

Evaluation of the efficiency of sequential electro-oxidation/adsorption and adsorption/electro-oxidation techniques in removing *Novacron Blue* from aqueous solution

Avaliação da eficiência das técnicas sequenciais de eletro-oxidação/ adsorção e adsorção/eletro-oxidação na remoção de Novacron Blue de solução aquosa

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Abstract

Dyes are among the biggest polluting sources in the world and due to their complex nature, a single chemical treatment of wastewater may not be adequate, thus being able to combine physical treatment to optimize the results of water decontamination. In this work it is proposed to use a process by sequential treatments using electro-oxidation/adsorption and adsorption/electro-oxidation of a synthetic effluent (aqueous solution) of the Novacron Blue dye using Pb/PbO₂ or Ti/Pt as an anode. The data showed that the individual treatment via electrochemical oxidation showed at pH 4.5 the total color removal in 150 minutes, regardless of the current densities used, causing a high energy consumption. The adsorption process at the same pH, however, showed a low color removal of 35.2% in 20 minutes (saturation time) of the adsorbent. The electro-oxidation/adsorption sequence proved to be more efficient in terms of TOC (total organic carbon) removal and less energy consumption than its reverse process, since expanded perlite was essential for the significant removal of the degradation by-products formed after electro-oxidation (identified by GC-MS). These data were confirmed by the analysis of total organic carbon (TOC) which showed a significant removal of organic matter, after the sequential treatments of electro-oxidation/adsorption. The results obtained through the analyzes carried out with the Pb/PbO₂ anode showed a higher TOC removal content (60.10%) when compared to the Ti/Pt electrode (51.98%), for all current density and pH values analyzed. The expanded perlite also showed good capacity to reduce the concentration of residual Pb (from the electrode).

Keywords: perlite; dyes; electrooxidation

Resumo

Os corantes estão entre as maiores fontes poluidoras do mundo e devido à sua natureza complexa, um único tratamento químico da água residuária pode não ser adequado, podendo assim combinar o tratamento físico para otimizar os resultados da descontaminação da água. Neste trabalho propõe-se a utilização de um processo por tratamentos sequenciais utilizando eletro-oxidação/adsorção e adsorção/eletro-oxidação de um efluente sintético (solução aquosa) do corante Novacron Blue utilizando Pb/PbO₂ ou Ti/Pt como ânodo. Os dados mostraram que o tratamento individual via oxidação eletroquímica apresentou em pH 4,5 a remoção total da cor em 150 minutos, independente das densidades de corrente utilizadas, ocasionando um alto consumo de energia. O processo de adsorção no mesmo pH, entretanto, apresentou uma baixa remoção de cor de 35,2% em 20 minutos (tempo de saturação) do adsorvente. A sequência de eletrooxidação/adsorção mostrou-se mais eficiente em termos de remoção de COT (carbono orgânico total) e menor consumo de energia do que seu processo reverso, uma vez que a perlita expandida foi essencial para a remoção significativa dos subprodutos da degradação formados após a eletrodeposição. oxidação (identificada por GC-MS). Esses dados foram confirmados pela análise de carbono orgânico total (COT) que mostrou uma significativa remoção de matéria orgânica, após os tratamentos sequenciais de eletro-oxidação / adsorção. Os resultados obtidos nas análises realizadas com o ânodo de Pb/PbO₂ apresentaram maior teor de remoção de TOC (60,10%) quando comparado ao eletrodo de Ti/Pt (51,98%), para todos os valores de densidade de corrente e pH analisados. A perlita expandida também apresentou boa capacidade de reduzir a concentração de Pb residual (proveniente do eletrodo).

Palavras-chave: perlita; corantes; eletro-oxidação

1 INTRODUÇÃO

Environmental pollution is responsible for serious and often irreparable damage to land. There are three main types: soil, water and air pollution, but the biggest water polluting agents are industries due to the excessive use of pesticides, fertilizers, pharmaceutical components, and other organic compounds such as paints and dyes in the textile industry (Natarajan, 2018). The industries are considered a sector with a great production of wastewater because it contains high amounts of harmful chemicals that are often discarded without any previous treatment in water bodies, causing innumerable environmental problems (Noreen et al., 2020).

Dyes are among the largest polluting sources in the world. They are used on a large scale, not only in the textile industry but also in food, cosmetics, agriculture, pharmaceuticals and papermaking. It is estimated that around 7×10^5 tonnes of dye are produced annually and that 10 to 15% of the fraction of dye used in manufacturing and dyeing in the textile industry is lost in the form of washing water, that is, waste water, becoming effluent highly harmful to the aquatic environment. Synthetic dyes present in water bodies are easily visible in minimal concentrations (<1 ppm or mg/L), preventing the passage of light in the water and interfering with the growth and life of aquatic organisms. Wastewater containing dyes discharged into nature is dangerous for human health, animals and the environment. Thus, the degradation of dyes as well as the removal of color, are crucial points for environmental remediation (Katheresan, Kansedo & Lau, 2018; Mu et al., 2019; Natarajan, 2018; Noreen et al., 2020).

Novacron Blue is an azo dye, that is, it has in its chemical structure the organic group $-N = N-$ (azo group), responsible for its strong and persistent coloring, they are the most toxic dye class among those produced in the world. It is a dye widely used in the textile industry, mainly in dyeing jeans. Dyes such as

novacron blue are stable even in extreme conditions (acids and alkalis) and medium temperatures, thus being present in aquatic media Novacron Blue is not easily removed from wastewater and requires attention before being released into water bodies (RÊGO et al., 2014; Zhuang et al., 2020). The literature mentions that it is of great importance that technologies that reduce the discharge, the coloring or that are able to totally degrade the dyes of the aqueous medium before being launched in aquatic environments to reduce the environmental impact (MU et al., 2019; Natarajan, 2018; Noreen et al., 2020). The dyes are not removed in the aqueous medium under natural conditions, they require physical and/or chemical or biological treatment conditions: adsorption, photocatalysis, use of membranes, oxidation, microorganisms and electrolysis. Some methods such as adsorption, coagulation and flocculation are not effective, as they only change the phase of the contaminant (liquid to solid), not being able to destroy the organic molecule. Electrochemical methods, for example, electro-oxidation, have an energy cost associated with the process, and the formation of intermediate by-products generally harmful to the environment. Biological methods require time and a large territorial area for their execution, including that some dyes are resistant to aerobic treatment, which brings a disadvantage to their application (Katheresan, Kansedo & Lau, 2018; Natarajan, 2018; SILVA et al., 2021).

Electrochemical technology has developed greatly over the past 10 years as an alternative use for wastewater treatment, since it offers promising advantages for the prevention of problems related to industrial effluent pollution. The main advantage of this technology is its environmental compatibility. Other advantages are: versatility, security, selectivity, simplicity of automation, friendly to the environment and low investment costs (Bensalah, Quiroz alfaró & Martínez-huitle, 2009; Gilpavas, Dobrosz-gómez & Gómez-garcía, 2018; Rêgo et al., 2014). The main challenge for the electrochemical technology to be used in the treatment of industrial effluents, in general,

is to reduce the energy consumption of the process so that it can decrease its operating cost and, thus, make it competitive with other chemical treatments. already (ROCHA *et al.*, 2012).

Electrochemical oxidation is the most used technique for removing organic contaminants in aqueous solutions due to its extraordinary reactivity, low cost and high energy efficiency. Contaminants are degraded and by-products are generated, making the adequately low total organic carbon (TOC) values are not achieved in these single treatment processes. Therefore, recent research has focused on various treatment techniques to clean wastewater, and thus achieve complete detoxification of contaminated water (Ganesan, Amirthalingam, & Arivalagan, 2019; Gilpavas, Dobrosz-gómez & Gómez-garcía, 2018).

In electrooxidation, no chemical reagent has to be added, since the electron is the “clean reagent” and does not generate residues after its execution, and the search for good anodic materials with excellent catalytic activities, low operating cost and high stability for application in tests electro-oxidation has been gaining prominence (RIBEIRO, 2013).

The material used as an anode in the oxidation process has an influence on the treatment efficiency, and the literature highlights that first class materials, called “active” anodes such as platinum-based materials (Pt), iridium oxide (IrO_2) and ruthenium oxide (RuO_2), are anodic materials with high stability and chemical and mechanical resistance. It is important to remember that platinum (Pt) electrodes are expensive, and to reduce their cost, the electrodes are produced by supporting platinum on the titanium plate (Ti/Pt). On the other hand, for electrochemical degradation processes there are also “non-active” electrodes in which the organic species is directly oxidized by hydroxyl radicals generated on the electrode surface, usually resulting in a faster and more complete combustion of organic matter: boron doped diamond electrode (BDD), SnO_2 and PbO_2 (TOC) (Malpass *et al.*, 2008; Miwa *et al.*, 2006).

The anode most widely used in electrooxidation

is Pb/PbO_2 due to its high electro-catalytic performance, corrosion resistance, long service life, high conductivity, high stability in very acidic media and low financial cost (Elaissaoui *et al.*, 2018; Ribeiro, 2013). For almost all pollutants, PbO_2 presents faster mineralization than platinum (Pt), iridium oxide (IrO_2), ruthenium oxide (RuO_2) and tin oxide (SnO_2) (CARVALHO *et al.*, 2011).

Due to the complex nature of the dyes, a single chemical treatment of wastewater, such as electro-oxidation, may not be adequate, thus being able to associate a physical treatment to optimize the results of dye removal. In this way, a sequential treatment technique, such as adsorption, is perfectly viable. Adsorption is a physicochemical phenomenon in which an inorganic material (adsorbent) can be used to remove pollutants in aqueous solution, in this case called a solid-liquid adsorption process. The selected adsorbent material must be easy to acquire, low cost and effective in removing degradation by-products, an important characteristic that biological treatment methods cannot achieve (GANESAN, AMIRTHALINGAM & ARIVALAGAN, 2019).

Expanded perlite is a natural aluminosilicate, consisting of 75.0% SiO_2 , low cost and abundant with great efficiency in removing organic molecules due to its active sites on its surface, the silanol groups (Si-OH). It is a promising material and widely used in the removal of dyes and adsorption of other organic molecules in an aqueous medium (ALMEIDA, *et al.*, 2017; ALMEIDA *et al.*, 2019).

In this work it is proposed to use sequential electrochemical oxidation/adsorption and adsorption/electrooxidation treatments of synthetic effluent (aqueous solution) of Novacron Blue dye. The proposal is to use two different electrode types: Ti/Pt and Pb/PbO_2 for the electro-oxidation step as they are one of the most used as anodes in electrochemical degradation processes. The objective is to evaluate the influence of the order of execution of the sequence of treatments of the synthetic effluent (electro-oxidation/adsorption or adsorption/electro-oxidation) in

the color removal efficiency, TOC reduction efficiency and energy cost.

2 MATERIALS AND METHOD

2.1 Materials

The reagents used in this study were sulfuric acid (H₂SO₄) 98.0% (Vetec), sodium hydroxide (NaOH) 99.0% (Vetec), sodium sulfate (Na₂SO₄) 99.5% (Vetec) and for chromatographic analysis, high purity acetonitrile grade GC-MS (Sigma-Aldrich). The textile dye used was commercial Novacron Blue (C₃₄H₂₄N₆Na₄O₁₄S₄) (Fig.1).

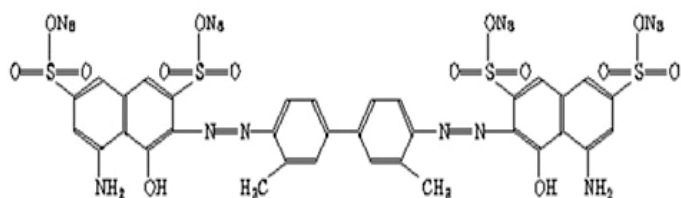


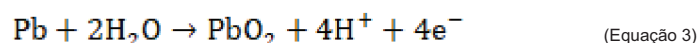
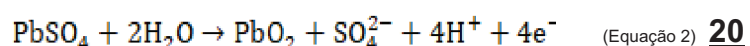
Figure 1. Chemical structure of Novacron Blue dye
Fonte: elaborada pelos autores

2.2 Preparation of aqueous solutions (synthetic textile effluents)

Novacron blue synthetic solutions were prepared by dissolving them in 0.25 mol/L sodium sulfate (Na₂SO₄) solution, since this salt is present in many textile wastewaters. The concentration of the dye used was 190 mg/L, in order to simulate the value of the concentration used in the textile industry. The pH values (1, 4.5 and 8) were adjusted with solutions of sulfuric acid (H₂SO₄) 0.5 mol/L and sodium hydroxide (NaOH) 0.25 mol/L. Industrial effluents from textile dyes generally contain concentrations between 100 and 150 mg/L of dissolved salts and pH 10, for this reason, the electrochemical and adsorption processes were tested by varying pH values to determine their influence on color removal.

2.3 Working electrode and electrochemical cell

The electrochemical cell was made up of an electrocatalytic material (Ti/Pt or Pb/PbO₂) as an anode and a 15 cm² plate of Ti as the cathode. The anodes had a square shape, with 10 cm² of geometric area. The inter-electrode distance was 1.5 cm. The Pt anode was a platinum coated Ti plate with a total area of 10 cm² (the Ti/Pt anode was supplied by De Nora S.P.A. Milan, Italy). The Pb/PbO₂ was prepared as follows: the Pb plate was immersed in a solution with a concentration equal to 10% sulfuric acid at room temperature in a beaker. In this system, a current density of 10 mA/cm² was applied for 40 minutes. After this process, it is observed that the Pb plate is converted to Pb/PbO₂ according to equations 1, 2 and (MARTÍNEZ-HUITLE *et al.*, 2004):



2.4 Electrochemical oxidation tests

The electro-oxidation tests were carried out for preliminary evaluation of the efficiency of the method for removing the color of the dye in aqueous solution. The tests were performed in an electrochemical cell with a reaction compartment whose capacity was 250 mL. The Novacron Blue oxidation experiments were carried out under galvanostatic conditions using a power supply. The influence of current density (20, 30 and 60 mAcm⁻²), with pH 4.5 and room temperature were the experimental conditions employed in the process.

2.4.1 Adsorption Test

The individual adsorption tests were performed using 500 mg of expanded perlite (adsorbent) in 50 mL of the synthetic solutions of the novacron blue dye (190 mg/L), placed in a 125 mL conical flask, under orbital agitation (160 rpm) on an incubator table at room

temperature. This study was carried out to evaluate an adsorption balance with a variation of pH 1; 4,5 and 8 and to investigate the efficiency of this removal method for Novacron Blue. Each aliquot removed was centrifuged to avoid the presence of material in suspension and the color decay (Equation 4) was evaluated by molecular UV-vis spectroscopy, by the absorbance at the maximum dye absorption length (600 nm).

2.4.2 Electrochemical oxidation/adsorption treatment

The aqueous solution of the Novacron Blue dye was subjected to treatment with sequential electrochemical oxidation and adsorption techniques. The electrochemical oxidation treatment was carried out in an electrochemical cell with a reaction compartment whose capacity was 250 mL. The Novacron Blue oxidation experiments were carried out under galvanostatic conditions using a power supply (Minipa brand and model MPL-3305M).

The experiments were carried out at 30 °C to study the effect of the applied current density (20, 40 and 60 mA/cm²), using Ti/Pt or Pb/PbO₂ as anode and varying the pH (1, 4.5 and 8) in a time of 0 to 60 minutes, while the effect of temperature (30, 40 and 60 °C) was studied only at a current density (20 mA/cm²) for all the pH values already mentioned and in a time interval from 0 to 40 minutes. Then, gas Chromatography Analyzes coupled with Mass Spectrometry (GC-MS) were performed to determine the reaction intermediate products and measures of Total Organic Carbon (TOC) to verify if the organic load was reduced during the electrochemical treatment.

As for the adsorption tests after electrochemical oxidation treatment, 50 ml of sample already submitted to electro-oxidative treatment, 500 mg of expanded perlite, under agitation of 160 rpm in an incubator table were also used. The expanded perlite used as an adsorbent in this work comes from Argentina and is supplied by Schumacher Insumos. The perlite was sieved in granulometry corresponding to 100 mesh (\pm

150 μ m), without any previous chemical treatment.

In order to influence the temperature in the adsorption process (30, 40 and 60 °C), pH values 1, 4.5 and 8 were tested in a time interval from 0 to 10 minutes, based on the saturation equilibrium time of the adsorbent (expanded perlite). Figure 2 shows the sequential treatment (electro-oxidation/adsorption) of the Novacron Blue dye.

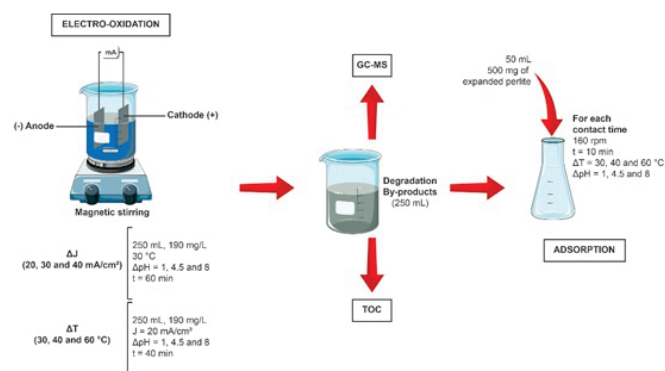


Figure 2. Experimental procedure for the sequential electro-oxidation/adsorption treatment

Fonte: elaborada pelos autores.

2.4.3 Adsorption/electrochemical oxidation treatment

In this work, the reverse process to that previously reported was also used, using sequential electrochemical adsorption/electro-oxidation techniques. At this point, after the solutions went through the adsorption process, they were subjected to the electrochemical oxidation process, as follows below.

The adsorption tests were performed using 2500 mg of expanded perlite in 250 mL of the synthetic solutions of Novacron Blue (190 mg/L), in an orbital stirring of 160 rpm, in an incubator table. A 250 mL conical flask was used and the adsorption was carried out in a time of 0 to 20 minutes at a temperature of 30 °C. The influence of the effect of the pH variation of the solution (pH 1, 4.5 and 8) and the effect of the temperature influence (30, 40 and 60 °C) on the dye adsorption process with the expanded perlite as an adsorbent were analyzed. After each contact time, an aliquot was removed and centrifuged to avoid the

presence of suspended material and the color removal was analyzed using a molecular absorption spectrophotometer in the UV-Vis region (UV-1800 Shimadzu) by decreasing the absorbance, in the maximum dye absorption wavelength (600 nm). The sequence of the adsorption/electro-oxidation process was outlined in Fig.3.

After the solutions went through the adsorption process, they were subjected to an electro-oxidative process, in order to verify the influence on color removal and current efficiency. The oxidations were carried out in an electrochemical cell with a reaction compartment, with a capacity of 250 mL. The dye oxidation experiments were carried out under galvanostatic conditions using a power supply (MPL-3305M).

To assess the effect of current density on the process, a fixed temperature of 30 °C was used, varying the applied current density (20, 40 and 60 mAcm⁻²) and pH (1; 4.5 and 8) in a time from 0 to 60 minutes. While the effect of temperature (30, 40 and 60 °C) was studied only at a current density (20 mAcm⁻²) for the pH values already mentioned and in a time interval of 0 to 40 minutes. Finally, the measurements of Total Organic Carbon (TOC) were made to verify if the organic load was reduced after the electrochemical treatment.

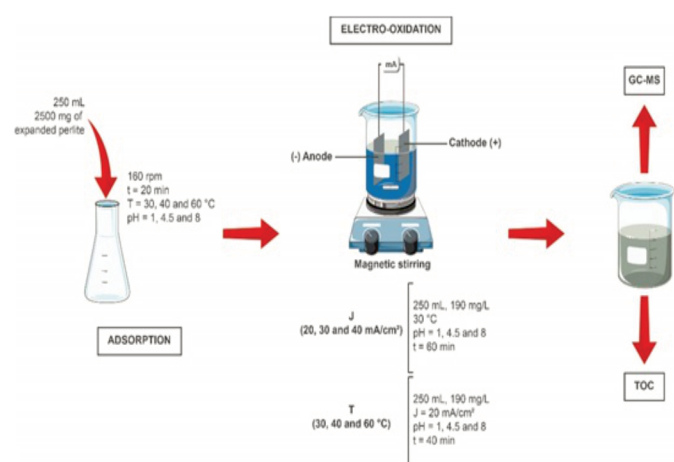


Figure 3. Experimental procedure for sequential adsorption/electro-oxidation treatment
Fonte: elaborada pelos autores.

2.5 Analytical methods

2.5.1 Electric conductivity

The electrical conductivity analyzes were performed on a conductivity meter (Tecnal model Tec-4MP) with two platinum electrodes, using a standard solution of 146.9 $\mu\text{S}/\text{cm} \pm 0.5\%$ (25 °C) for the calibration of the equipment.

These analyzes were carried out in order to assess whether the expanded perlite was adsorbing the support electrolyte ($\text{Na}_2\text{SO}_4 - 0.25 \text{ mol/L}$) and thus decreasing the ionic strength of the reaction medium. The samples of interest were read and after each reading the electrode was washed with distilled water and dried with absorbent paper

2.5.2 Color removal

Color removal was analyzed using a spectrophotometer (UV-1800 Shimadzu) and accompanied by a decrease in absorbance. Experimentally, the percentage of color removal was calculated by the expression (MARTÍNEZ-HUITLE & BRILLAS, 2009) according to Equation 4:

$$\text{Color removal (\%)} = (\text{ABS}_0 - \text{ABS}_t / \text{ABS}_0) \times 100 \quad (\text{Eq 4})$$

ABS_0 and ABS_t are the absorbances before and after an electrolysis time t at the maximum wavelength of the Novacron Blue (600 nm).

The energy consumption per volume of treated effluent was calculated and expressed in kW.h.m⁻³. The average cell potential, during electrolysis, is taken to calculate energy consumption, according to Equation 5 (MARTÍNEZ-HUITLE & BRILLAS, 2009):

$$\text{Energy consumption} = (V \times A \times t) / (1000 \times V_s) \quad (\text{Eq 5})$$

Where t is the electrolysis time (h), V is the cell voltage (Volts), A is the current (Amperes) and V_s the sample volume (m³).

2.5.3 Total Organic Carbon (COT)

The Total Organic Carbon Analyzer

(Analytik Jena Multi N/C 3100) measures the amount of Total Carbon (T.C) and Inorganic Carbon (I.C) in the sample. The TOC is given by subtracting T.C. and I.C. For the determination of total carbon, the injected sample is taken to a combustion tube at 680 °C containing platinum supported on alumina and undergoes catalytic oxidation to CO₂. For the determination of inorganic carbon, the injected sample reacts with 25% phosphoric acid, and all inorganic carbon is converted to CO₂. The CO₂ produced, both in catalytic oxidation and from inorganic carbon, is quantified by infrared absorption. The concentration of T.C. and I.C. are obtained by interpolation using analytical curves (peak area x concentration) previously made by injection of standards.

2.5.4 Gas Chromatography coupled to Mass Spectrometer (GC-MS)

Gas Chromatography analyzes coupled to a Mass Spectrometer (Thermo Scientific®) were carried out in order to identify the intermediate compounds formed from the electrochemical oxidation analyzes of the Novacron Blue dye.

The samples were prepared by diluting 10 µL of the sample after electrochemical oxidation in 1 mL of acetonitrile and the final mixture was filtered using anhydrous sodium sulfate to remove traces of water and then injected into the chromatograph.

Table 1 shows the conditions that were used to perform the GC-MS analyzes for the Novacron Blue sample after electrooxidation.

Table 1.
Conditions used in GC-MS analyzes

Heating ramp	40 °C (5 min)
	12 °C/min to 100 °C (0 min)
	5 °C/min to 200 °C (0 min)
	20 °C/min to 270 °C (5 min)
Column	VF-5ms, 15m x 0.25mm x 0.25 µm Manufacturer: Varian
Stationary phase composition	5% fenil-arilene, 95% dimetilpolisiloxane
Injector temperature	220 °C
Injection mode	Splitless
Carrier gas and gas flow	Helium, 0,8 mL/min
Ion source temperature	220 °C
Transfer line temperature	280 °C
Mass range	35 to 500 m/z

2.5.5 Atomic Absorption Spectrometry (AAS)

In order to ascertain the presence of lead residue in the electrochemical oxidation/adsorption analyzes, atomic absorption spectrometry analyzes were performed using an Atomic Absorption Spectrometer (model AA-6800 from Shimadzu). The tests were performed according to the APHA 3111B standard. For the calibration of the equipment, a reference standard traced to NIST was used, prepared volumetrically.

3 RESULTS AND DISCUSSION

3.1 Individual treatments to remove the color of Novacron Blue

3.1.1 Electrochemical oxidation test

Before performing the sequential processes (electrochemical oxidation/adsorption) in the treatment of synthetic textile effluents (aqueous solution of the dye), electrochemical oxidation and adsorption tests were carried out individually in order to observe the behavior of the dye against the electrocatalytic material (Ti/Pt or Pb/PbO₂) and adsorbent (expanded perlite).

Electrochemical oxidation tests were performed using Pb/PbO₂ or Ti/Pt electrodes, concentration of the aqueous solution of dye (synthetic effluent) of 190 mg/L, at pH 4.5 and current densities of 20, 40 and 60 mA/cm² at room temperature. The solutions were subjected to electro-oxidative treatment until the color was completely removed. Figure 4 shows the influence of the applied current density on the total color removal during the electrochemical oxidation of the synthetic effluent containing the Novacron Blue dye using Pb/PbO₂ and Ti/Pt anodes.

As can be seen, complete color removal, in all cases, was achieved in a time of 150 minutes regardless of the current density applied and the type of anodic material. This shows that the complete elimination of the color occurs through its reaction with radicals (OH) that are electro-generated on the surface

of the electrodes, indicating a break in the azo bond (chromophore group, -N=N-) of the dye, removing its strong color and persistent (COMNINELLIS & PULGARIN, 1993; MARTÍNEZ-HUITLE & BRILLAS, 2009).

The current density determines the production of oxidizing species in the reaction medium. The increase in the current density provides an increase in the speed of the reactions in the electrodes, generating more OH, which consequently reduces the value of total organic carbon (TOC), increasing the mineralization of the organic pollutant, in this case the Novacron Blue (Dos santos et al., 2020).

between the dye molecules and the active sites on the electrode surface (Singh, et al., 2016). When using Pb/PbO₂ as an anode there is an increase in the mineralization content of the said dye. This can be explained by the fact that this type of anode is one of the classic examples of material with overpotential oxygen evolution, so it is extremely useful for the electrochemical removal of organic compounds. This overpotential favors the electrochemical combustion of organic compounds since they can be completely mineralized, thus ensuring a quick chemical reaction with low molecular weight products until conversion to CO₂ (MARTÍNEZ-HUITLE & BRILLAS, 2009, 2015; PANIZZA & CERISOLA, 2008).

3.1.1.1 Energy consumption for electro-oxidation

Table 2 shows the energy cost required for the complete removal of color from the Novacron Blue dye in 150 minutes under different current density conditions using the Pb/PbO₂ or Ti/Pt electrode as an anode. It can be seen that, during the electrolysis of the synthetic solution of the dye, the energy consumption of the process is proportional to the current density applied. Thus, as the color removal is total (100%) in the three current density values studied and in the same test time (150 min), the current density used in the other sequential electro-oxidation/adsorption tests was fixed at 20 mA/cm² due to the lower energy cost associated with the process. Lower current density values are preferred for more efficient electro-oxidative treatments, although they lead to a slower TOC reduction (DOS SANTOS *et al.* 2019). As for the type of anodic material, the energy cost was not very variable between the Pb/PbO₂ and Ti/Pt electrodes, demonstrating that the electro-oxidation had an energy cost practically equivalent regardless of the anode used. Due to the need for a long electrooxidation test time (150 minutes) to completely remove the color of the dye, the energy consumption and, consequently, the cost associated with the process was high, making the use of electrooxidation as an individual removal process unviable for the dye.

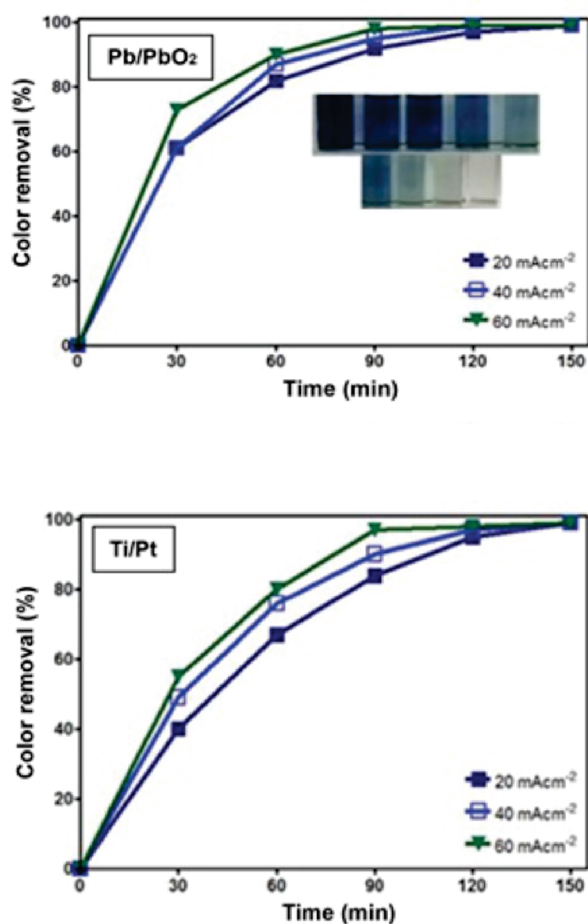


Figure 4. Influence of current density on the removal of Novacron Blue color by electrochemical oxidation at pH 4.5.

Fonte: elaborada pelos autores.

The increase in current density provides maximum O₂ evolution in the reaction medium, increasing the degradation and the rate of interaction

Table 2

Energy consumption for anodic oxidation of the novacron blue dye at different current densities

Electrode	Current density (mA/cm ²)	pH	Energy consumption (kWh/m ³)	Cost (R\$)/m ³
Pb/PbO ₂	20	4.5	31.09	15.73
	40		91.48	46.29
	60		152.47	77.15
Ti/Pt	20	4.5	30.89	15.63
	40		92.76	46.94
	60		150.09	75.95

Experimental conditions: Dye concentration: 190 mg/L; Temperature: 30 °C; Electrolyte: Na₂SO₄ 0.25 mol/L.

Fonte: elaborada pelos autores.

3.1.2 Adsorption test

Figure 5 shows the study of the adsorption balance based on the influence of pH on the color removal during the process of adsorption of the synthetic effluent containing the Novacron Blue dye using expanded perlite as an adsorbent. From these results, there was no complete removal of the color, because in 20 minutes the adsorbent saturation process is observed. Thus, at pH 1 there was a 30.0% removal, at pH 4.5 a 35.2% removal and at pH 8 a 39.5% removal. These data indicate that for the conditions of concentration, mass of the adsorbent and temperature it was not possible to achieve the total removal of the color of Novacron Blue using only the adsorption treatment.

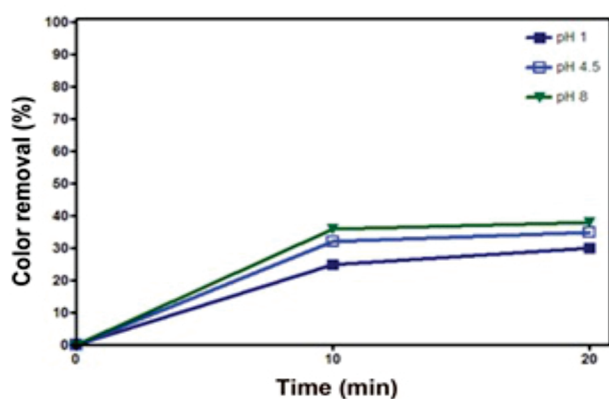


Figure 5. Influence of pH on the color removal of Novacron Blue by the adsorption process.

Fonte: elaborada pelos autores.

The adsorption process is a physical-chemical phenomenon that depends on factors related to the adsorbent (expanded perlite) and adsorbate (dye molecules): such as adsorbent porosity, size of the adsorbate molecule and especially the type of interaction between the dye and the adsorbent material. The adsorption test showed a quick saturation of the active sites of the adsorbent, that is, of the silanol groups (Si-OH) present on the surface of the expanded perlite, this indicates a high interaction with the Novacron Blue molecules and mainly attributed to the considerable size large number of dye molecules that quickly saturate the adsorbent, lowering the adsorptive efficiency of expanded perlite (ALMEIDA et al., 2017).

After performing the treatments in isolation, the treatment was applied sequentially (electrochemical oxidation/adsorption), in order to observe the influence of the sequence on the behavior of some conditions, such as: minimization of the total treatment time, decreased consumption energy and consequent financial cost, possibility of color retention and intermediary compounds of electrochemical oxidation by the adsorbent (expanded perlite) used, thus promoting a lowering of the levels of total organic carbon.

3.2 Sequential treatment:

electro-oxidation/adsorption of Novacron Blue

When performing the individual treatments, it was observed that it was not possible under the conditions analyzed to obtain a favorable color removal of the dye considering only a single type of treatment (electro-oxidation or adsorption). The experiments involving electrochemical oxidations obtained total color removal, but it took a long time (150 minutes) for this to happen, which resulted in high energy consumption, making the process economically unfeasible. The adsorption using the expanded perlite as an adsorbent was not able to promote the total removal of the color from the synthetic effluent of the dye under the mentioned conditions. Therefore, it is

3.2.1 Influence of pH in the sequential electro-oxidation/adsorption process

Figure 6 shows the result of the percentage of color removal from Novacron Blue, using the Pb/PbO₂ or Ti/Pt electrode for all studied pH values. There is an influence of the pH in the removal of the color because it is observed that in values of acid pH there is a greater facility in the removal of the color in the electro-oxidative treatment. Other works observing these aspects have also been developed and the authors explain that in this case there is a greater production of OH that accelerates the oxidation of organic compounds (MARTÍNEZ-HUITLE & BRILLAS, 2009; Carvalho et al., 2011; ROCHA et al., 2012).

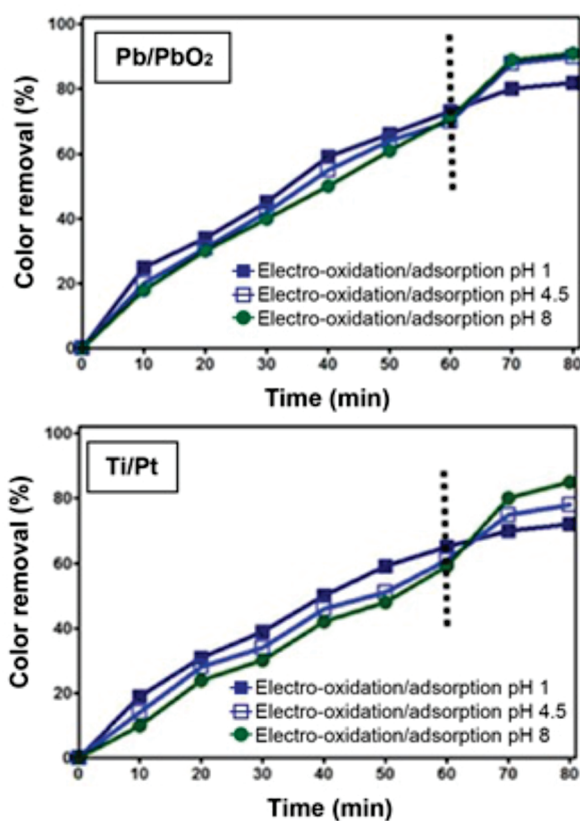


Figure 6. Influence of the pH of the synthetic effluent of Novacron Blue during the sequential electro-oxidation/adsorption treatment (current density 20 mAcm⁻²)

Fonte: elaborada pelos autores.

An important point to be discussed on the influence of pH on the electrochemical oxidation process are the types of molecules present in the reaction medium when changing the pH of the medium. As can be seen in Fig. 6, the process of degradation

(color removal) of the Novacron Blue dye is higher in acidic pH (pH 1), this is because in this pH value chemical species less resistant to attack by hydroxyl radicals (OH) are present in the reaction medium, increasing the efficiency of the electro-oxidative process. Azo dyes present an important balance when they undergo pH variation in aqueous solution, the azohydrazone tautomerism (Reaction 1) in which the hydrazone species (R-NH-N = R) is more stable in alkaline pH than the azo species in the dye (RN = NR), stable at acid pH. This justifies the small decrease in the efficiency of removing the color of Novacron Blue at alkaline pH, due to the presence of the hydrazone species. At pH 1 the azo species of the dye is the most stable and predominant in equilibrium, being more easily degraded by breaking the azo bond (chromophore group, -N=N-) of the dye, removing its strong and persistent color via electrochemical oxidation (Hunger, 2007; Xia et al., 2019).



Reaction 1. Azohydrazone tautomerism

Where -N=N- is the azo group of Novacron Blue, H is the hydrogen atom and R represents the other organic groups of the dye molecule (Fig. 1) just to simplify the equilibrium reaction.

As shown in Fig. 6, color removal is more efficient the lower the pH of the medium. Another factor deserves to be discussed about the chemical structure of Novacron Blue: at acid pH the amino groups (NH₂) of the chemical structure of the dye are protonated (Fig. 1), offering the dye molecules a cationic character, conferring instability and consequently they are more easily oxidized, as it increases the reactivity of the molecule with the radicals formed during electrolysis. This better justifies the degradation of the azo form (R-N=N-R) of the dye (Vasconcelos et al., 2016).

Already from 60 minutes after electrooxidation, the adsorption test starts, and the pH most efficient was pH 8. According to Almeida et al., (2019), the predominant species even with pH variations on the

silica surface, like expanded perlite, it is the Si-OH groups that interact with the by-products of degradation of the electro-oxidation of the dye, described in section 3.3.3 of this work.

The efficiency of the electro-oxidation/adsorption process for the Pb/PbO₂ and Ti/Pt anodes were summarized in Table 3. The removal of the color, as well as the degradation process was more efficient when using the Pb/PbO₂ anode reaching almost all (99.0%) with pH 1 and current density of 60 mA/cm² in 80 minutes of total treatment. This shows the efficiency of the sequential treatment.

Table 3

Novacron Blue color removal efficiency by sequential electro-oxidation/adsorption treatment

pH	Current density (mA/cm ²)	Color removal efficiency (%)	
		Ti/Pt	Pb/PbO ₂
1	20	72	92
	40	87	94
	60	90	99
4.5	20	78	90
	40	89	95
	60	92	96
8	20	85	91
	40	88	96
	60	94	98

Experimental conditions: Dye concentration: 190 mg/L; Adsorption time: 20 minutes; Electro-oxidation time: 60 minutes; Temperature: 30 °C; Electrolyte: Na₂SO₄ 0.25 mol / L.

Fonte: elaborada pelos autores.

Because the Ti/Pt anode is of the “active” type and the oxidizing species originating from it are the MO type oxides, due to the interaction between the electrode (M) and the hydroxyl radicals (OH) generated on the electrode surface, lowering the efficiency of the dye electrooxidation compared to the “non-active” Pb/PbO₂ electrode. On the other hand, with the surface of an “inactive” anode, this type of interaction is so weak that it allows the direct reaction of OH with organic compounds more quickly. Then, in the Pb/PbO₂ electrode, the radicals (OH) formed by the oxidation of water can be converted into molecular oxygen, or contribute to the complete oxidation of organic

compounds (Araújo, 2014; Malpass et al., 2008; Miwa et al., 2006).

3.2.2 Influence of temperature on the sequential electro-oxidation/adsorption process

In electrochemical oxidation experiments, the following parameters were considered: current density of 20 mA/cm², time of 40 minutes. For the adsorption experiments, the following parameters were considered: mass of the adsorbent (expanded perlite) 500 mg, contact time 10 minutes. The study of the influence of temperature on the sequential treatment (electro-oxidation/adsorption) was carried out at different pH values of the medium already mentioned (pH 1; 4.5 and 8). Fig. 7 shows the influence of temperature on the treatment of Novacron Blue by anodic oxidation/adsorption.

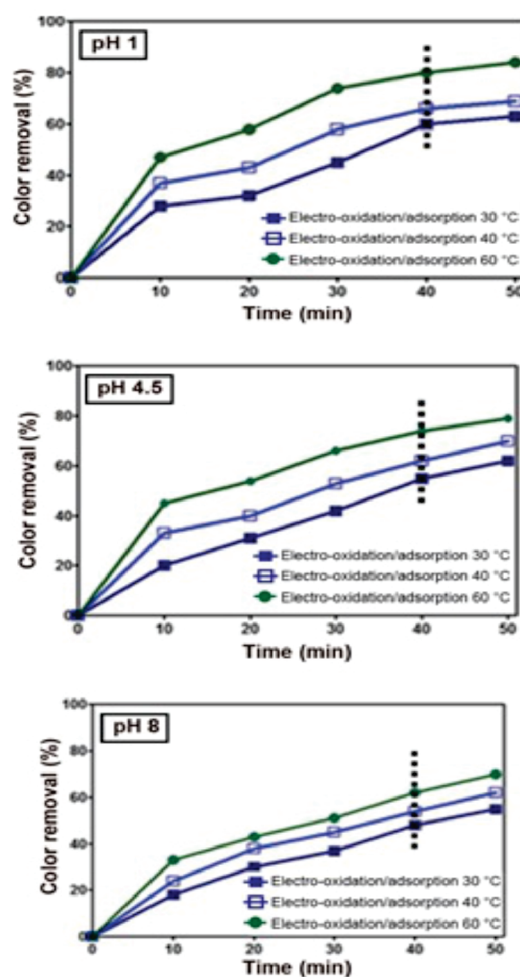


Figure 7. Influence of temperature in the process of treatment of synthetic effluent of Novacron Blue using electro-oxidation/adsorption (current density 20 mA/cm²) with Pb/PbO₂ anode

Fonte: elaborada pelos autores.

The results obtained show that the increase in temperature had a significant impact on the kinetics of the electrochemical oxidation and adsorption reactions of novacron blue, since the color removal increases considerably as the temperature increases (30, 40 and 60 °C). With this increase, it is possible to observe the reduction in time, both for electrolysis and adsorption, necessary for color removal. The results indicated an increase in color removal from 63% to 84% (pH 1), from 62% to 79% (pH 4.5) and from 55% to 70% (pH 8) for the tests with electrode Pb/PbO₂ (Fig.7). The color removal increased from 52% to 70% (pH 1), from 55% to 68% (pH 4.5) and from 48% to 67% (pH 8) using Ti/Pt electrode (Fig.8).

The increase in temperature increases the current efficiency, favoring the generation of oxidizing radicals (OH) improving the efficiency of the chemical oxidation process. This increase in temperature favors the mineralization of organic matter, which are complex chemical reactions that require more energy for their occurrence (VASCONCELOS, *et al.* 2016). Other authors have also observed that the increase in temperature influences both the electrochemical oxidation process (ROCHA *et al.*, 2012; Tavares *et al.*, 2012) and the adsorption process (Doğan, *et al.*, 2004; Govindasamy, 2009)

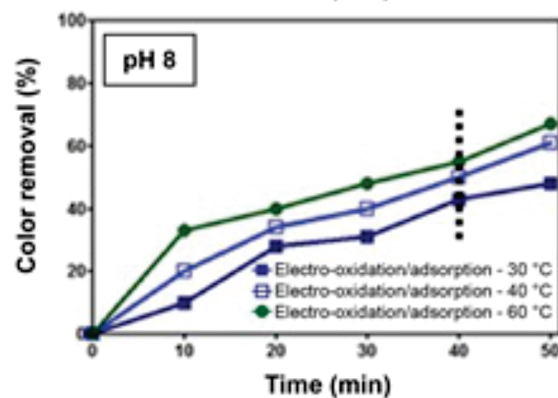


Figure 8. Influence of temperature in the process of treatment of Novacron Blue synthetic effluent using electro-oxidation/adsorption (current density 20 mA/cm²) with Ti/Pt anode

Fonte: elaborada pelos autores.

3.3 Sequential adsorption/electro-oxidation treatment of Novacron Blue

3.3.1 pH influence

In this situation, the reverse treatment was considered, firstly the one of adsorption in a time of 20 minutes for the Novacron Blue and then the one of electro-oxidation in a time of 60 minutes, also using the electrodes of Ti/Pt and Pb/PbO₂ for all studied pH values.

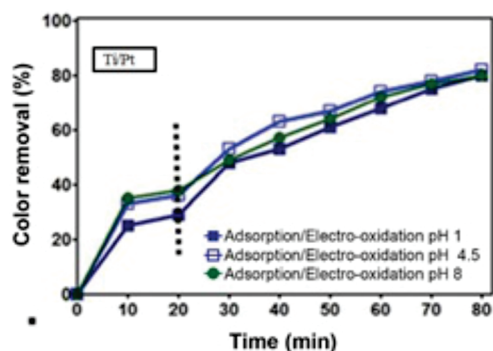
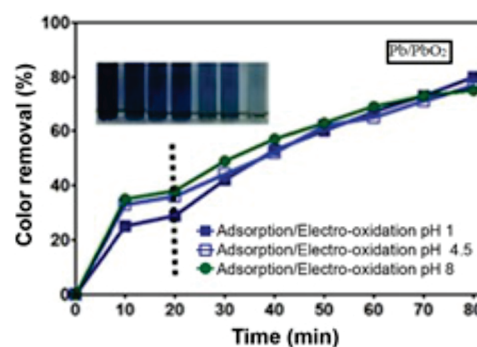
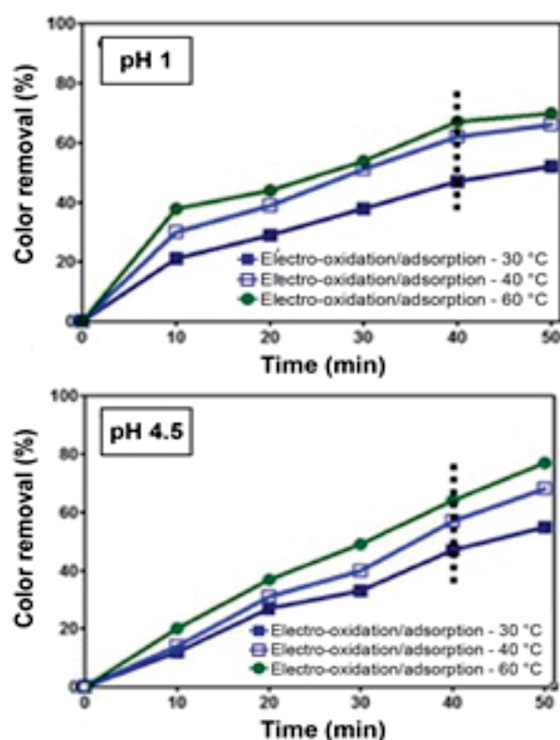


Figure 9. Influence of the pH of the synthetic effluent of Novacron Blue during the sequential adsorption/electro-oxidation treatment (current density 20 mA/cm²)

Fonte: elaborada pelos autores.

The results showed (Fig.9) that the increase in pH values had a satisfactory influence on the adsorption experiments. The increase in pH favors the adsorption step as it ensures the Bronsted acid-base interaction between the perlite silanol groups (Si-OH) and the amino groups (-NH₂) of the dye (ALMEIDA, *et al.*, 2017). As for the electro-oxidation stage, as already discussed, the pH does not cause very significant variations, however in acid pH the process is a little more favored due to the higher production of radicals OH, this is because in this pH value less resistant chemical species (azo form of the dye) to attack by hydroxyl radicals (OH) are present in the reaction medium, increasing the efficiency of the electro-oxidative process (HUNGER, 2007; XIA *et al.*, 2020).

Table 4 summarizes the efficiency of the sequential adsorption/electro-oxidation process for novacron blue using the Pb/PbO₂ and Ti/Pt anodes.

Table 4

Efficiency of the sequential adsorption/electro-oxidation process for Novacron Blue using Pb/PbO₂ and Ti/Pt anodes

pH	Current density (mA/cm ²)	Color removal efficiency (%)	
		Ti/Pt	Pb/PbO ₂
1	20	80	80
	40	82	87
	60	93	95
4,5	20	77	82
	40	86	89
	60	90	94
8	20	75	80
	40	89	93
	60	87	94

Experimental conditions: Dye concentration: 190 mg/L; Adsorption time: 20 minutes; Electro-oxidation time: 60 minutes; Temperature: 30 °C; Electrolyte: Na₂SO₄ 0.25 mol/L.

Fonte: elaborada pelos autores.

As the Pb/PbO₂ anode is of the “non-active” type, it allows the direct oxidation of organic molecules by hydroxyl radicals (OH), being more efficient than the Ti/Pt electrode as the results of this study show TOC (Araújo, 2014; Malpass *et al.*, 2008; Miwa *et al.*, 2006; ROCHA *et al.*, 2012). The Pb/PbO₂ anode achieved a Novacron Blue removal efficiency of 95% removal in 60

minutes of testing, while the Ti/Pt anode removed 93% of the dye (at a current density of 60 mA/cm²).

3.3.2 Influence of temperature

The Fig. 10 shows the influence of temperature on color removal as a function of time, considering the sequential adsorption/electrochemical oxidation processes. For the adsorption experiments, the following parameters were considered: mass of the adsorbent 500 mg, contact time of 10 minutes considering the same pH values (1, 4.5 and 8). In the electrochemical oxidation experiments, the following parameters were considered: current density of 20 mA/cm², time of 40 minutes under the same pH conditions already mentioned.

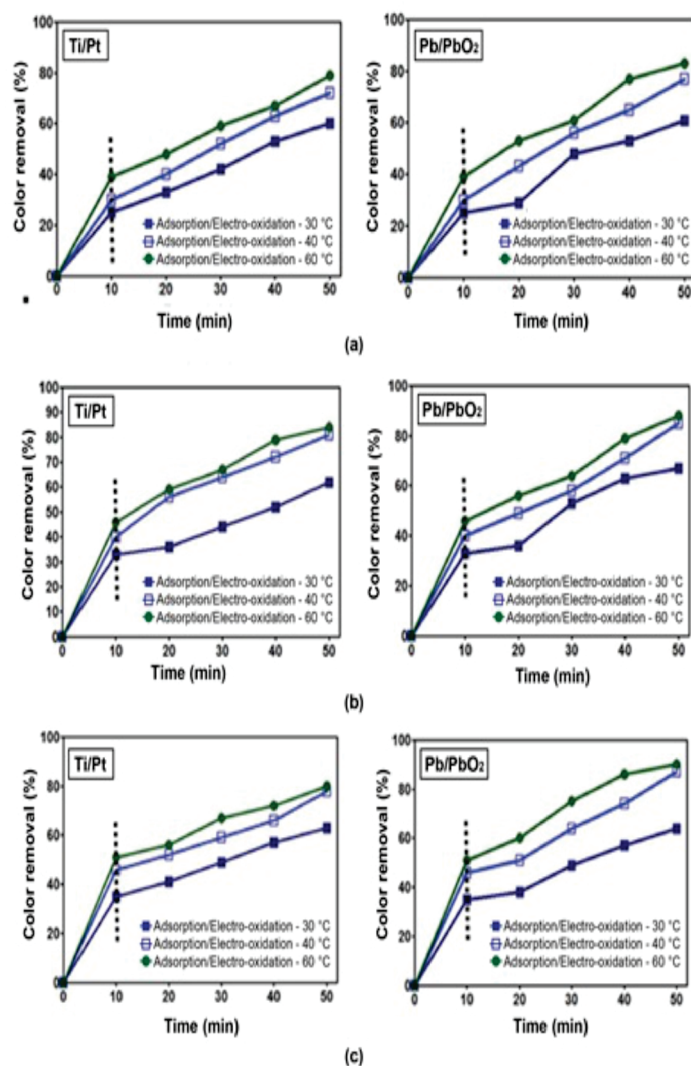


Figure 10. Influence of temperature on color removal for sequential adsorption/electro-oxidation processes at (a) pH 1, (b) pH 4.5 and (c) pH 8

Fonte: elaborada pelos autores.

The results obtained show that the increase in temperature (30, 40 and 60 °C) also influenced in a satisfactory way the inverse treatment process (adsorption/electro-oxidation). The color removal of the Novacron Blue dye increased from 60% to 79% (pH 1), from 70% to 84% (pH 4.5) and from 63% to 80% (pH 8) using platinum electrode. When using lead oxide electrode, the results increased from 61% to 83% (pH 1), from 67% to 88% (pH 4.5) and from 64% to 90% (pH 8), as shown in Table 5.

Table 5

Influence of temperature on removing the color of the Novacron Blue dye during sequential adsorption/electrochemical oxidation treatment

pH	Temperature (°C)	Color removal efficiency (%)	
		Ti/Pt	Pb/PbO ₂
1	30	60	61
	40	72	77
	60	79	83
4.5	30	70	67
	40	81	85
	60	84	88
8	30	63	64
	40	78	87
	60	80	90

Experimental conditions: Dye concentration: 190 mg/L; Adsorption time: 20 minutes; Electro-oxidation time: 60 minutes; Current density: 20mA/cm²; Electrolyte: Na₂SO₄ 0.25 mol/L.

Fonte: elaborada pelos autores.

The use of the adsorption/electro-oxidation treatment sequence favored the removal of the Novacron Blue color as described in Table 5, and the results for both anodes were quite similar (Ti/Pt and Pb/PbO₂). The adsorption process is an efficient technique for removing color from dyes in aqueous solution, the use of this process before electrochemical oxidation adds an advantage to this treatment in terms of reducing the color of the synthetic effluent. The active sites of expanded perlite, the silanol groups (Si-OH), have an affinity for the Novacron Blue molecules, mainly for the amino groups (-NH₂) of their structure, which in alkaline pH ensure their Bronsted acid-base interaction already observed in the literature when

dealing with the interaction of silicas and organic molecules (ALMEIDA *et al.*, 2017; ALMEIDA *et al.*, 2019). This adsorptive capacity of the perlite with Novacron Blue removes part of the dye molecules from the aqueous solution, until reaching its saturation balance (in 20 minutes), as it has already been seen that the adsorption alone does not have a considerable efficiency, and the process electrochemical complements the treatment with degradation and consequent removal of the color from the azo dye.

3.4 Energy consumption and cost estimation

Tables 6 and 7 show the energy cost required to remove the color of the Novacron Blue dye in 60 minutes under different conditions of current densities (20, 30 and 60 mA/cm²) and temperature (30, 40 and 60 °C) at pH values (1, 4.5 and 8) using the lead electrode (Pb/PbO₂) and Ti/Pt as an anode.

In Table 6, during the electrolysis of the synthetic solution using the Pb/PbO₂ electrode, the energy consumption of the process is shown to be proportional to the current density applied and the increase in the pH value. At pH 1 there was an increase from 9.26 kWh/m³ (20 mA/cm²) to 37.10 kWh/m³ (60 mA/cm²). At pH 4.5 there is an increase from 11.14 kWh/m³ (20 mA/cm²) to 48.37 kWh/m³ (60 mA/cm²). At pH 8 there is an increase from 8.02 kWh/m³ (20 mA/cm²) to 50.65 kWh/m³ (60 mA/cm²).

Table 6

Energy consumption by volume of synthetic effluent of Novacron Blue treated during anodic oxidation (Pb/PbO₂) for different current densities and pH values

pH	Current density (mA/cm ²)	Energy consumption (kWh/m ³)	Cost (R\$)
1	20	9.26	4.69
	40	21.18	10.72
	60	37.10	18.77
4.5	20	11.14	5.64
	40	28.90	14.62
	60	48.37	24.48
8	20	8.02	4.06
	40	31.19	15.78
	60	50.65	25.63

Experimental conditions: Pb/PbO₂ electrode. Dye concentration: 190 mg/L; Temperature: 30 °C; Electrolyte: Na₂SO₄ 0.25 mol/L.

Fonte: elaborada pelos autores.

In Table 7, it can be seen that, during the electrolysis of the synthetic solution using the Ti/Pt anode, the energy consumption of the process is shown to be proportional to the current density applied and the increase in the pH value. At pH 1 there was an increase from 8.70 kWh/m³ (20mA/cm²) to 36.00 kWh/m³ (60mA/cm²). At pH 4.5 there is an increase from 10.88 kWh/m³ (20mA/cm²) to 47.12 kWh/m³ (60mA/cm²). At pH 8 there is an increase from 8.52 kWh/m³ (20mA/cm²) to 51.68 kWh/m³ (60mA/cm²). The results show that the increase in current density led to an increase in energy consumption and, consequently, to the cost associated with the electrochemical process. It is observed that at pH 8, even without very significant variation, energy consumption was higher for both anodes (Pb/PbO₂ and Ti/Pt) at this pH due to the presence of species more resistant to oxidative treatment (hydrazone form of Novacron Blue), resulting in lower efficiency and higher energy consumption at this pH.

Table 7

Energy consumption of Novacron Blue treated by anodic oxidation (Ti/Pt) for different current densities and pH values

pH	Current density (mA/cm ²)	Energy consumption (kWh/m ³)	Cost (R\$)
1	20	8.70	4.40
	40	20.59	10.42
	60	36.00	18.22
4.5	20	10.88	5.51
	40	28.47	14.41
	60	47.12	23.84
8	20	8.52	4.31
	40	33.12	16.76
	60	51.68	26.15

Experimental conditions: Ti/Pt electrode. Dye concentration: 190 mg/L; Temperature: 30 °C; Electrolyte: Na₂SO₄ 0.25 mol/L.

Fonte: elaborada pelos autores.

Table 8 shows the energy consumption for the Novacron Blue dye using the Pb/PbO₂ anode, taking into account the temperature variation during the electro-oxidative process over a period of 40 minutes and a current density of 20 mA/cm² for all pH values studied. It is also possible to observe that as the

temperature increases, energy consumption decreases satisfactorily for all pH values studied.

Table 8

Energy consumption for anodic oxidation (Pb/PbO₂) of Novacron Blue dye for different temperatures and pH values

pH	Temperature (°C)	Energy consumption (kWh/m ³)	Cost (R\$)
1	30	9.26	4.69
	40	6.18	3.13
	60	5.90	2.99
4,5	30	11.14	5.64
	40	8.64	4.37
	60	7.91	4.00
8	30	8.02	4.06
	40	5.23	2.65
	60	4.92	2.49

Experimental conditions: Pb/PbO₂ electrode. Dye concentration: 190 mg/L; Current density: 20 mAcm⁻²; Electrolyte: Na₂SO₄ 0.25 mol/L.

Fonte: elaborada pelos autores.

Table 9 shows the energy consumption for the Novacron Blue dye, taking into account the temperature variation during the electro-oxidative process, with Ti/Pt anode over 40 minutes and a current density of 20 mA/cm² for all the studied pH values. It is possible to observe that at pH 1, there was a reduction from 8.70 kWh/m³ to 5.04 kWh/m³. At pH 4.5 consumption was reduced from 10.88 kWh/m³ to 7.29 kWh/m³. At pH 8, the reduction was from 8.52 kWh/m³ to 4.98 kWh/m³, when the temperature varied from 30 to 60 °C.

Table 9

Energy consumption for anodic oxidation (Ti/Pt) of the Novacron Blue dye for different temperatures and pH values

pH	Temperature (°C)	Energy consumption (kWh/m ³)	Cost (R\$)
1	30	8.70	4.40
	40	5.83	2.95
	60	5.04	2.55
4,5	30	10.88	5.51
	40	7.29	3.69
	60	6.89	3.49
8	30	8.52	4.31
	40	5.70	2.88
	60	4.98	2.52

Experimental conditions: Ti/Pt electrode. Dye concentration: 190 mg/L; Current density: 20 mA/cm²; Electrolyte: Na₂SO₄ 0.25 mol/L.

Fonte: elaborada pelos autores.

As already discussed, pH did not significantly affect the efficiency of the electro-oxidative process because the pH effect is not a very relevant parameter in terms of electrochemical oxidation efficiency (VASCONCELOS *et al.*, 2016). It is important to highlight that this reduction in the energy cost that occurs when there is an increase in temperature can be explained by the fact that as the temperature rises, less time will be necessary for an increase in the percentage of color removal to occur, thus, less time will be needed in the electro-oxidation process and a consequent saving in the cost of the process. These calculations were performed considering the cost of electricity in Brazil in the amount of R\$ 0.506 (R\$ = Brazilian (Real currency), excluding the amount of Brazilian taxes) per kWh (Data from ANEEL – National Electric Energy Agency/Brazil). The expense of the process was studied in order to show the viability of the process as a green alternative.

3.3 Efficiency of the analytical method

3.3.1 Electrical conductivity analysis

In order to ascertain whether the expanded perlite was decreasing the ionic strength because it was adsorbing the support electrolyte (Na_2SO_4) used in the solution thus causing an increase in the resistance of the reaction medium and consequently a decrease in the efficiency of the electrochemical process, conductivity analyzes were performed solution of Na_2SO_4 solution (0.25 mol/L) before and after adsorption.

The values were obtained through electrical conductivity analysis, which are as follows: before adsorption (27.23 mS/cm), in 10 minutes of adsorption (26.67 mS/cm), 20 minutes (26.19 mS/cm) and 30 minutes (26.09 mS/cm). Therefore, the displayed values show that there was no adsorption of Na_2SO_4 by the expanded perlite, thus not affecting the electrochemical oxidation process due to a possible adsorption of the electrolyte.

3.3.2 Total organic carbon (TOC) analysis

3.3.2.1 TOC results for the electro-oxidation/adsorption sequence

In order to observe the removal of organic matter after electrochemical oxidation experiments, TOC analyzes were performed. Table 10 summarizes the results of removal of TOC after the sequential electro-oxidation/adsorption treatment when using as an anode Pb/PbO_2 and Ti/Pt at different pH (1, 4.5 and 8) in the current densities evaluated in this study. Analyzes of samples submitted to the adsorption process after electro-oxidation were also carried out in order to assess whether there was influence of adsorption on the removal of organic matter.

Current density is the driving force for electrochemical reactions. The increase in current density (60 mA/cm^2) provides maximum production of hydroxyl radicals (OH) in the reaction medium, increasing the degradation of dye molecules (SINGH *et al.*, 2016; DOS SANTOS *et al.*, 2020). This explains the increased removal of the TOC with increased current density (Fig.11).

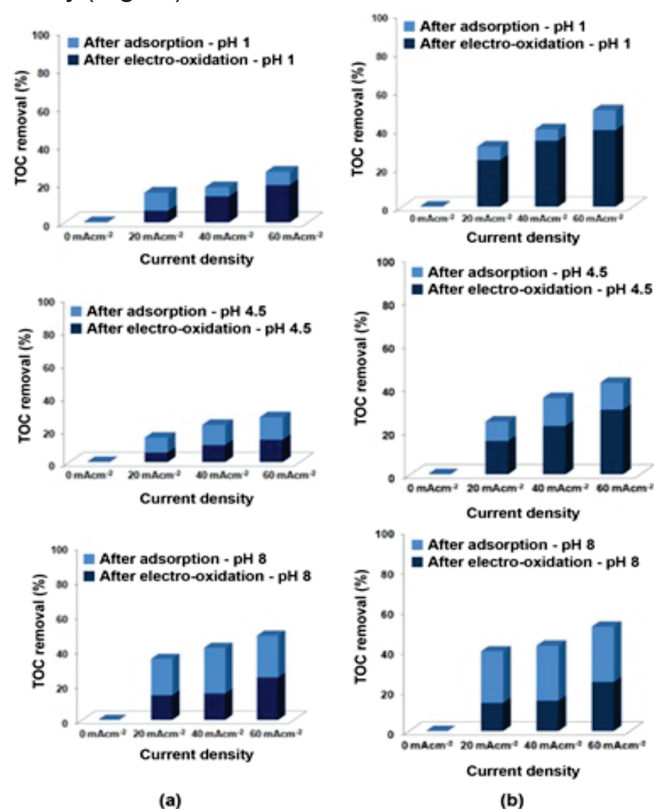


Figure 11. Percentage of TOC removal for the novacron blue dye after sequential electro-oxidation/adsorption treatment at different current densities for the (a) Pb/PbO_2 and (b) Ti/Pt electrodes
Fonte: elaborada pelos autores.

Thus, considering the electro-oxidative treatment, it was found that the Pb/PbO₂ electrode showed a higher percentage of TOC removal compared to the values obtained for the Ti/Pt electrode, considering all the current density values studied after time 60 minutes. Previous work shows that this can be explained because the Ti/Pt anode is an “active” electrode, the oxidizing species originating from it are the MO type oxides, due to the interaction between the electrode (M) and hydroxyl radicals (OH) electro-generated on the electrode surface, lowering the efficiency of the dye electro-oxidation compared to the “non-active” Pb/PbO₂ electrode. Thus, the Ti/Pt electrode can only cause the azo bond to break (-N=N-) of Novacron Blue (chromophore group), removing the color from the aqueous synthetic effluent, but presenting a low mineralization efficiency of organic matter when compared to the “non-active” electrode (Pb/PbO₂). Pb/PbO₂ allows the direct oxidation of dye molecules by the attack of hydroxyl radicals (OH) being more efficient in the degradation process by generating by-products and mineralizing the organic load, causing a better reduction in TOC (Araújo, 2014; Malpass et al., 2008; Miwa et al., 2006; ROCHA *et al.*, 2012).

It is observed that in all pH values, the removal of TOC was greater after the sequential adsorption process with the expanded perlite after electro-oxidation. This indicates that the intermediate compounds formed after the Novacron Blue degradation process were adsorbed by the expanded perlite used in this study as an adsorbent. It is also observed that this increase was more intense at pH 8 where it is known that the increase in pH favors the adsorption step as it ensures the Bronsted acid-base interaction between the silanol groups of the perlite (Si-OH) and the amino groups (-NH₂) of the dye (ALMEIDA *et al.*, 2017).

Another point to be highlighted for lower efficiency in reducing TOC with Ti/Pt anode compared to Pb/PbO₂, is that the possible intermediates formed as by-products of electro-oxidation degradation with Ti Pt can accumulate on the surface of the electrode and

cause a decrease in its efficiency. Therefore, for there to be total elimination of organic compounds in the Ti/Pt electrode it would be necessary to significantly increase the oxidation time with which there would be an increase in energy consumption, which would make the process unfeasible –(Chou et al., 2010; Oliveira et al., 2019).

Table 10
Results of removal of TOC after the sequential electrooxidation/adsorption treatment when using as Pb/PbO₂ and Ti/Pt anodes

pH	Anode	Current density (mA/cm ²)	TOC removal (%)
1	Ti/Pt	20	31.09
	Ti/Pt	60	50.00
	Pb/PbO ₂	20	20.12
4.5	Pb/PbO ₂	60	37.17
	Ti/Pt	20	24.29
	Ti/Pt	60	42.22
8	Pb/PbO ₂	20	21.09
	Pb/PbO ₂	60	35.65
	Ti/Pt	20	39.09
	Ti/Pt	60	51.98
	Pb/PbO ₂	20	40.08
	Pb/PbO ₂	60	60.10

Fonte: elaborada pelos autores.

Another point to be highlighted for lower efficiency in reducing TOC with Ti/Pt anode compared to Pb/PbO₂, is that the possible intermediates formed as by-products of electro-oxidation degradation with Ti Pt can accumulate on the surface of the electrode and cause a decrease in its efficiency. Therefore, for there to be total elimination of organic compounds in the Ti/Pt electrode it would be necessary to significantly increase the oxidation time with which there would be an increase in energy consumption, which would make the process unfeasible –(Chou et al., 2010; Oliveira et al., 2019).

Thus, the data obtained demonstrate that the sequential treatment contributed satisfactorily to the removal of organic matter because of the influence of adsorption, which favored the partial removal of intermediate compounds formed as products of electrochemical oxidation.

3.3.2.2 TOC results for the adsorption/electro-oxidation sequence

TOC analyzes were also carried out for experiments that followed the reverse treatment process, where first the adsorption treatment was carried out and then the electro-oxidative treatment. Table 11 summarizes the results of TOC removal after the sequential adsorption/electro-oxidation treatment when using as an anode Pb/PbO₂ and Ti/Pt at different pH (1, 4.5 and 8) at the minimum current densities (20 mA/cm²) and maximum (60 mA/cm²) of this study. In this case, in the TOC analysis, only the electro-oxidative treatment was considered since the adsorption treatment was carried out in the first place and it does not generate intermediate compounds.

The results obtained through the analyzes performed with the Pb/PbO₂ anode showed a higher TOC removal content when compared to those performed with the Ti/Pt electrode, for all the current density and pH values analyzed (Fig. 12). As already discussed, Pb/PbO₂ allows the direct oxidation of dye molecules by the attack of hydroxyl radicals (OH) being more efficient in the degradation process by generating by-products and mineralizing the organic load, causing a better reduction in TOC (ARAÚJO, 2014; MALPASS et al., 2008; MIWA et al., 2006; ROCHA et al., 2012).

However, as shown in Table 11, the efficiency of reducing the TOC due to the inversion of the sequential treatment process (adsorption before electro-oxidation), affected the effectiveness of the reduction of organic matter in the synthetic effluent, despite having favored the process of removing the dye color. This is perfectly explainable since the expanded perlite played a fundamental role in the process of removing the degradation by-products after the electro-oxidative oxidation of Novacron Blue, reducing the TOC with good efficiency (60.10%) due to the interaction of the Si-OH groups of the adsorbent with the intermediate compounds formed after electrooxidation with the Pb/PbO₂ electrode (identified by GC-MS).

Table 11

Results of TOC removal after sequential adsorption/ electro-oxidation treatment when using Pb/PbO₂ and Ti/Pt as anode

pH	Anode	Current density (mA/cm ²)	TOC removal (%)
1	Ti/Pt	20	10.33
	Ti/Pt	60	21.46
	Pb/PbO ₂	20	25.18
	Pb/PbO ₂	60	38.36
4,5	Ti/Pt	20	7.78
	Ti/Pt	60	19.54
	Pb/PbO ₂	20	21.18
	Pb/PbO ₂	60	42.16
8	Ti/Pt	20	17.39
	Ti/Pt	60	29.65
	Pb/PbO ₂	20	31.24
	Pb/PbO ₂	60	47.75

Fonte: elaborada pelos autores.

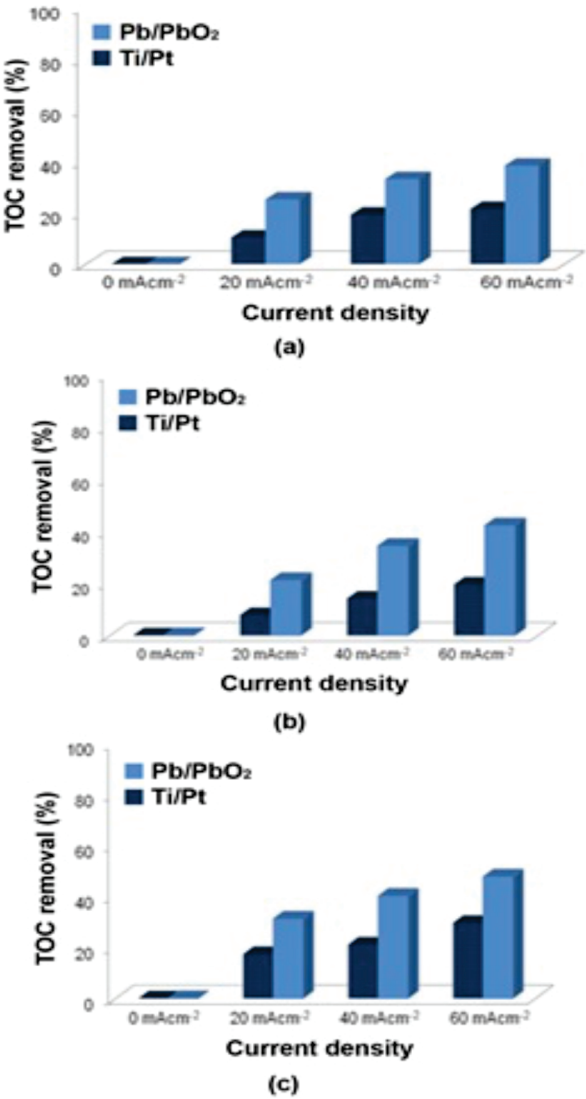


Figure 12. Percentage of TOC removal for Novacron Blue dye after sequential adsorption/electro-oxidation treatment at different current densities in (a) pH 1, (b) pH 4.5 and (c) pH 8

Fonte: elaborada pelos autores.

3.3.3 Analysis of electrochemical oxidation products and efficiency of the adsorption process by GC-MS

In order to observe the by-products formed after the electrochemical oxidation experiments, GC-MS analyzes were performed for all pH values (1 and 4.5) at a current density of 20 mA/cm² in a time of 60 minutes of electrolysis for the study with the Pb/PbO₂ anode as this was the one with the best results of the electro-oxidative process (color removal efficiency, TOC reduction efficiency and energy cost). Analyzes of the samples submitted to the adsorption process after electro-oxidation were also carried out in order to assess whether there was influence of the adsorption in the removal of the formed intermediate compounds.

Figure 13 shows the intermediate compounds formed during the electro-oxidation (with the Pb/PbO₂ anode) of the Novacron Blue dye. The results obtained after 60 minutes of electro-oxidation to pH 1 showed the formation of aniline, 3-methyl benzoic acid, phthalic acid, 1,6-dimethyl naphthalene and the hydroxybenzene sulfonate ion. At pH 4.5, with the exception of the hydroxybenzene sulfonate ion, the formation of the same compounds that appeared at pH 1 is observed, but the presence of naphthalene appears.

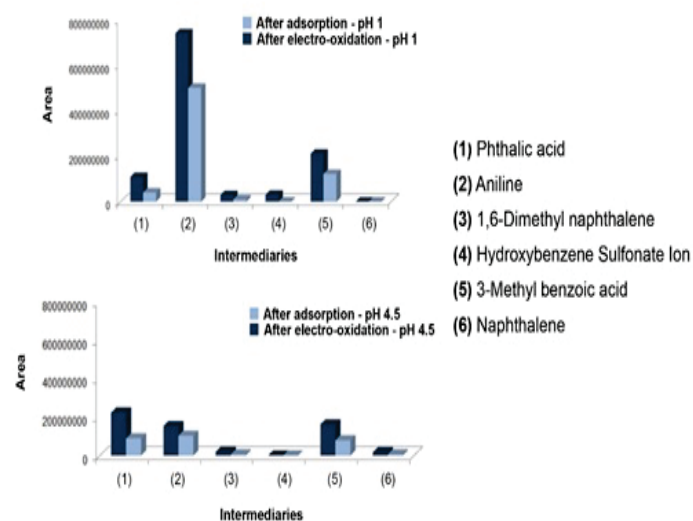


Figure 13. Electro-oxidation degradation products of Novacron Blue dye identified by GC-MS using Pb/PbO₂ anode
Fonte: elaborada pelos autores.

These products can be explained considering that in the Pb/PbO₂ electrode the reactions between the radicals (OH) and the organic compounds occur directly on the electrode surface, promoting a greater reaction speed and forming degradation compounds due to the electrooxidation of the dye molecule directly (MARTINEZ-HUITLE *et al.*, 2004; PANIZZA & CERISOLA, 2007; BENSALAH, QUIROZ ALFARO & MARTÍNEZ-HUITLE, 2009; ROCHA *et al.*, 2012).

Observing the results of the adsorption after the electrochemical oxidation it is noticed that in all the cases of pH analyzed the adsorption with the expanded perlite was essential for the significant removal of the formed intermediates. These results indicate that the sequential treatments, in addition to contributing to the color removal of both dyes, also contribute to the removal of the formed intermediate compounds, since in this case, the expanded perlite adsorbed the by-products resulting from electrooxidation. These data were confirmed by the analysis of total organic carbon (TOC) which showed a significant removal of organic matter, after the sequential treatments of electro-oxidation/adsorption.

3.3.4 Evaluation of the removal of Pb residues by atomic absorption spectrometry (AAS) from electrooxidation

In order to observe the presence of lead in the treated effluent after the electrochemical oxidation/adsorption treatments using Pb/PbO₂ electrodes, atomic absorption analyzes were performed. These analyzes were obtained considering the mentioned pH values with a current density of 40 mA/cm², both after electro-oxidation and after adsorption in order to verify the influence of perlite on the adsorption of the said metal.

Figure 14 shows the results obtained through that technique. It was possible to observe that there was a small detachment of lead (in the order of ppm) from the electrode to the effluent during the electro-oxidative treatment. However, it is also observed that these values suffer a reduction when, after

electrochemical oxidation, the effluent goes to the adsorption treatment, in this way it is possible to verify that the expanded perlite acts by significantly adsorbing the lead that is in solution.

Thus, it has to be said that for the synthetic effluent of the Novacron Blue dye, the lead concentration values range from 2.34 to 1.87 mg/L (pH 1), 2.97 to 1.84 mg/L (pH 4.5) and 2.48 to 1.74 mg/L (pH 8), according to Fig. 14.

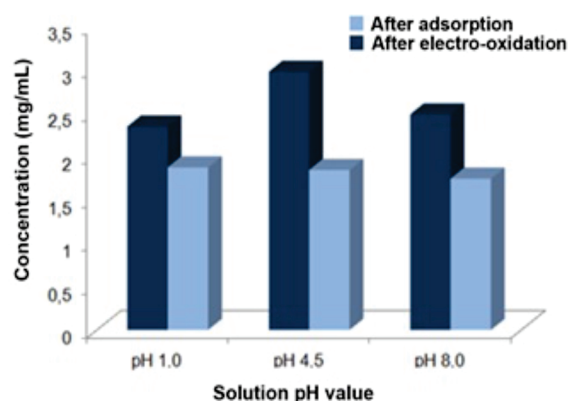


Figure 14. Total lead concentration obtained by Atomic Absorption Spectrometry using Pb/PbO₂ anode in the electro-oxidation of Novacron Blue dye

Fonte: elaborada pelos autores.

Therefore, expanded perlite acts as a good adsorbent for intermediate compounds formed after electrochemical degradation of the dye, as well as removing residual Pb ions from the electrode, making the sequential electro-oxidation/adsorption process a viable treatment for removing Novacron Blue from aqueous effluents.

4. CONCLUSIONS

The process of removing the Novacron Blue from aqueous solution by the sequential electrochemical oxidation/adsorption and adsorption/electro-oxidation technique proved to be effective considering the parameters analyzed in this work, since the isolated techniques were effective, as electro-oxidation alone requires a longer time test, resulting in a higher energy cost for total color removal

(150 minutes), and adsorption was unable to remove the color completely due to the fast saturation of the adsorbent. The electro-oxidation/adsorption sequence showed better results (color removal efficiency, TOC reduction efficiency and energy cost). The adsorption treatment was the indispensable tool in this study, since the expanded perlite (a low cost natural aluminosilicate) proved to be efficient in removing the degradation by-products generated after electro-oxidation of the dye, confirmed by the reduction of the total organic carbon of the samples. Therefore, the sequential electrochemical oxidation/adsorption technique for the treatment of wastewater containing Novacron Blue was highly effective and an excellent proposal for the environmental remediation of water bodies.

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Interest conflicts

The authors declare that they have no conflicts of interest.

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