Electrolytic treatment in the effluent of a rubber antiozonant chemical industry

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ABSTRACT

The electrolytic process was applied in the effluent treatment of a rubber chemical antiozonant industry aiming to transform molecules of persistent wastes. In the characterization of effluent, was evidenced high content of organic material as amino aromatic, ketones, oils and greases that are toxic and extremely pollutant wastes. The influence of various factors was studied using steel and $TiRuO_2$. *The results showed molecular changes. The excellent conditions of electrolyze handling had been: 0,5 A; pH 9,0; agitation of 200 r.p.m. and process of time: 20 min. The conductivity had its higher value in the time of 30 min. In the time of 10 min of electrolyze a higher precipitation of the waste was verified, allowing for a more transparent and colorless effluent of UV-visible Spectra of electrolyzed raw effluent, with* $TiRuO_2$ *electrode had shown more intense changes than electrolyzed effluents with steel electrodes. Electrolysis produces changes in molecules of Flexzone 3P (n-fenil-n-isopropil-p-fenilenodiamina) and Flexzone 7P (n-fenil-n'-1,3-dimetil-butil-p-fenilenodia-mina). Finally, it was concluded that the electrolytic was viable to produce molecular changes in the effluent of a rubber chemical industry.*

Key Words: electrolytic process, biodegradation, wastes persistant electrodes.

INTRODUCTION

The increasing concern with environment preservation has made possible many progresses in the field of the environmental sciences.

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Technologies and procedures have been devised to attain a rational use of the hydric and energetic resources aiming the recycling of materials, reduction in water waste and in the costs of conventional treatments.

The characterization of industrial liquid effluents warns about the risks to public health, damage to the ecosystem, toxicity of substances as well as the effectivity of measures aiming to reduce pollution, which are necessary to the evaluation of the quality of the environment.

The electrolytic system has showed to be efficient as an alternative way for the treatment of different types of industrial effluents as well as for the treatment of drinking water, which is a proof of its versatility (Angelis *et al.*, 1998; Israilides *et al.*, 1997).

The importance of its use comes from the fact that it reduces the toxicity through the transformation of the recalcitrant substances (aromatic rings, etc.) into more easily biodegradable substances. In this way, the electrolytic treatment may enhance the efficiency of the biological conventional treatment (aerobiosis lagoon, anaerobiosis, etc) and even can be used as a substitute for these treatments.

The cost of treating water is directly proportional to the contaminants that it should remove. Most of the effluents contain organic compounds that will use the dissolved ions to form non-soluble particles.

The electrolytic treatment produces electroxidation of the organic materials both by the electrode and the oxy-reduction potential. In addition, there is no need to use chemical products for neutralization and it aids in the processes of decantation, coagulation and flocculation, as well as allowing the treated water to be reutilized in the process. This shows that this sort of treatment is compatible with the conservation of the environment (Aoki, *et al.*, 1993).

Besides optimizing the conventional process, leaving out some steps, it requires the use of a smaller area, which is most welcome to industries localized in urban areas. Reasons for that are the decrease in the period of detention of the effluents in front of the electrodes and the improvement in the aeration since it is not required a large system, that is, around 1/10 of the space used by a secondary treatment system (Smith, E. C., 1972).

Therefore, the knowledge of the reactions occurring in a given effluent will indicate the most adequate material to be used in the composition of the electrode, which is the main responsible for the cost of the operation once it is recognized that electricity costs are low.

This study aims to observe the molecular transformation due to the electrolytic process applied to effluents in a chemical industry. The analyzed samples included the raw effluent as well as isolated substances from the effluent by spectrophotometry by visible U-V.

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MATERIAL AND METHODS

The electrolyzed effluent pertains to the chemical industry working with antiazotants for rubber collected from the raw effluent, that is, before the conventional biological treatment. Electrolyses were performed in the same day of sample collection totaling 30.0 l of raw effluent.

In this effluent the following antiozonants substances were identified: aromatic amines with n-phenil-n-isopropil-p-phenilenodiamine (FLEXZONE 3P), n-phenil-n'-1,3-dimetilbutil-p-phenilenodiamine (FLEXZONE 7P). These substances were also separately electrolyzed to verify the electrolytic effect in relation to the molecular transformation in the spectrum of visible U-V.

Electrolytic process

The experimental system consisted of a source of continuous current (Dawer), model FCC-3005D connected to a group of steel electrodes (C + Fe). The steel electrode, used for volumes above 2.0 l was made of steel plaques with low level of heavy metals, connected in an intercalated way. For volumes above 40 ml it was used two plaques with a gap of 15 mm separated by a Nylon ® screw. During electrolysis the electrode was immersed in an electrolytic basin under constant stirring by stirring equipment with paddles (Marconi). After each period of electrolysis there was substitution of the effluent. The continuous current was of 2.0 A with a tension varying from 3.5 to 4.0 V. The electric tension was registered during the electrolysis directly in the power source.

Ruthenium oxide electrode

The Ti/TiRuO_2 electrode (Dimensionally Stable Anodes), used for volumes of 40 ml, was made of two plaques of titanium covered by a mixture of TiO_2 and RuO_2. Both plaques had a gap of 5.0 mm. Preparation of these plaques followed the patent De Nora (1970) – which is at present in public domain – and was based also in the work of De Battisti *et al.* (1997).

Simulated effluent

For the preparation of the simulated effluent it was used the substances with greater concentration in the industrial effluent, which was the product (aromatic amines) of the syntheses done by the industry of antiozonant for rubber. It was prepared two simulated effluents each with 1000 ml of sodium sulfate solution 0.10M, containing 14.2 g (P. A. - MERCK) of Na_2SO_4 and 5 ml of acetone (P. A. - BAKER) and one of the substances such as Flexzone 3P and Flexzone 7P.

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Analyses

In the spectrophotometer analysis of the raw effluent, as well as of the simulated solutions, steel and $TiRuO_2$ electrodes were used with constant stirring in a stationary system (batchwise type), that is, after each electrolysis period the effluent was changed. Aliquots of 40 ml were electrolyzed at each period of time. The continuous current applied was of 0.5 A and the electric tension varied from 7.0 to 8.0 V both for the steel and $TiRuO_2$ electrode. The effluents were electrolyzed in the following periods of time: zero, 10, 20, 30 and 40 minutes.

RESULTS

Visible U-V spectrum of the raw effluent

The determination of the absorbency in the region of the visible U-V was made with the electrolyzed raw and filtered effluents in the time periods of 10, 20, 30 e 40 minutes.

Steel electrode

It is possible to observe in FIGURE 1 that in the longer periods of electrolysis the substances suffer greater chemical transformation.

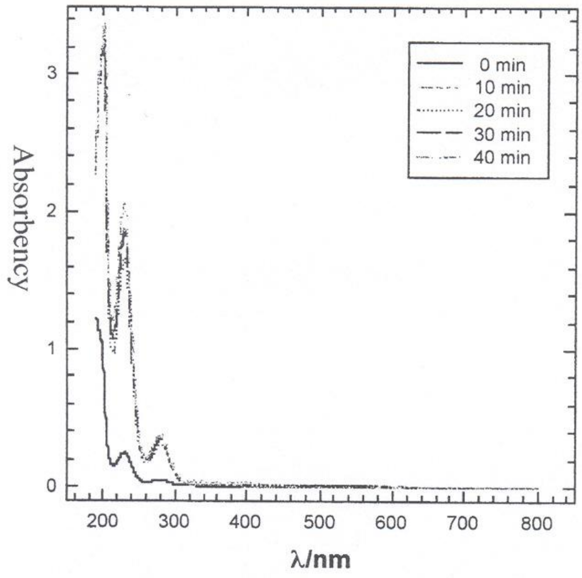

FIGURE 1 – Spectrum of visible UV for raw effluent after different periods of electrolysis. Steel electrode, I = 0.5 A e T= 26°C.

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$TiRuO_2$ electrode

Visible U-V spectrum of the electrolyzed rough effluent by $TiRuO_2$ shows more intense transformation. After 20 minutes of electrolysis, as can be seen in FIGURE 2, substances in the effluent are transformed since the peak in the spectrum are deeply modified in the intensity of absorbency and in the region of the wavelength.

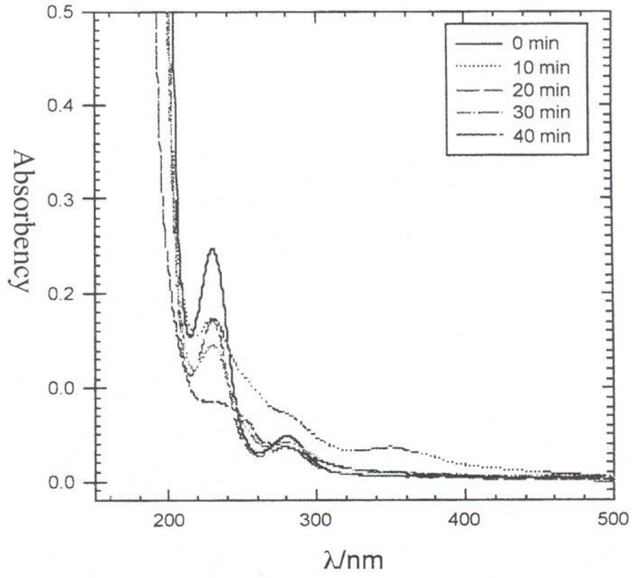

FIGURE 2 – Spectrum of visible UV for raw effluent after different periods of electrolysis. $TiRuO_2$ electrode, I = 0.5 A e T= 26°C.

Visible UV spectrum for Flexzone 3P

The aromatic cycles are usually more resistant to biodegradation by microorganisms (Comninellis & Nerini, 1995). By means of electroxidation the electrolytic process allows transformation in the molecule, most probably by opening the aromatic ring.

Steel electrode

FIGURE 3 shows the spectrum of visible UV for Flexzone 3P without electrolysis and for different periods of electrolysis with steel electrode.

The 290 nm peak is characteristic of Flexzone 3P molecule. After the electrolysis it is observed a peak of 470 nm possibly as a result of a subproduct. This can be a phenol type molecule, i.e., the Flexzone 3P molecule may be broken in the ring junction forming two molecules, one observed at 290 nm and the other at 470 nm.

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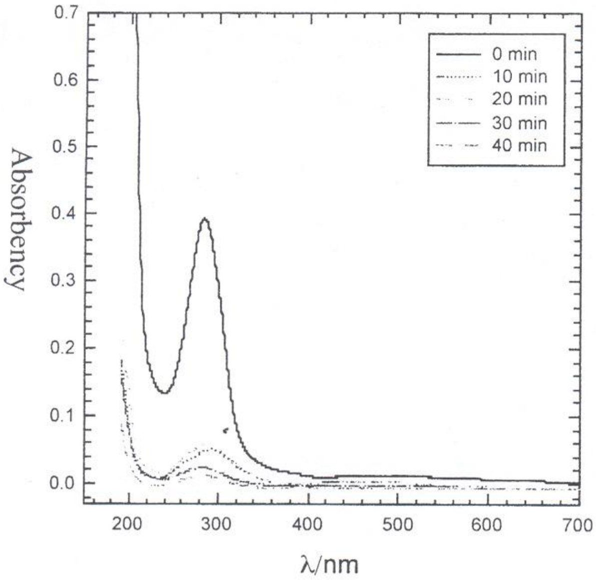

FIGURE 3 – Spectrum of visible UV for simulated effluent with Flexzone 3P (100 ppm of 3P + Na_2SO_4 0.1 M) in different periods of electrolysis. Steel electrode, I = 0.5 A and T= 26°C.

$TiRuO_2$ electrode

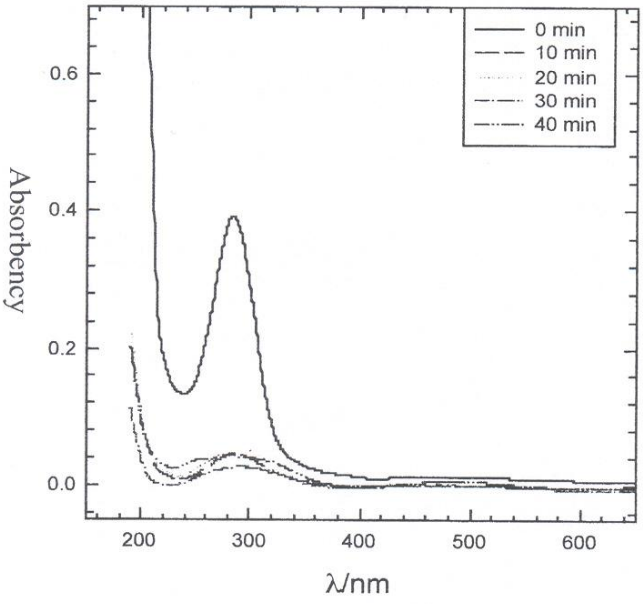

FIGURE 4 – Spectrum of visible UV for simulated effluent with Flexzone 3P (100 ppm of 3P + Na_2SO_4 0.1 M) in different periods of electrolysis. $TiRuO_2$ electrode, I = 0.5 A and T = 26°C.

Electrolysis induces a transformation in the Flexzone 3P molecule. After 10 minutes there is a peak close to 480 nm that indicates intramolecular modification or the formation of other substances. The opening of the aromatic ring is strongly suggested by the decrease in the absorbency intensity after the electrolysis. The benzene aromatic cycle such as phenol, absorb in the regions from 270 to 290 nm, as can be seen in the solutions of Flexzone 3P without electrolysis. After the electrolysis the intensity of absorbency and the peak region are modified.

Visible U-V spectrum for Flexzone 7P

- Steel electrode

It can be seen that for Flexzone 7P (FIGURE 5) there was a reduction in the peak in the spectrum after the electrolysis. This indicates the formation of several byproducts. In addition the aromatic rings that absorbs close to 300 nm were modified or opened since the intensity of absorbency has decreased producing a displacement of the wavelength for the absorbency peaks.

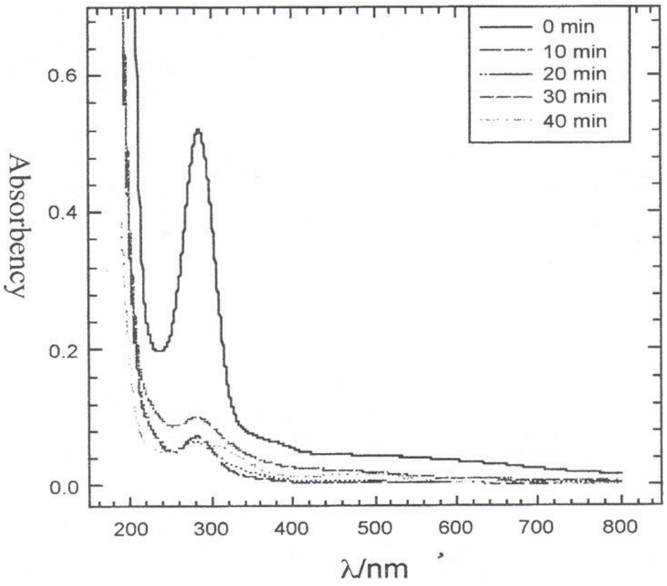

FIGURA 5 – Spectrum of visible UV for simulated effluent with Flexzone 7P (100 ppm + Na_2SO_4 0.1 M) in different periods of electrolysis. Steel electrode, I = 0.5 A and T= 26° C.

$TiRuO_2$ electrode

FIGURE 6 shows the spectrum of the visible U-V for Flexzone 7P without electrolysis and in various periods of electrolysis. Again for the

Flexzone 7P there was decrease in the intensity of absorbency and displacement of the peaks, which indicates transformation in the molecules after the electrolysis.

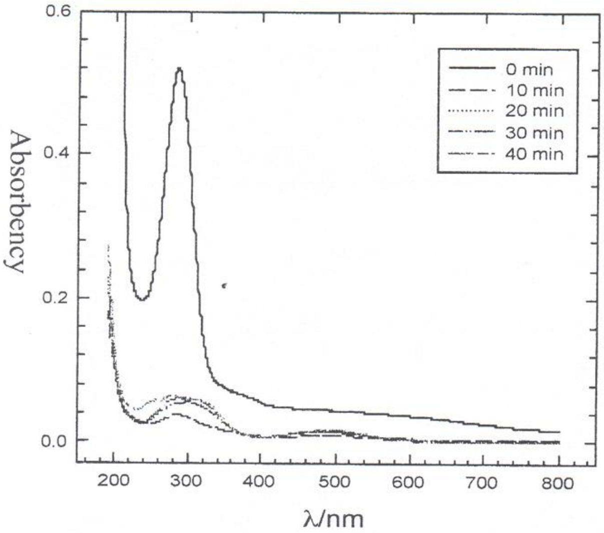

FIGURE 6 – Spectrum of visible UV for simulated effluent with Flexzone 7P (100 ppm + Na_2SO_4 0.1 M) in different periods of electrolysis. $TiRuO_2$ electrode, I = 0.5 A and T= 26°C.

DISCUSSION

Spectra of visible U-V of the rough effluent electrolyzed with $TiRuO_2$ electrode showed more intense transformation than that of the effluent electrolyzed with steel electrode. It is possible to conclude that with increasing time of electrolysis the existing substances undergo greater chemical transformation, showing a sensible decrease in the absorbency of the spectrum peaks and in the region of wavelength similar to the ones for the rough effluent not electrolyzed.

Electrolysis produces modification in the molecules of Flexzone 3P and Flexzone 7P. The strongest hint that opening of the aromatic ring and that molecular transformation has occurred is the diminution of the absorbency intensity and the displacement of the peak regions.

Both the steel and $TiRuO_2$ electrode induced modification in both studied molecules. However, the strongest transformation was seen while using the $TiRuO_2$ electrode.

As a general conclusion, the electrolytic process is an efficient method for modifying persistent molecules present in the residual waters of industries producing antiazotants for rubber and, therefore, these can become more biocompatible with the environment.

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