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Electrolytic Treatment Applied to the Industrial Effluent Containing Persistent Wastes Monitored by Bartha Respirometric Assays

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ABSTRACT

The effluent of a rubber chemical antioxidant and antiozonant producer industry, with high content of organic material was subjected to electrolytic process. To evaluate the speed of stabilization of the eletroctrolyzed effluents, and to evaluate the biodegradation the respirometric test of Bartha and *Pramer was used. The monitoring of the biodegradation of the effluent, after different periods of electrolysis show that the ideal time of electrolysis was 10 and 25 min. It was concluded that the eletrolytic process was viable to diminish the adaptation time of the microorganism to the effluent and consequently increased the biodegradation of effluent.*

Key word: Electrolytic process; biodegradation; wastes pollutant; electrodes

INTRODUCTION

A persistent residue being discarded may go through some different transformation processes, but many substances that promote toxic and bio-cumulative effects may remain in the environment for many years, without experiencing changes in their structures (Fewson, 1988). The synthetic compounds, in general, show greater resistance to the degradation of the compounds of natural origin and, the degree of persistence in the environment is related with physical, chemical and biological factors (Skladany and Metting Junior, 1993). Effluents generated by chemical manufacturing processes are frequently difficult to be degradated. Therefore, its characterization is important for the knowledge of the effectiveness of measurements to control and to reduce pollution, which are necessary to evaluate the quality of the environment. The electrolytic system has shown to be an efficient alternative way for the treatment of different types of industrial effluent; therefore, it reduces the toxicity through the resistant substance transformation (aromatical rings, etc) in biodegradable substances. This can be carried out through the electro-oxidation of the organic substance, either through the electrode or the potential of oxide-reduction. Therefore, it helps the processes of decantation, coagulation and flocculation, and if applied before the conventional biological treatment, it allows to increase the efficiency of the aerobiose and anaerobiose lagoons. Also it avoids the use of chemical products for neutralization, and the treated water may be reused in the process, showing to be a compatible treatment with the conservation of the environment (Angelis et al., 1998). The usual aromatical compounds degradation aerobic

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process is very well known. The biodegradation reactions may break the chains of organic compounds, mineralizing them and, many times, modifying its toxicity (Painter, 1995). Thus, the action of the microorganisms as effective agents for the destruction and recycling of the organic materials in the biosfera are sufficiently accepted. Microbe respiration is indicative of the biological activity, which is in an important tool to evaluate the potential of organic compounds biodegradation (CETESB, 1990). The biodegradability of chemical substances in aqueous medium, simulated in laboratory through respirometric tests in closed erlenmeyers showed that the degradation rate was dependent of the effluent type used, of the amount and quality of the nutrients applied bacterium and organic substances (Gotvajn and Koncan-Zagorc, 1999). This work aimed at evaluating the speed of stabilization of the effluent generated by a chemical industry, which produced antioxidants for rubber, submitted to an electrolytical process with steel electrodes. The Bartha and Pramer (1965) respirometric, in liquid medium was used to compare the biodegradation velocity of the electrolyzed and non-electrolyzed effluent under the action of bacteria.

MATERIAL AND METHODS

1. Effluent

The studied effluent was sampled from the inlet-settling lagoon (Fig. 1). Electrolysis was carried out the same day the samples were taken. This effluent had the following substances: aromatic amine as n-phenil-n-isopropyl-p-phenilenodiami ne, n-phenil-n'-1.3-butyldimetyl-p- phenilenodia-mine; antioxidants as 1,2-dihidro-2,2,4-trimetilquinoleína polimerizada, ketones, oils and greases.

2. Electrolytic Process

The experimental electrolytic system consisted of one electrolytic cell, one continuous current source (Dawer model Fcc-3005d), connected to a set up of steel electrodes (SAE 1020) and one paddle agitator (Marconi). The steel electrode, used in the electrolysis of the referred effluent, was formed by 6 steel plates (Usiminas Co. - Brazil), alternately conected, each one with a thickness of 3 mm.

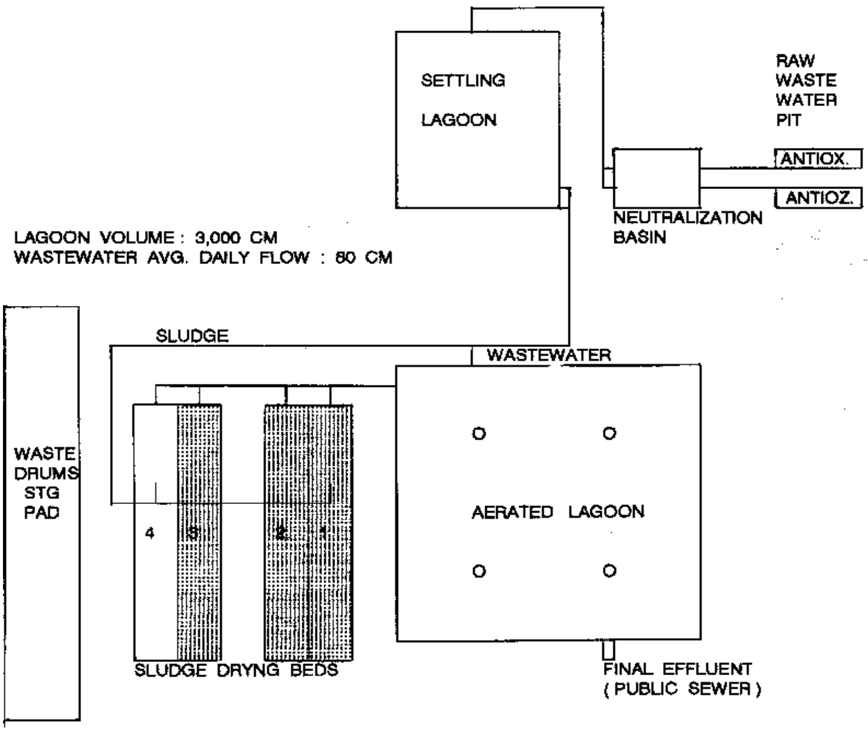

Figure 1 - Diagram of effluent treatment applied by the chemical industry.

Six plates with geometric area of 475 cm^2 and spaced by 0.1 mm were finally placed. The electrode was plunged in an electrolytic cell, with capacity of 2.0 L under agitation and at constant room temperature, and submitted to a 2.0 A direct current and 3.5 - 4.0 Volts (Fig. 2). After different electrolysis durations (0, 10, 25, and 50 min), effluent temperature and pH were measured.

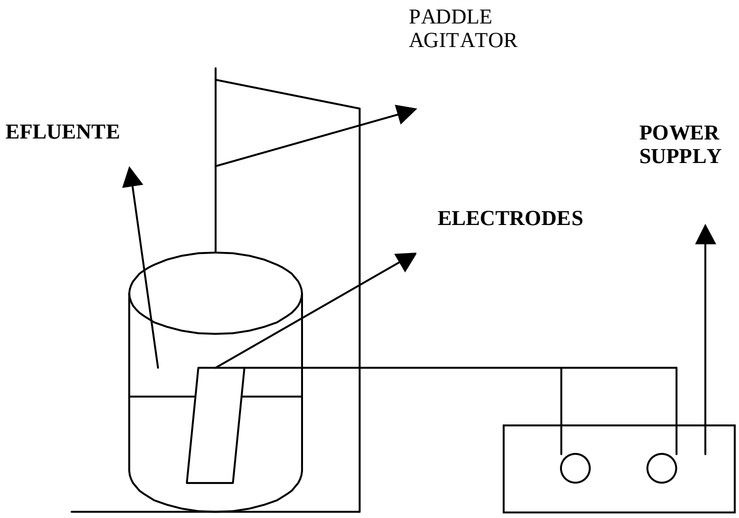

Figure 2 - Schematic design of the electrochemical cell

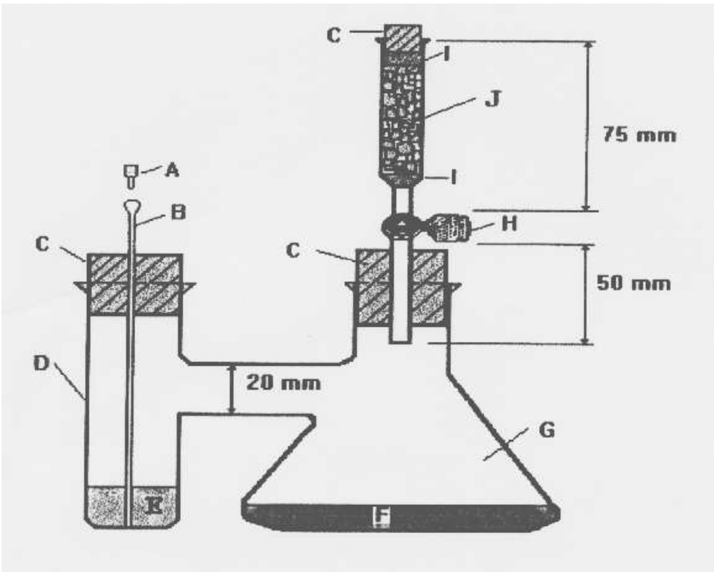

Figure 3 - Model of the system used for the Respirometer

A - Cover the cannula; B - Cannula; C - Tight closed rubber cork; D - Lateral arm; E - Solution the KOH; F - Sample the mixture to be degraded residue-ground; G - bottle cup of 300 mL; H - Valve; I - Layer has supported (glass woll); J - Filter of CO_2

3. Respirometric Test

The technical standard L6.350 issued by CETESB (1990) considers that the measurement of CO_2 produced in respirometrics can be done in continuous flow analysis systems or in closed systems. The respirometric method consists of determining the quantity of CO_2 generated by the process of organic substance degradation. It's considered that the generation of CO_2 and the biodegradation of the organic material are correlated (Siviero, 1999). This respirometric assay was carried in Bartha and Pramer flask (Fig. 3). It was added 100.0 mL of the electrolyzed effluent plus 1.0 mL of inoculums bacteria in each flask. The effluent was electrolyzed in three different times, 10, 25 and 50 min. and one flask contained non-electrolyzed effluent (control).

4. Preparation and Standardization of Inoculum

All samples were put together in one container and diluted with deionated water for 0, 25, 50, 75 and 100% v/v concentrations. 8.0 mL from each concentration were taken and added to 50.0 mL of the non-treated effluent plus 2.0 mL of the nutrient broth from Difco Laboratories (Fig. 4). All the flasks were kept on shaker (Phoenix AT56) at 280 rpm and 30 ºC for 72 hours. Then samples of 3.0 mL from each flask were taken to verify the growth of the culture. The concentration of 50% v/v showed a better growth rate and 1.0 mL of this culture was used in the respirometric test.

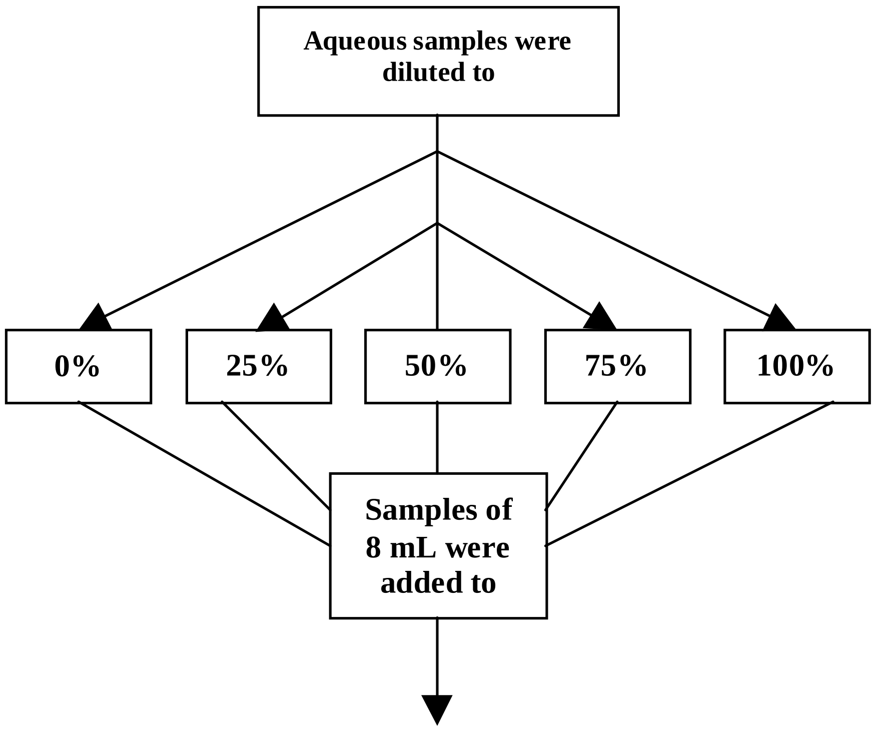

Figure 4 - Flow-diagram of preparation of inoculums

5. Respirometer Preparation

The preparation of the Bartha standard respirometer followed rules estabilished by Technical Standard L6. 350 issued by CETESB (1990).
Each respirometer had:

- 100.0 mL of the eletrolysed effluent;
- mL of bacteria Inoculum.

All samples were placed in closed respirometer and were incubated twice, including the control effluent (without electrolytic treatment) at 28 ± 1°C. The generation of CO_2 was determined in

Bartha flask. CO_2 generated in the process after the incubation period was calculated in accordance with Technical Standard L6.350 issued by CETESB (1990), by means of the consumed volume of HCl in the titration of KOH. The period between one to another titration was determined based on the obtained results.

RESULTS AND CONCLUSION

1. CO_2 Production

Fig. 5 shows the evolution of the biodegradation of the electrolyzed raw effluent in different periods of time and of the non-electrolyzed effluent through quantifying the CO_2 content. During first 20 days, electrolyzed effluent allowed a moderate production of CO_2, when compared to the non-electrolized effluent. The electrolysis durations that allowed for the moderate degradation rate of the organic material were 10 min and 25 min. The non-electrolyzed effluent produced more CO_2 than the electrolyzed effluent after 25 days (Fig. 5).

2. Accumulated CO_2

The accumulated production of CO_2 in flasks during 120 days for different periods of time of applied electrolysis in the raw industrial effluent at temperature of 28ºC ± 1ºC can be observed in Fig. 6. For three different durations of applied electrolysis, 10 min, 25 min and 50 min, and also in the control (without electrolysis), biodegradation occurred, meaning that testing conditions helped microbial activity. In this sense, for the three tested times and in the control sample, production of CO_2 occurred. Fig. 6 showed that the sample treated for 25 min presented CO_2 quantity similar to the sample treated for 10 min, which produced more CO_2 until the 69th day, i. e., the response to biodegradation was more intense under this electrolysis duration. After the 69th day, the control sample (without electrolysis) produced more CO_2 than the electrolyzed effluent.

The electrolyzed effluent that was treated for 50 min was less efficiently biodegraded by the inoculums when compared to all others, during the first 80 days; afterwards, this effluent passed the other two treatment times (10 and 25 min) with regards to the quantity of CO_2.

For the control sample, biodegradability showed to be lower during the first 40 days in the respirometric assays, when compared to the electrolyzed effluents. On the other hand, the control sample presented a higher accumulative rate of CO_2 after 70th day. The electrolyzed effluent for 10 min showed to be the one that produced CO_2 at a faster rate during the first 69 days. Probably, the electrolysis changed persistent substances into more biodegradable ones, helping microorganisms which do not require adaptation and latent times, causing the beginning of biodegradation to accelerate. Besides that the electrolysis allowed to reduce the toxicity of the effluent, in a way to reduce the retention time of the residue during conventional biological treatment. It could be concluded that the electrolytic treatment could be an efficient method to treat effluents, once it accelerates. biodegradation, reducing adaptation time of microorganisms in relation to the effluent that not received the electrolytic treatment in the first days of biodegradation (0 to 40 days).

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RESUMO

O efluente de uma indústria produtora de antioxidante e antiozonante para borracha, caracterizado por alta concentração de matéria orgânica e aminas aromáticas que são poluentes e tóxicos, foi tratado através do processo eletrolítico de forma a melhorar as condições para a biodegradabilidade de seus resíduos persistentes. A avaliação da velocidade de estabilização dos efluentes eletrolisados e não eletrolisado, em meio líquido, biodegradação, sob a ação de bactérias, foi utilizado o respirômetro de Bartha and Pramer. A aferição da biodegradabilidade dos efluentes, após os diferentes tempos de eletrólise, permitiu determinar o tempo ótimo de exposição à eletrólise.

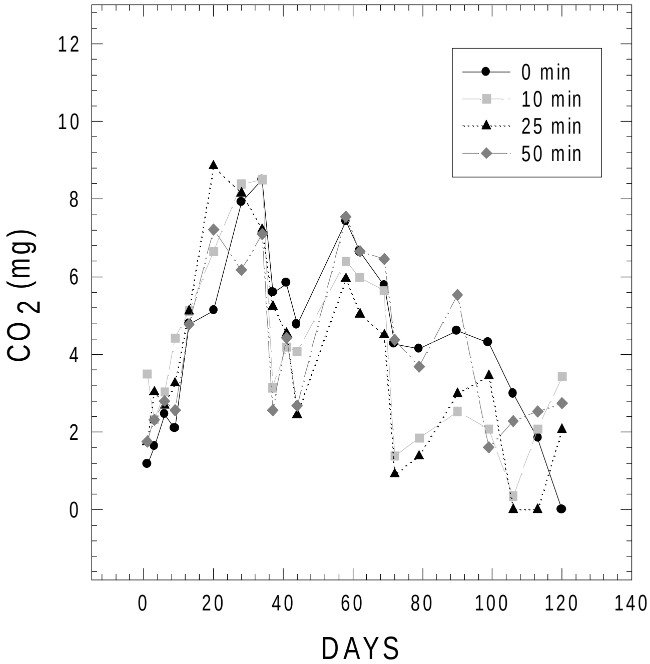

Figure 5 - Evolution of the CO_2 production in function of the number of days in the respirometric assay for the method of Bartha.

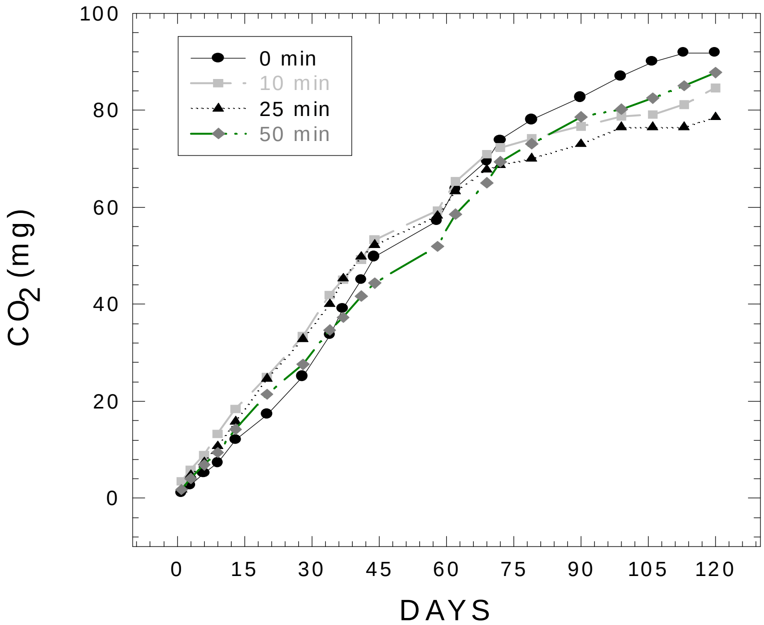

Figure 6 - CO_2 accumulated during the respirometric assay in function of the number of days.

Os tempos de eletrólise que permitiram uma maior degradação da matéria orgânica foram de 10 min e 25 min. Pode-se concluir que o tratamento eletrolítico é um método viável para a diminuição do tempo de adaptação dos microrganismos ao efluente e conseqüentemente acelerar a biodegradação do efluente da indústria química.

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