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Electrolytic Treatment of Oily Residues from Mechanical Industry

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***Abstract* – Electroflocculation can be defined as a process that is the association of electroflotation and electrocoagulation in the treatment of industrial effluents. It is an alternative technology employing electrolysis reactions that enables the removal of oily liquids and emulsions from mechanical industries, which are comprised mainly of mixtures of temporary protective oils, lubricating oils and mineral oils. The functioning principle of the electrolytic process consists of applying an electrical potential to an aqueous solution using carbon steel electrodes, promoting the dissolution (corrosion) of this metal with the generation of ions and gases (oxygen and hydrogen), which form flocculation-coagulation reactions suitable for oily residues at the proper pH. This article reports the laboratory experiments and results of treatment in a small unit showing the reduction of the value of Chemical Oxygen Demand (COD) and the excellent oily mass removal in industrial effluents.**

***Keywords* — Electroflocculation, Electroflotation, Electrocoagulation, Industrial Effluents, Environmental.**

INTRODUCTION

The industry for oil production in Brazil seeks to adapt its business and technological management in constant harmony with preservation of the environment. In this way, unceasingly allied techniques and technologies are sought with knowledge of materials, design, manufacturing facilities, industrial assembly and anticorrosive techniques, so that all of the equipment intended for oil production has an intrinsic reliability that will ensure, directly or indirectly, environmental preservation.

In the specific case of a mechanical company which manufactures and assembles various equipment for the production of petroleum and gas, Brazilian environmental compliance is critical for managing the correct final disposal of industrial waste generated, mainly those from oil as greases, lubricating oils, hydraulic fluids, temporary protective anti-corrosives, and cutting and machining fluids, etc.

As the aim is to not pollute water in the environment, a good economy and its scarcity can now be seen as an opportunity for a business that will enforce the rationale use of water and consequently the treatment of industrial effluents. The first step was the promulgation of the Law of Waters, n° 9.433/97 (01/08/1997), which allowed a price for water that is captured today free of water bodies, because today you pay only the cost of treatment and distribution [1, 2].

In this way, the treatment of oily liquid wastes from a mechanical industry which manufactures equipment for oil production is extremely relevant as an environmental management system.

This paper aims to show that the electrolytic process of oily liquid waste treatment will enable current information to be gathered showing, qualitatively and quantitatively, its contribution as an effective alternative treatment aimed at the reduction of Chemical Oxygen Demand (COD) and oily mass.

II. ELECTROLYTIC TECHNOLOGY ASSOCIATED WITH THE REMOVAL OF OILY MASS AND CHEMICAL OXYGEN DEMAND

Electroflocculation can be defined as a process that is the association of electroflotation and electrocoagulation in the treatment of industrial effluents.

A. Electroflotation

Electroflotation is an electrochemical process that allows the generation of micro-bubbles of oxygen (O_2) and hydrogen (H_2), respectively, at the anode and cathode, following the reactions:

Cathode (-): $2\,H_2O + 2\,e^- \rightarrow H_2 + 2OH^-$

Anode (+): $H_2O - 2\,e^- \rightarrow \frac{1}{2}\,O_2 + 2\,H^+$

According to Scott [3], the main advantages of electroflotation are focused on the following points:

- The formation of tiny dispersed gas bubbles (O_2 and H_2) allows the flotation and removal of very suspended fine particles, oil, colloids, etc.;
- The gas micro-bubbles generated in electrodes collide with the oily particles in suspension and are then adsorbed; by having a lower density, they promote the flotation effect and therefore clarification of the effluent, according to the mechanism shown in Figure 1;
- It is possible that the generation of oxygen at the anode promotes oxidation and the consequent breaking down or destruction of any resistant organic molecules. Similarly, the hydrogen produced on the cathode can function as a reducing agent of organic molecules.

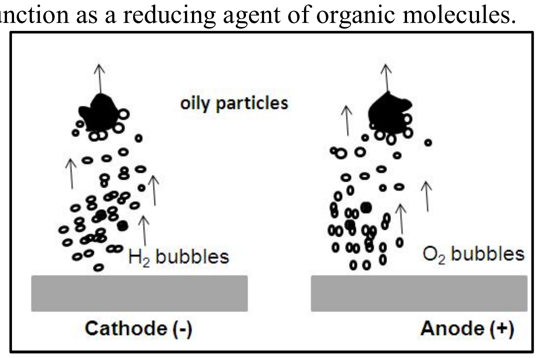

Fig.1. Electroflotation of oil particles

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B. Electrocoagulation

The electrocoagulation process comprises the *in situ* generation of coagulants by dissolving electrically either iron or aluminum from electrodes (anodes) while hydrogen (H_2) generation is achieved at the cathode. The following are reactions that occur in carbon steel anodes, in the cathode and the respective coagulation reactions that can occur in the pH range of 6.5 to 9.0 [4,5,6,7].

For carbon steel anode (+):

$Fe - 2e^- \rightarrow Fe^{2+}$

Coagulation reactions:

$Fe^{2+} + 2\ OH^- \rightarrow Fe(OH)_2$ (alkaline conditions)

$2\ Fe^{2+} + ½\ O_2 + H_2O \rightarrow 2\ Fe^{3+} + 2\ OH^-$ (acidic conditions)

$Fe^{3+} + 3\ OH^- \rightarrow Fe(OH)_3$

The reaction at the cathode (-) is:

$2\ H_2O + 2e^- \rightarrow H_2 + 2OH^-$

III. Materials and Methods

The electroflotation-electrocoagulation experimental unit consisted of a 2 L glass beaker batch (Figure 2) or a polyethylene continuous reactor with a capacity of 7 L (Figure 3), with anodes and cathodes of carbon steel in a rectangular shape, installed horizontally in the middle of the beaker or polyethylene continuous reactor.

As shown in Figure 4, the carbon steel electrodes (cathodes and anodes) are separated by ceramic rings. The electrodes for the batch system (beaker) are made up of carbon steel plates of 120x80x2mm, while the plates for the polyethylene continuous reactor are 250x80x2mm.

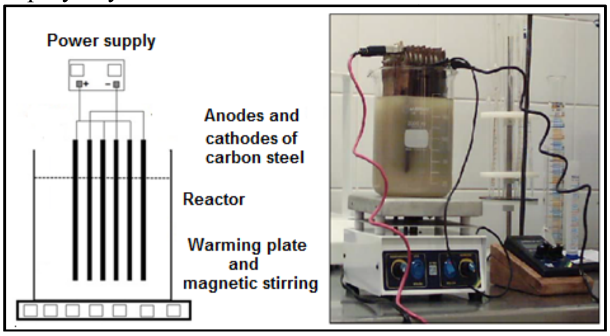

Fig.2. Schematic diagram and electroflotation-electrocoagulation experimental batch

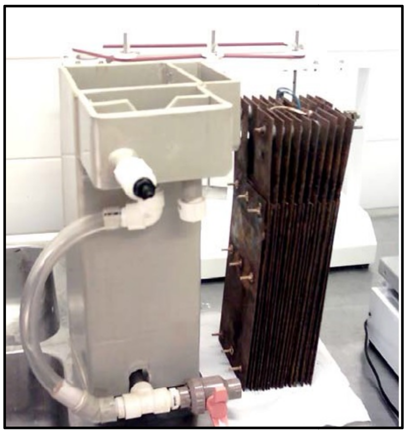

Fig.3. Polyethylene continuous reactor

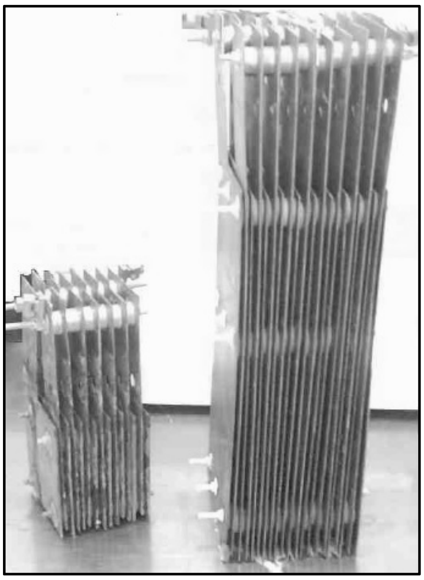

Fig.4. Carbon steel electrodes

The electrodes are connected to a DC power supply providing 0-20 V (2-5A) to batch process (beaker) and DC power supply providing 0-50V (15-20A) to the polyethylene continuous reactor. The DC power supply has galvanostatic operational options for controlling the current density.

The batch processing time was 30 minutes. The flow for the continuous process was 100 mL/min for a total period of 60 minutes. The pH for processing varied from 4.0 to 6.0, while in the final decantation, pH ranged from 8.0 to 9.0. The temperature was maintained from 30-40°C. Samples of 100 L were taken from each industrial effluent stream to be used as standards of effluent samples from the premises of the industrial assembly of equipment for oil production. Sample "A" was constituted of cutting oils, the residues of protective oils, lubricating oils and grease residues, while the "B" sample was composed basically of oils and hydraulic fluids.

In evaluating the electrolytic treatment, the COD (Chemical Oxygen Demand) test was taken as the base representing the limit of possibility of oxidation of wastewater and the volume of oil electro-float removed. The COD test oxidises the whole sample through the use of potassium dichromate in acidic medium, by taking measurements after the use of reagent. The final outcome of the test is expressed as the amount (in mg) of oxygen (the potassium dichromate-$K_2Cr_2O_7$) used for the oxidation of a litter of effluent and can be understood as a measure of organic matter, expressed in oxygen. All experiments were repeated three times and the experimental error was estimated as 3%.

IV. Results and Discussion

Figure 5 represents the electrolytic treatment performed with the "A" samples, which were constituted, basically, of cutting oils, residues of protective oils, lubricating oils and grease residues. The average volume of oily mass floated on the electrolytic treatment was higher than 80%, and the volume of deposited mass was 10% on average.

The removal efficiency (%) of COD was defined as follows:

Removal efficiency (%) = 100 (COD_I – COD_F/COD_I), where COD_I is the initial and COD_F is the final treatment. The average removal efficiency was 70%.

Figure 6 represents the three steps of the electrolytic treatment of the standard batch sample "B". This sample of effluent basically consisted of mixtures of oily residues and hydraulic fluids with dye. Hydraulic fluids used in petroleum operations are based on ethylene glycol and bactericides with an intense green dye to identify possible leaks.

Fig.5. Electrolytic treatment with sample "A"

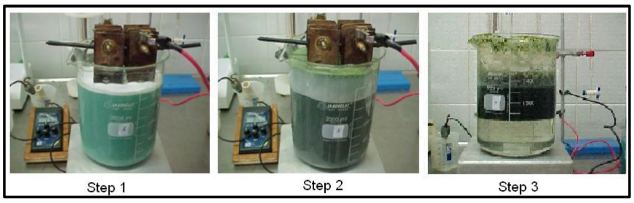

Fig.6. Aspect of the three stages (early, after 15 minutes and the separation of the phases) of the electrolytic treatment of batch standard sample "B".

Step 1 represents the start of the treatment, while step 2 is after 15 minutes, where the color change and formation of conditioned material at the top can be observed. In step 3, good separation of the aqueous phase from the oily phase and removal of the green dye can be seen

More than 90% of the oily phase and dyes was removed; however, the reduction of COD was in the order of 20%, showing the difficulty of degradation (oxidation) of the ethylene glycol constituent of hydraulic fluid.

The laboratory tests performed on standardized samples "A" and "B" showed that electrolytic processing favored the reduction of oils, greases, surfactants and the content of zinc ($Zn^{2+)}$ as a metal contaminant. The addition of polyelectrolyte in samples promoted the better separation of oily masses.

The removal efficiency increased with increasing voltage; the optimal voltage applied in this work was 5 V. However, it is important to note that the high electrical consumption prevents the electrolytic process from becoming viable.

It was also noted that reducing the conductivity of the process can cause a passivation in the electrodes depending on the oily mass present. Small additions of sodium chloride increase the conductivity of the medium and therefore favor the reactions in carbon steel electrodes.

The mechanism shown in Figure 7, representing the electrolytic process of flotation, coagulation and precipitation in the treatment of effluents, is based on studies conducted by the authors referenced [4, 5, 6.7].

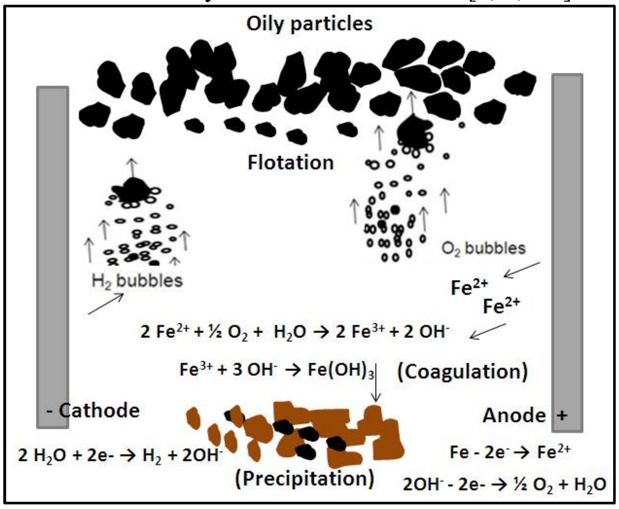

Fig.7. Mechanism of the electrolytic process of oily effluents

V. Conclusion

On the basis of the tests and chemical analyses carried out, electrolytic treatment of effluents from a mechanical engineering perspective specialized in the production of equipment for oil production, the following conclusions can be drawn:

- The average volumes of oily mass floated on electrolytic treatment were higher than 80% in the samples constituted of cutting oils, residues of protective oils, lubricating oils and grease residues, while in effluentsconsisting of hydraulic fluids contaminated with oil, the removal was greater than 90%;
- The electrolytic process removed about 70% of the COD in oily effluents; however, in residues of hydraulic fluids, this was in the order of 20%, showing the difficulty in the degradation (oxidation) of the ethylene glycol constituent of hydraulic fluid;
- The addition of polyelectrolytes as an aid to flocculation arguably produces excellent results in clarification, therefore decreasing the total treatment time required.

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