally faster in assays that underwent 10 and 25 minutes of electrolytic treatment, as they initially produced more CO₂. Therefore, the electrochemical treatment followed by bioremediation is an efficient treatment for an effluent from a rubber antioxidant and antiozonant chemical industry containing the Naugard Q[®] compound.

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