Involvement of controlled Corrosion of Steel and Aluminum in the Treatment of Industrial Wastewater: Case of the Removal of Evans Blue in Aqueous Solution

F. Adjie BAH¹, G. KENNE DEDZO¹, E. FOTO², and C. P. NANSEU - NJIKI¹

¹Laboratory of Physical and Analytical Chemistry (LCPA) of the University of Yaoundé I, Cameroon
²Laboratory Hydrosciences Lavoisier, UNESCO Chair on Water Management, University of Bangui, Faculty of Sciences BP 908 Bangui, Central African Republic

Copyright © 2019 ISSR Journals. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

ABSTRACT: The present work focuses on the electrocoagulation treatment of an Evans blue solution (B.E). Of the four bottom salts (KCl, NaCl, Na₂SO₄, K₂SO₄) used for the treatment, it appears that, for an optimum charge density of 2.33 F/m³ and a voltage set at 1.5V, potassium chloride (KCl) provides the best abatement rate (95.5%). The variation of the pH of the solution reveals that the best abatement rates are obtained for the basic pH. pH 9 is optimal for treatment whereas for pH values above 10, inefficiency is noted. The speed of the treatment increases with the density of the applied current, the treatment is efficient and the energy cost is limited for a current density value set at 20 mA/cm². For the same set values of charge density and voltage, the abatement rate is inversely proportional to the concentration of B.E, and aluminum is better suited as electrode material, compared to iron.

KEYWORDS: electrocoagulation, Evans blue, abatement rate, charge density, current density.

1 INTRODUCTION

The development of technology, and the demographic pressure, the anthropic activities are at the origin of the perpetual sources of various pollutions among others the water pollution, generated by domestic, agricultural, industrial discharges etc. [1, 2]. Thus, the man, aware of the harmful consequences of his activities on nature and on himself, seeks solutions to limit pollution to a level considered acceptable. The setting of standards by international organizations such as the World Health Organization (WHO) contributes to raising human awareness to regulate the quantities of pollutants discharged into the environment [3]. In order to meet these fixed concentration limits, the man must resort to different methods of depollution. One of the electrochemical water treatment techniques is electrocoagulation, which involves the corrosion of a metal electrode (iron or aluminum), in order to generate in situ the metal hydroxides, main coagulating agents used during the processes chemical.

2 MATERIALS AND METHODS

2.1 MATERIALS

In this study, the electrocoagulation method is used to remove a dye in aqueous solution. We propose here to determine the optimal conditions for efficient removal of Evans Blue (B.E) by electrocoagulation. B.E is one of the dyes used in the textile industries. Effluents from these industries are often loaded with chemicals and must be treated before discharge to avoid environmental pollution [3]. Prolonged exposure to more than 10 mg/L of solution containing this dye may cause liver cancer in humans, as well as skin and eye contact irritation. Of chemical formula C₃₄H₂₄N₆Na₄O₁₄S₄, its molar mass is 960.82 g/mol and its structural formula is as shown below (Fig1)
2.1.1 Principle of Electrocoagulation (EC)

Electrocoagulation is based on the basic techniques of electrochemistry. An electric current is passed through the water to be treated containing metal electrodes, which makes it possible to produce the metal hydroxides in situ, it is the latter that will neutralize the pollutants present in the medium and facilitate the treatment [18]. The electrode material used for electrocoagulation must contribute to the elimination of pollutants with a good yield and not increase the toxicity of sludge and treated effluent [4]. Aluminum and iron are commonly used in relation to their affordability, availability and ionic form, which has a high valence that can rapidly cause colloid agglutination and therefore rapid settling [7].

The electrocoagulation process is summarized in the diagram below:

Fig. 1. Evans blue formula: Tetra sodium 6,6'- (3,3'-dimethoxy- (1,1'-biphenyl-4,4'-diyl) bis (azo) bis (4-amino-5-hydroxy-1,3-naphtalènedisulfonate).

Fig. 2. Diagram of the principle of electrocoagulation [18]
2.2 Methods

2.2.1 Modes of treatment in electrocoagulation

The different effluent treatment methods used in EC are:

Continuous mode: The effluent circulates continuously in the reactor, which makes it possible to homogenize the treated solution. This displacement of the effluent is generally caused by a pump or by a difference in altitude between the generator and the feed tank. The flow rate imposed on the effluent varies according to the different treatment parameters. This mode is used for large volumes of effluents to be treated.

Batch mode: The effluent is stable in the reactor. Homogenization can be provided by a magnetic stirrer. This mode is proposed for small quantities of waste water.

The different reactions taking place during the electrocoagulation process are as follows:

Mechanism [1]

| Anode: | Fe | → | Fe$^{2+}$ + 2e$^{-}$ (1) |
| Chuck: | 2H$_2$O + 2e$^{-}$ | → | 2OH$_{aq}$ + H$_2(g)$ (2) |
| Solution: | Fe$^{2+}$ + 2OH$_{aq}$ | → | Fe(OH)$_2(aq)$ (3) |
| Appraisal: | Fe + 2H$_2$O | → | Fe(OH)$_2(aq)$ + H$_2(g)$ (4) |

Mechanism [2]

| Anode: | 4Fe$_{(s)}$ | → | 4Fe$^{2+}_{(aq)}$ + 8e$^{-}$ (5) |
| Chuck: | 8H$_{aq}^+$ + 8e$^{-}$ | → | 4H$_2(g)$ (6) |
| Solution: | 4Fe$^{2+}_{(aq)}$ + 10H$_2$O + O$_2(g)$ | → | 4Fe(OH)$_3(aq)$ + 8H$_{aq}^+$ (7) |
| Appraisal: | 4 Fe$_{(s)}$ + 10 H$_2$O + O$_2(g)$ | → | 4 Fe(OH)$_3(aq)$ + 4H$_2(g)$ (8) |

A multitude of iron hydroxides and complexes form in solution such as Fe(OH)$_3(aq)$, Fe(OH)$_2^{2+}$, Fe(OH)$_3^{3+}$, Fe(OH)$_4^{4+}$ et FeO(OH), Fe(OH)$_2^{2+}$ [18].

With the aluminum electrode

| Anode: | Al$_{(s)}$ | → | Al$^{3+}$ + 3e$^{-}$ (9) |
| Chuck: | 2H$_2$O + 2e$^{-}$ | → | H$_2(g)$ + 2OH$^-_{aq}$ (10) |
| In acid medium: | 2H$_{aq}^+$ + 2e$^{-}$ | → | H$_2(g)$ (11) |
| Solution: | 4Al$^{3+}$ + 10H$_2$O + O$_2(g)$ | 4 Al(OH)$_3(aq)$ + 8H$_{aq}^+$ (aq) (12) |
| Assessment: | 4 Al$_{(s)}$ + 10 H$_2$O + O$_2(g)$ | 4 Al(OH)$_3(aq)$ + 4 H$_2(g)$ (13) |

The Al$^{3+}$ and OH$^-$ ions react to give the monomeric forms such as Al(OH)$_3^{3+}$, Al(OH)$_2^{2+}$, Al(OH)$_4^{4+}$ and polymers such as: Al$_2$(OH)$_3^{2+}$, Al$_3$(OH)$_5^{3+}$, Al$_4$(OH)$_7^{4+}$, Al$_6$(OH)$_9^{5+}$, Al$_{13}$(OH)$_{25}^{17+}$ which will be converted to Al(OH)$_3(aq)$.

Operating procedure of BE treatment used

From a stock solution of 10$^{-2}$ M B.E, a daughter solution of 25 µM B.E is prepared. In a beaker containing 200 mL, the KCl solution (0.1M) and the magnetic bar, 0.5 mL of the stock solution of B.E is removed and added to the beaker, and placed on a magnetic stirrer. The two active surface iron electrodes 5 cm$^2$ (h = 2.5 cm and l = 2 cm) are arranged vertically in the solution and connected to the generator by means of conducting wires. The charge density is varied from (0, 0.31, 0.777, 1.55, 2.33 and 3.10 F/m$^3$). At each charge density value, 200 μL of the beaker solution is removed and diluted to 1/10 if necessary. Afterwards, the measurement of the absorbance of the residual concentration is obtained from the previously established calibration line. The measurement of the voltage is made by reading it on the generator and the different abatement rates are obtained from the formula:

abatement rate = \[
\frac{(C_0 - C)}{C_0} \times 100
\]

Where $C_0$ is the initial concentration of B.E in µM and C is the measured concentration in µM.
We then measured 4, this is:

- Density of charge, Quantity of electricity per unit of volume of effluents to be treated: \( \rho = \frac{I.t}{96500V} = \frac{Q}{V} \) expressed in, F / m\(^3\); current intensity (A) \( t = \) electrolysis time (s), \( V = \) volume of the effluent (m\(^3\));

- pH, It acts essentially on the rate of formation of the precipitates of metal hydroxides, and consequently, on the coagulation;

- The density of the current, Ratio of the intensity of current by the active surface of the electrode:
  \( \sigma = \frac{I}{S}, \text{mA/cm}^2; \sigma = \) current density, \( I = \) current intensity (mA), \( S = \) electrode area (cm\(^2\)) and

- Conductivity, Ability of a solution to conduct electrical current, \( \mu S/cm \).

### 3 RESULTS AND DISCUSSION

#### 3.1 USE OF IRON ELECTRODES

##### 3.1.1 EFFECT OF THE SUPPORTING ELECTROLYTE ON THE ELIMINATION OF B.E BY ELECTROCOAGULATION

Removal of B.E by electrocoagulation with iron electrodes was performed using different carrier electrolytes: KCl, NaCl, Na\(_2\)SO\(_4\) and K\(_2\)SO\(_4\). By varying the charge density from 0 to 3.10 F / m\(^3\), the effect of each electrolyte on the removal of Evans blue was studied.

The following Fig3 shows the evolution of the abatement rate as a function of the charge density for each support electrolyte used.

![Fig. 3. Evolution of the abatement rate as a function of the charge density when using different types of support electrolytes for a charge density ranging from 0 to 3.10 F / m\(^3\).](image)

With regard to this figure, it is noted that the evolution of the abatement rate is similar for the four electrolytes used. In general, the abatement rate increases with the charge density.

When the value of the latter is 1.55 F / m\(^3\), the slopes are larger and the peaks are formed from 2.33 F / m\(^3\). This sharp increase in the abatement rate can be explained by the massive production of ferrous ions in solution that will combine with the hydroxide ions produced at the cathode, to form different types of complexes that can neutralize all the pollution load of the medium. This is illustrated by the equation:

\[
\text{Fe}^{(s)} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2(\text{s}) + \text{H}_2(\text{g})
\]
The flocs observed during B.E elimination treatments float in all cases. This phenomenon could be attributed to the production of dihydrogens at the cathode, which can, by their upward movement, cause flocs on the surface.

These formed flocs are green in color, and the treated solution of B.E becomes rusty at the end of the experiment or after filtration. These color changes are attributed to the respective formation of ferrous and ferric hydroxides according to the equation:

\[ 3\text{Fe}^{2+} + 8\text{H}_2\text{O} \rightarrow 4\text{H}_2\text{O}_2 + 2\text{Fe}^{3+} + 2\text{Fe}(	ext{OH})_3 \] (15)

In addition, it is found that the highest abatement rates are obtained with the electrolytes containing the chloride ions. A reduction of 98.8% is already obtained with NaCl, for an optimal charge density of 2.33 F/m³, followed by KCl with 95.5% for the same charge density value. These results are consistent with those found by Daneshvar et al, Ahyao et al [24,25] who worked on the treatment of yellow acid Cl 23 and the treatment of a daily effluent by electrocoagulation, which stipulate that chloride ions significantly reduce the adverse effects of other anions that may be present in the water and are very good conductors of electric current, which confirms the speed and effectiveness of treatment with these electrolytes. With NaCl, it is also found that the floc formation is very fast in solution and the metal deposition is considerable at the anode at the end of the treatment.

The following Fig4 shows the evolution of the voltage during the treatment during the use of the different electrolytes supports:

![Fig. 4. Evolution of the voltage for a charge density ranging from 0 to 3,10F / m³ during the use of the different support electrolytes.](image)

The voltage measurements made in the case of the use of the different electrolytes supports, show that it increases gradually and reaches a limit where it remains constant until the end of treatment. The greatest increase in tension is observed in the case of the use of NaCl (1.6V), followed by KCl (1.5V), the lowest value is noted in the case of the use of K₂SO₄ (1, 1V). This increase in voltage during the experiment is attributed to the increase in the resistance of the electrolyser, caused by the metal deposition at the anode (this deposit is even very visible on the anode at the end of each experience). The order of evolution of the voltage curve is also related to the conductivity of the solution. The more conductive the solution, the increase in voltage is high. Since the conductance of potassium is higher than that of Na, the solution of KCl (0.1M) is the best conductive solution with a limited number of ions in solution. The objective being to have a high abatement rate for low voltage values to optimize the treatment, the KCl (0.1M) will be maintained as the best supporting electrolyte and the value of the voltage found during its use (1.5V), for an optimal charge density set at 2.33 F / m³ which made it possible to have a 95.5% reduction.
3.1.2 **Effect of pH Variation**

To study the effect of pH on the treatment by electrocoagulation, the initial pH of the solution of Evans blue at 25 μM was measured, this pH is equal to pH = 6.45, the objective being to adjust its pH value in a range of 3, 5, 9, 10, and 11 with the KOH and HCl solutions. The study of the variations of the abatement rate when the voltage and the charge density are fixed respectively at 1.5V and 2.33 F/m³ has been made. KCl (0.1 M) was used as the supporting electrolyte. At each charge density interval, the concentration of the solution is measured from a spectrophotometer. The values of these different concentrations made it possible to calculate the different rates of abatement. At the end of the treatment, the final pH of the solution was also measured. Fig 5 shows the evolution of the abatement rates for the different fixed pH values.

![Fig. 5. Evolution of the abatement rate of the different pH values fixed for a charge density ranging from 0 to 2.33 F/m³ and a voltage set at 1.5V](image)

The analysis of Fig 5 shows that the best abatement rate is obtained in the case of basic pH, when the charge density is set at 2.33 F/m³, and the voltage at 1.5V.

For the initial pH value of the B.E solution set at 9, the reduction rate obtained is 98.90%, followed by pH 10, where 96.66% of the abatement rate was obtained.

While trying to continue the treatment at pH = 11, the solution of BE tends to a purple color, which explains the stop of the treatment with pH = 10, this situation made it possible to understand the literature which stipulates that with pH> 10, the absorption wavelength of BE changes, the amorphous Fe (OH)₃ (s) responsible for coagulation is not the majority and the cathode can be chemically attacked [9,20].

All of these results are consistent with those of Gousmi et al [26] who have applied the EC process to petroleum rejection, arguing that most of the metal hydroxides responsible for coagulation are formed at basic pHs. Thus the optimum pH value of BE treatment is set to 9.

Fig 6 below shows the evolution of the different pH values fixed during the treatment:
In general, it is noticed that for the experiments carried out in acid medium, an increase of the pH during the treatment is observed [7], this can be attributed to the reduction of the hydronium H⁺ ions responsible for the acidity of the water in H₂ gaseous at the cathode according to the equation:
\[ 2H^+ + 2e^- \rightarrow H_2(g) \] (16).

On the other hand for experiments in basic medium, it is a decrease of pH which is observed at the end, this is due to the consumption of the hydroxide ions by the ferrous ions and ferric ions (Fe²⁺ and Fe³⁺) to form the complexes of the hydroxides of iron, responsible for the coagulation of BE in solution [10]. The reduction of the OH⁻ in the medium thus causes the decrease of the pH according to the equation:
\[ Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3(s) \] (17)

3.1.3 Effect of the Variation of the Density of the Current

To study the effect of the current density on the treatment, a variation of it of (2, 10, 14, 20 and 30 mA / cm²) was performed, the charge density was set at 2.33 F / m³ using KCl as the supporting electrolyte. The evolutions of the reduction ratio and the voltage as a function of the current density are respectively given by the following FIGS. 7 and 8:
Fig. 7. Evolution of the abatement rate for a current density ranging from 0 to 30 mA/cm².

Fig. 8. Evolution of the voltage for a current density varying from 0 to 30 mA/cm².

It was noticed during this experiment, that the rate of abatement, as well as the voltage increase gradually with the current density applied, for the largest value of the latter (30 mA/cm²), the flocs start to form very rapidly and the release of dihydrogen at the cathode is more intense and very visible during treatment. The formed flocs take the green color, due to the formation of ferrous ions in solution. When the applied charge density reaches 1.55 F/m³, floc complete flotation is observed and the B.E. treated solution becomes very clear. An abatement rate of 100% of B.E is obtained while the measured voltage reaches 3V. This increase in tension is explained by the formation of a considerable metal deposit at the cathode which is noticed.

The results obtained make it possible to conclude that the density of the current influences the formation speed of the flocs, and therefore the rate of treatment with EC. The higher it is, the faster the treatment [27]. However it is important to
emphasize that the current density should be moderate to avoid excessive energy cost of treatment. For this study a current density set at 20 mA / cm² which allowed to have a reduction rate of 97.7% of the BE would be sufficient.

3.1.4 Effect of variation in B.E concentration

To study the influence of the concentration on the EC treatment of the B.E solution, solutions of B.E of 10 μM, 35 μM and 50 μM were prepared. With these solutions, variations in the abatement rate and voltage were studied by fixing the charge density at 2.33 F / m³, the voltage at 1.5 V and the current density at 20 mA / cm². The following Fig 9 illustrates the different results obtained in this case.

![Fig 9. Effect of the evolution of the abatement rate as a function of the different BE concentrations for a charge density ranging from 0 to 2.33 F / m³, a current density and a voltage set respectively at 20 mA / cm² and 1.5V](image)

The analysis of this Fig shows that as the concentration of BE increases, the abatement rate decreases from 85.69% to 29.85% when the charge density is varied from 0 to 2.33 F / m³. The results obtained show that the applied charge density is effective for lower concentrations of B.E. and less effective for higher B.E. concentrations. This means that for a given treatment, the charge density to be applied must be proportional to the quantity of the pollutant in solution. The concentration of the pollutant must be known in order to better adapt the various electrolysis parameters [28]. Therefore, following this finding, we can conclude that for this study, for a better efficacy of treatment with EC, a BE concentration limited to 10 μM, which allowed us to obtain 85.69% The abatement is sufficient to optimize the treatment. The treated solution of B.E becomes rust after filtration, due to the oxidation of ferrous ions to ferric ions.

3.2 Use of aluminum electrodes

3.2.1 Effect of the supporting electrolyte (KCl) on the elimination of B.E by electrocoagulation

To study the effect of the nature of the electrode on the elimination treatment of the BE, aluminum electrodes are used, keeping the same operating mode and the same electrolysis parameters previously fixed in the case of the iron electrodes. (for a charge density ranging from 0 to 2.33 F / m³, a voltage and a current density set respectively at 1.5V and 20 mA / cm².) In a 200 mL beaker used as an EC reactor and containing a magnetic bar, the solution of KCl (0.1M) is poured and all placed on a magnetic stirrer, 0.5mL of the stock solution of the BE (10⁻²M) is removed and added to the solution. aluminum surface 5cm², as in the case of iron electrodes (H = 3cm and l = 1.67cm) are arranged vertically and connected to the generator through the conductor son. The changes in the rates of BE and of tension are studied when the densities The load is varied from 0 to 2.33 F / m³.
These results are illustrated by Figures 10 and 11.

**Fig. 10.** Evolution of the abatement rate as a function of the charge density for a current density and an initial voltage set respectively at 20 mA/cm$^2$ and 1.5 V when using the aluminum electrodes.

**Fig. 11.** Evolution of the voltage when using the aluminum electrodes for a charge density set at 20 mA/cm$^2$

During this study, we find that the discoloration of the B.E solution is pronounced as soon as a charge density greater than 0.31 F/m$^3$ is applied. The gas bubbles formed at the cathode are of low proportion compared to those obtained in the case of the use of iron electrodes. Very fast flotation of the formed flocs is observed. These flocks keep the blue color until the end of the treatment and tend to come off as soon as the applied charge density reaches 1.55 F/m$^3$ and even during the sampling for
filtration. After filtration, the color of the solution is clear. At the end of the treatment, a metal deposit at the cathode is noticed, but this deposit is less important than that observed when using the iron electrodes.

Fig 10 shows that the abatement rate reaches a maximum value when the charge density reaches 1.55 F/m³, above this value, a decrease in the abatement rate is observed up to a value of 96.56% at the end of the experiment.

This makes it possible to assert that the optimal charge density for an EC treatment of the B.E solution, in the case of the use of the aluminum electrodes, is 1.55 F/m³. Ineffectiveness of the treatment which is materialized by the detachment of the flocs in solution is observed at the end of the treatment. These results are consistent with those reported by several authors. Donfack, Tchamango et al [5, 23], who all work with aluminum electrodes to treat by electrocoagulation, an artisanal tannery effluent and a daily effluent have demonstrated the effectiveness of these electrodes.

A slight decrease in tension is observed during the treatment (Fig11), this is attributed to a decrease in the resistance of the electrolyser, which explains the low density of flocs observed at the anode at the end of the treatment. Fig12 below shows the case where the abatement rates obtained when using these different electrodes (iron and aluminum) were compared.

### 3.2.2 Comparison between the reduction rates obtained when using the different electrodes

![Graph: Comparison of the B.E abatement rates obtained when using the iron and Al electrodes](image)

**Fig. 12.** Comparison of the B.E abatement rates obtained when using the Iron and Al electrodes

The comparison between the use of the different electrodes shows that, for a charge density of 2.33 F/m³, aluminum gives the best result of the abatement rate with 96.56% whereas with the iron this rate is 95.5%. With the iron, during the treatment, there is evolution of the color of the formed flocs passing, of the original color of the BE to the green, however the excess of iron in solution confers a rust color corresponding to the transformation of the ions Ferric ions, this often decreases the effectiveness of EC treatment with iron as an electrode. With aluminum, the flocs formed retain the color of the B.E, but for a prolonged period of treatment, the flocs are likely to become detached in the solution thus reducing the effectiveness of the treatment. These results are consistent with those found by Donfack and Jarmanny et al [5,10], all of whom used EC to treat artisanal tannery effluent and effluent from a textile industry, respectively, and all demonstrated efficacy. aluminum electrodes. To do this, DO and Chen [29] point out that the optimal conditions of EC vary with the choice of electrodes (iron or aluminum). This choice also depends on the following parameters:

- The initial concentration of the pollutant
- The nature of the pollutant
- The stirring speed of the medium and
- The density of the applied current.
Thus, different measurements must be taken and all the parameters must be mastered for a better result of the E.C treatment for each type of electrode used.

### 3.3 Use Of The Optimal Conditions Of Treatment

The parameters set in the case of the different experiments carried out during the elimination of the BE by electrocoagulation, made it possible to have a low energetic consumption, to determine by the formula of the energy consumption (or the specific energy consumed) SEEC:

\[
SEEC = \frac{(U \times I \times t_{ec})}{V} \text{ in kWh/m}^3
\]

The results are conferred in the following table:

<table>
<thead>
<tr>
<th>Processing optimization parameters</th>
<th>Density of charge, F/m^3</th>
<th>Current density, mA/Cm^2</th>
<th>Voltage, V</th>
<th>pH</th>
<th>Energy consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.33</td>
<td>20</td>
<td>1.5</td>
<td>9</td>
<td>93.75</td>
</tr>
</tbody>
</table>

### 4 Conclusion

Ultimately, this manipulation made it possible to optimize the treatment of the B.E solution by electrocoagulation. For this, a respective study of the effect of the nature of the background salt, the initial pH, the density of the applied current and the concentration of the B.E solution was made. KCl was chosen as the best supporting electrolyte because it gave a good result of reduction rate to optimize the treatment (95.5%) for a voltage limited to 1.5V and a charge density set at 2,33F/m^3. The best yields are obtained for the basic pH values and the pH 9 is chosen as the optimal pH with 98.90% of abatement rate, the treatment is efficient for low concentration values (10 μM) of the pollutant and for a current density set at 20 mA/cm^2 making it possible to moderate the energy consumption whose value for these various fixed parameters is 93.75 kWh/m^3. This low energy cost is attributed to the low charge density applied (2.33F/m^3) in this study, which allowed to obtain better values of rate of abatement. The comparison with the use of aluminum electrodes has shown that the latter is the best proposed electrode because it has demonstrated its treatment efficiency compared to iron, for all electrolysis conditions.

### References


