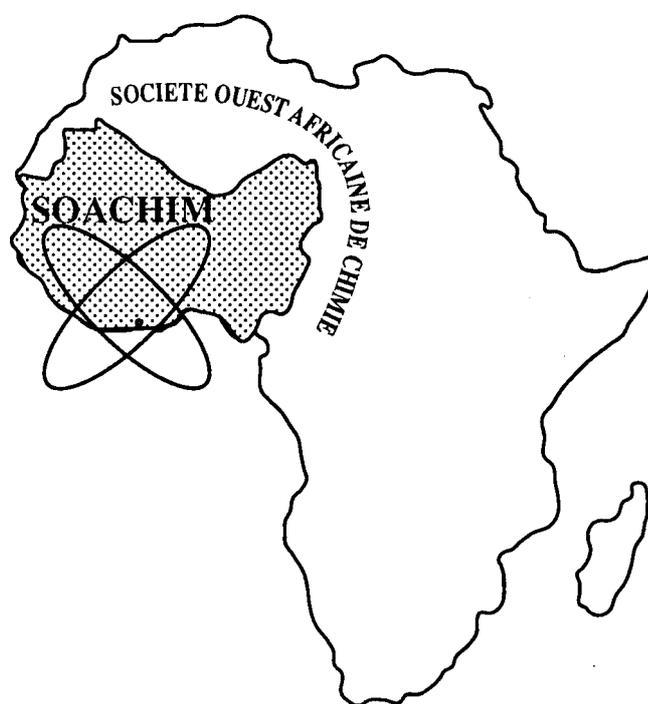# Removal of crystal violet by electrocoagulation: Optimization and reaction mechanisms involved

Maryam Khadim Mbacké, Cheikhou Kane, Ibrahima Diouf, Codou Mar Diop

Removal of crystal violet by electrocoagulation: Optimization and reaction mechanisms involved

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Abstract : Solutions of crystal violet are treated by electrocoagulation using a batch reactor. All the authors working with aluminum electrodes in the electrocoagulation process have shown that dissolution occurs at the cathode. The most probable reaction is a chemical attack by hydroxyl ions (generated during water reduction) on the aluminum cathode.To avoid these reactions the coulometric efficiency is increased; a stainless steel cathode and an aluminum anode are used in this study.The influence of various process parameters (pH, conductivity, interelectrode distance, current density and initial concentration) on treatment efficiency was investigated to optimize the system. The results indicated that slightly acidic solutions (pH=5.43) containing a dye concentration of 100 mg/L, can be clarified (removal of CV>99%; abatement of 98% of the Chemical Oxygen Demand (COD) in less than 1 hour of electrolysis and can be achieved at relatively low current density (250 A/m²). Finally, tests complexations with EDTA were performed on the treated solution and sludge formed and the results were used to write different reaction mechanisms involved in the electrocoagulation process.

Key-words: Electrocoagulation; crystal violet; aluminum; complexation.

Elimination du cristal violet par électrocoagulation: Optimisation et mécanismes réactionnels mis en jeu

Résumé:Des solutions de cristal violet sont traitées par électrocoagulation en utilisant un réacteur discontinu. Les travaux sur l'électrocoagulation avec des électrodes en aluminium ont montré une attaque de la cathode par les ions hydroxydes. Pour éviter ces contraintes qui augmentent le rendement faradique, une cathode en acier inox a été utilisée. L'influence des divers paramètres opératoires (pH, conductivité, distance inter-électrodes, densité de courant et concentration initiale) sur l'efficacité du traitement a été étudiée afin d'optimiser le système de traitement. Les résultats ont montré que des solutions légèrement acide (pH=5,43) contenant une concentration en colorant de 100 mg/l sont traitées (rendement CV 99% ; abattement de la DCO 98%) après 1heure d'électrolyse avec une densité de courant de 250A/m^2.Des tests de complexations ont été effectués sur les solutions traitées et les boues formées et les résultats sont utilisés pour écrire les différents mécanismes réactionnels impliqués dans le processus d'électrocoagulation.

Mots-clé : Electrocoagulation, cristal violet, aluminium, complexation

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1. Introduction

Environmental pollution due to industrial toxic effluents constitutes a major current problem; for example the textile effluents are associated with the introduction of toxic components into the food chains of humans and animals. Over 10000 synthetic dyes are extensively used in a large variety of industries, with an annual worldwide production higher than $7x10^5$ tons; Among them 5-10% is lost in the industrial effluents [1], implying their removal before the effluent rejection.

The dye used in this study was crystal violet ($C_{25}H_{30}N_3Cl$, 407.98 g/mol, CI 42555, Class: basic dye 3). Crystal violet is a cationic dye, providing a deep violet color, and widely used for textiles such as cotton and silk. Structure of crystal violet molecule is shown in **Figure 1** and **Figure 2**.

To remove the synthetics dyes and their derivatives content in wastewater, various techniques exist and could be used. They include chemical coagulation, precipitation, electroflotation, adsorption on activated carbon, ion exchange through a liquid–liquid membrane, fixation of the pollutant through a biological membrane and ultrafiltration [2-6]. Recently some techniques based on the trapping by mercury have been developed [7]. Not that all these techniques present some limitations (cost of chemicals used, removal efficiencies unsatisfactories for example); moreover, their implementation requires important equipment contributing to raise treatments costs. As an example, chemical coagulation requires some reagents (iron and aluminum hydrolysable salts), a permanent pH adjustment and this leads in general to secondary pollution [8].

Textile industry produces dyes very loaded wastewaters of which treatment imply various combinations of biological-chemical-physical conventional methods, because a simple technique does not allow a complete elimination of these pollutants [9]. On the other hand, these parameters could significantly changes in the various countries implied to the textile production or treatments, due to several factors (scarcity of space, land cost, complexity of handling, availability of chemicals,…) [10]. Consequence of this is the continuously increasing cost of the treatment of textile waste effluents.

Finally, required quantity of chemical, space [11-12] and energy consumption have to be extremely reduced in order to propose an optimized and applicable process.

Electrocoagulation (EC) process can be performed to treat industrial wastewaters because of its simplicity, versatility and environmental compatibility. Compared to conventional techniques, EC has some advantages, such as a simple equipment, minimization of chemicals, rapid sedimentation of the electrogenerated flocks, less sludge production, and finally a relatively rapid operation. In addition, the technique, very safe, allows treatments without risks, nor side pollution. Therefore, it was shown that EC could be used as an promising effective and reliable method for efficient reducing or removing a large variety of pollutants from industrial effluents (food processing, textile industry, etc.) [12].

Electrocoagulation has been used successfully used for the treatment of wastewater from dairy [13], alcohol distillery [14] and textile industries [16, 17].

H Zhian demonstrates that electrocoagulation allows decolorization of effluents containing heavy dye like Acid red 88 and led to removal efficiency close to 100% [18].
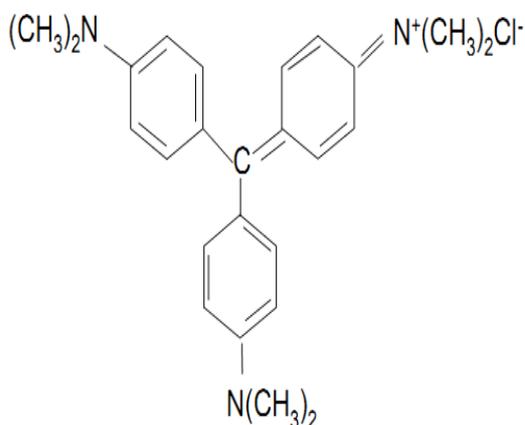
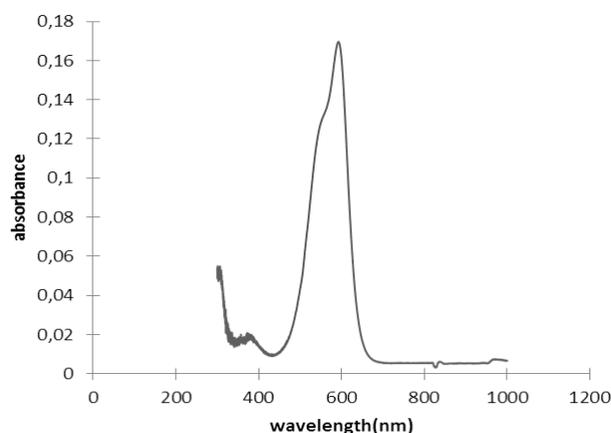**Figure 1**: The structure of crystal violet

**Figure 2**: Experimental absorption spectra for crystal violet in water

2. Material and methods
2.1 Principle of Electrocoagulation (EC) and Experimental

Aluminum or iron are usually used as sacrificial anodes, and their electrochemical dissolution allows generation of the corresponding cations according to the reaction (1).
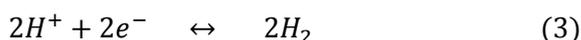
$$Al \leftrightarrow Al^{3+}{}_{aq} + 3e^- \qquad (1)$$

Stainless steel plates involved as cathode producing gaseous hydrogen (2).

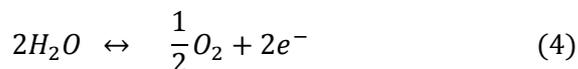$$2H_2O + 2e^- \leftrightarrow 2OH^-{}_{aq} + H_{2(g)} \qquad (2)$$
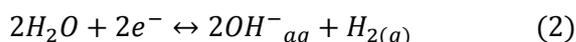
Electrolysis of water occurs at the anode and cathode. In the case of an acidic medium, there are the following reactions:
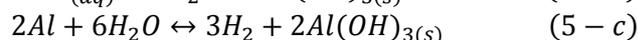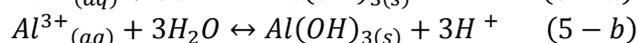
Oxidation of water at the anode

$$2H^+ + 2e^- \quad \leftrightarrow \quad 2H_2 \qquad (3)$$

Reduction of water at the cathode

$$2H_2O \quad \leftrightarrow \quad \frac{1}{2}O_2 + 2e^- \qquad (4)$$

The electrogenerated metallic ions (here Al^{3+}) are hydrolyzed in the electrochemical cell to produce aluminum hydroxide according reactions (5-a) and (5-b) or (5-c).

$$Al^{3+}{}_{(aq)} + 3OH^- \leftrightarrow Al(OH)_{3(s)} \qquad (5-a)$$
$$Al^{3+}{}_{(aq)} + 3H_2O \leftrightarrow Al(OH)_{3(s)} + 3H^+ \qquad (5-b)$$
$$2Al + 6H_2O \leftrightarrow 3H_2 + 2Al(OH)_{3(s)} \qquad (5-c)$$

Overall reaction (5-c) can be assumed to take place, without changes in the pH or the ionic straight in the bulk. Note that, pH and ionic strength of the solution controls the solubility ofthe produced hydroxide, which is insoluble at pH range from ~5 to ~8 [19]; Thus, Al(OH)$_3$, so called coagulants, can interact with charged (or not) species of dye particles in the water and adsorbs them ; in fact Al(OH)$_3$neutralizes the electrostatic charges on disperses particles to reduce the electrostatic interparticle repulsion so that the van der Waals attraction predominates, thus enhancing agglomeration; consequence is that flocks appears (6), which, thanks to the gaseous hydrogen produced at the cathode, float [20]. It is believed that the main pollutant removal mechanism observed during electrocoagulation is adsorption and

entrapment onto the amorphous aluminum hydroxide precipitate formed [21].
Finally, except aluminum consumption, the electro-coagulation processes do not require the addition of any chemicals.

$$\alpha\, Al(OH)_{3(s)} + \beta\, dyes\; molecules$$
$$\leftrightarrow flocks \qquad (6)$$
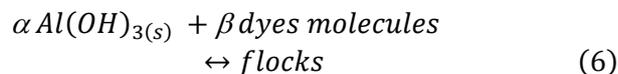
2.2 Experimental dispositive

Crystal violet (CV,CI 42555) electrocoagulation experiments was carried out in stirred batch (V=0.1 L), under constant voltage applied between the anode and the cathode, using a DC power supply (*GPC-3030D, 3A, 5V*). Two metallic plates (2cm x 7cm; 14 cm^2/face) made in aluminum (anode) and stainless steel (cathode), were used as electrodes, and the distance between them was varied from 0.5 cm to 2 cm using a PVC rod.
Solutions of CV were prepared at concentration (varying from 100 to 140 mg/L) using deionized water containing sodium chloride (as supporting electrolyte) and the pH was adjusted by adding HCl or NaOH 10^{-1}M. All the chemicals used were of analytical grade.
The pH and the conductivity of the solution were monitored using a pHmeter*210-HANNA INSTRUMENTS and* a conductimeter *EC214-HANNA INSTRUMENTS*.
Dye concentration was spectroscopically determined using the Beer-Lambert law (A=$\varepsilon \times \ell \times C$) applied at 592 nm, where ε is the molar absorptivity, ℓ is the solution thickness and C the CV concentration.
Electrolyzed solutions were filtrated ("PTFE 13MM 0.45µM/PP") and the chemical oxygen demand (COD) was determined by Rodier methods, in order to confirm the spectroscopically determined concentrations of the residual dye.
The dye removal efficiency Φ was estimated by equation:

$$\Phi = 1 - \frac{c}{c_0} \qquad (7)$$

where C_0 and C are respectively the initial and the temporal concentrations of crystal violet dye.
As indicated previous these concentration are spectroscopically determined.

3. Results and discussions
3.1 Typical parameters followed during experiments of crystal violet electrochemical decolorization

This experimental session focuses on the electrocoagulation of aqueous solutions containing the crystal violet; various operating parameters were investigated and their effects on the removal efficiency of the crystal violet were examined. Electrolysis time that ranged from 10 to 60 minutes, for applied voltage (ranged from 1.4 to 2.0 V) in potentiostatic mode, or current densities (ranged from 150 to 250 A/m^2) in galvanostatic mode (with solutions containing an initial concentration of CV (ranged from 20 to 140 mg/L), for an inter-electrodes distance (ranged from 0.5 to 2 cm), solution pH (range from 3.5 to 5.5) and electrolyte concentration (ranged from 0.2 to 1 g/L)).

Figure 3 shows typical current potential curves obtained on an aluminum anode and stain steel cathode using a PG 580 potentiostat model.

The curves (Fig. 3) show that, operating with NaCl alone or in the presence of crystal violet, oxidation potential of the aluminum starts in the chosen operating conditions at around -0.65V/SCE. The oxidation potential of the aluminum slightly decreases in presence of CV, probably because some complexation by the dye of the anodic products (operating cell voltage ΔV~5V).
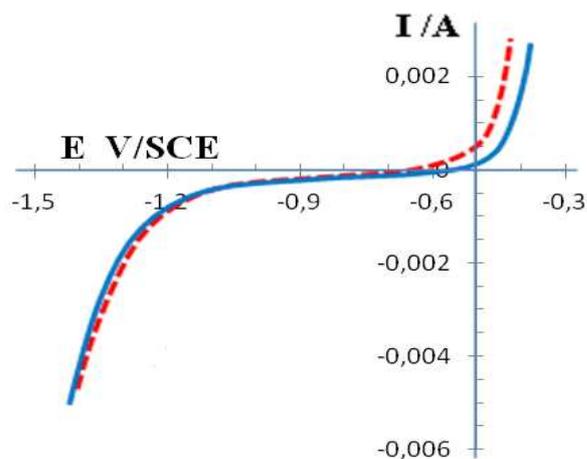

Figure 3: Evolution of potential versus current on NaCl (1g/L) ─ and in the presence of crystal violet (100mg/L) ....pH$_{t=0}$=5.43;   Cathode: stain steel; Anode: Al.
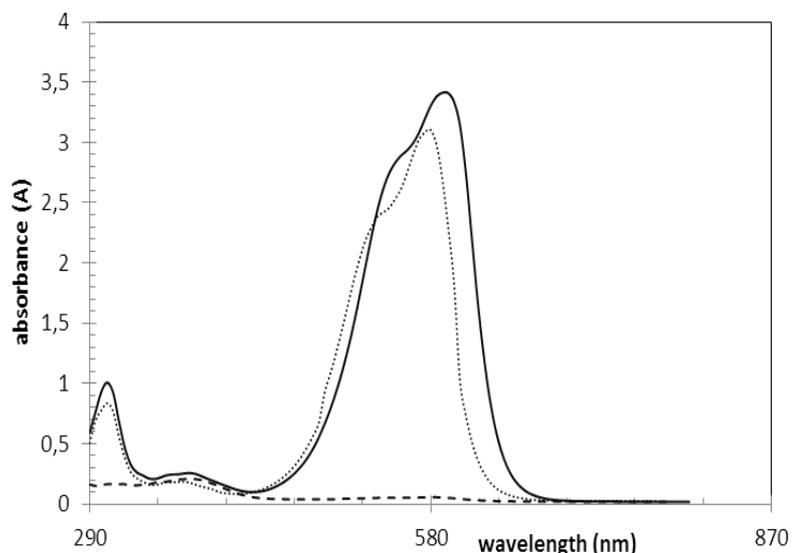

Figure (4) : (I) UV-Visible absorption spectra.
─aqueous solution of the Cristal violet (100mg/L);
….aqueous solution of the Cristal violet (100mg/L) containing NaCl 1g/L;
----aqueous solution of the Cristal violet (100mg/L) containing NaCl 1g/L after 60 min of electrolysis.pH$_{t=0}$=5.43
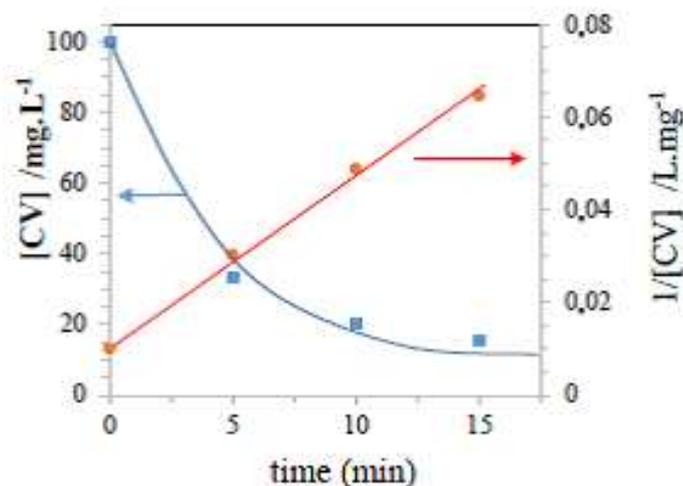
Figure (5): ──Evolution of the Cristal violet concentration versus time

──{1/[CV]} $_{(L.mg^{-1})}$ = 0.0037 × t + 0.0097 R² = 0.995

[CV]° = 100 mg / L ;$i_{applied}$= 250 A/m² ; inter-electrode distance: 0.5 cm; The solution conductivity is maintained to 4.27 mS/cm with NaCl to 1 g / L;

The UV-visible absorption spectra obtained with **the Cristal violet** alone (**Figure 4──**) shows a broad peak at 592 nm and two weak peaks around 300 and 400 nm. When adding NaCl in the CV solution (to increase the conductivity), the UV-visible absorption spectra obtained (**Figure 4** ….), indicates the same look with a small decrease in absorbance at 592 nm. The UV-visible absorption spectra obtained after 60 min of electrolysis (**Figure 4** ----), shows the magnitude of the massif at 592 nm strongly decreased. The calculated after 60 minutes of treatment operative performance shows that more than 99% crystal violet present in the initial solution are removed.

During electrolyses, the absorbance of a sample filtered was measured and the residual concentration of the CV was deduced. Typical curves providing the temporal evolution of the CV concentration during 15 minutes of electrolyseswere indicated in (**Figure 5 ──**). Results, obtained with an initial pH= 5.43, show that during the first 5 minutes of processing more than 50% of the dye are removed and recovery rate obtained for 15 min electrolysis durations is higher than 80%.This curve (pH=5.43) will used as the 'reference results' to discuss comparatively every other results indicated in the follow text. Note that a linear evolution was observed between the reverse of the CV concentration (1/[CV]) and the time (**Figure 5 ──**){1/[CV]} $_{(L.mg^{-1})}$ = 0.0037 × t + 0.0097 R² = 0.995, meaning that the apparent reaction rate order is equal to 2. The apparent rate constant for the removal rate of crystal violet was estimated in these conditions equal to 0.0037 L.mg^{-1}.min^{-1}.

3.2 Impact of different operating parameters on the rate of discoloration

3.2.1 Effect of initial pH

The pH of the solution changes during the process because the hydrogen evolution and the generation of OH$^-$ ions at the cathode; nevertheless, overall balance (reactions 5) indicates the consumption, in the bulk, of the generated OH$^-$ by the generated Al^{3+} ions, so the pH in the bulk must remain constant. According to literature [21], the pH is the most important parameter which conditions the efficiency of the electrocoagulation process; it has an effect on the conductivity of the solution, dissolution of the electrodes, speciation of hydroxides and ζpotential of colloidal particles. Aset of experiments are carried out to investigate the effects of the initial pH (in the range from 3 to 9) on the removal of crystal violet from the solution. (**Figure 6 and 7**). **Figure 6** shows the temporal evolution of the pH of electrolyzed solutions of the CV at various initial pH in the range from 3 to 10. Results shows that, whatever the initial pH of the solution, it increases during the electrolyses and it stabilizes around 9 in the first minutes of treatment, due to the buffering effect of the electrocoagulation process. Solution becomes slightly basic under the effect of electrolysis (production of OH$^-$ in the cathode, of which a little part does not react with the aluminum ions produced in the anode). **Figure 7** shows the effect of the initial pH of the solution on the temporal evolution of the residual concentration of the crystal violet.
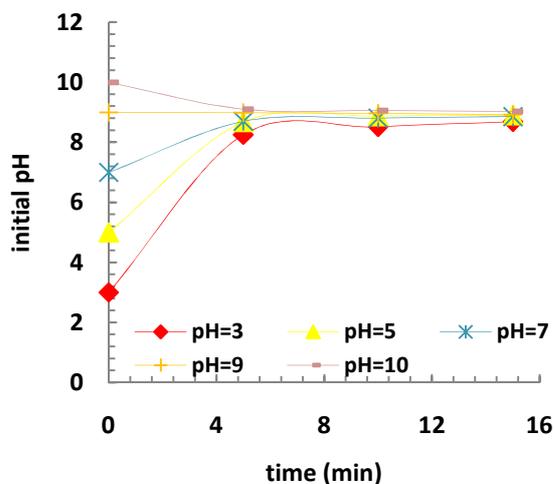
Figure 6: Evolution of initial pH over time
i = 250A/m^2; ied = 0.5 cm;
conductivity= 4.27mS/cm;
initial CV concentration=100mg/L

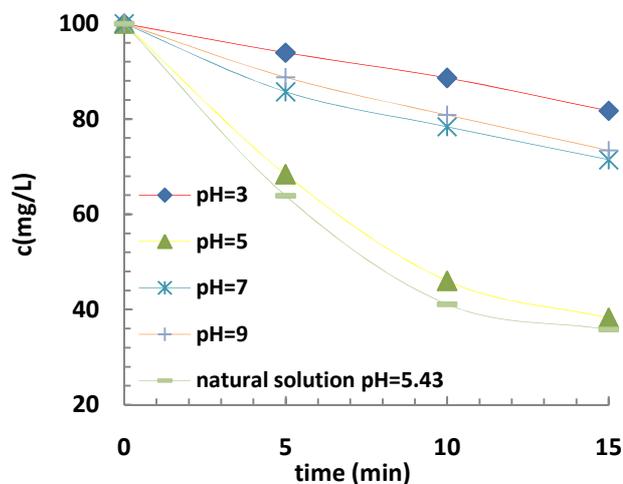**Figure 7**:Evolution of crystal violet concentration over
time with different initial pH;i = 250A/m^2;
ied = 0.5 cm; conductivity = 4.27mS/cm;
initial CV concentration=100mg/L

Results are compared versus the experiment achieved at pH=5.43, e.g. more than 80% of CV was removed from the solution in less than 15 minutes. Increasing or decreasing the pH, cause the coagulation rate to decrease; indeed for electrolysis achieved at an initial pH 5, CV's recovery rate is 78% at 15 minutes electrolysis duration and this recovery rate drop to 50% for an initial pH=3.
Similarly the recovery rate drops from 80% to 42% when the pH increases from 5.43 to 9.

According to the Pourbaix diagram at pH in the range 2 to 3, cationic monomeric species Al^{3+} and $Al(OH)_2^+$ are predominant, and their affinity to complex/flocculate with the CV is low [21], that explain the low obtained recovery rates at these pH. In the same manner recovery rates at higher pH are also lower because the presence of aluminates ions ($Al(OH)_4^-$) with a poor coagulation performance; that is in agreement with the amphoteric character of aluminum hydroxide $Al(OH)_3$ of which solubility increases as the solution becomes either more acidic or alkaline [14].
When the pH is between 4 and 9, the Al^{3+} and OH^- generated at the electrodes react to form oligomeric species such as $Al_6(OH)_{15}^{3+}$ $Al_7(OH)_{17}^{4+}$, $Al_{13}(OH)_{34}^{5+}$, to finally transform into a compound amorphous water-insoluble $Al(OH)_{3(S)}$, via a polymerization kinetics / complex precipitation. These solids particles fix the CV and leds to a satisfactory high recovery rate of the dye ; the discoloration is faster in this pH range. Note that in

this pH range, the solid $Al(OH)_3$ can appears at the anode and causes a slight inhibition of the aluminum oxidation (especially under potentiostatic conditions), that requires strong stirring conditions to remove the deposit from the electrode.
On the other hand, the color and the ionic charge of the dye strongly depends of the pH; for practically neutral solutions (pH>5, λ_{max} = 592 nm) one of thenitrogen atoms keeps a positive charge and interactions between aluminum hydroxide and dye are favored [14]. Reducing the pH (pH<2) causes both other nitrogen atoms to be protonated and to get additionnal positive charges (all three nitrogen atoms carry a positive charge for pH=1, λ_{1max} = 420 nm and λ_{2max} = 620nm). Simultaneously, aluminum is present under octahedric formcomplexs ($Al(H_2O)_6^{3+}$) and instead attractive interactions, it exists repulsives interactions between the dye and the aluminumions.

3.2.2 Effect of the applied voltage

In the EC process, the voltage is an important parameter because it defines (indirectly) the floculant produced flux. As indicated above, at constant applied voltage ($\Delta V=\Delta V_{min}+\Delta_a-\Delta_c+RI$) the current will remain constant, if other terms remain constant :
➢ Δ_a, the anodic overvoltage, is assumed constant because the uniform dissolution of the aluminum plate shaped anode; moreover produced $Al^{(III)}$is assumed to leave the electrode because the vigorous stirring of the suspension,

➢ Δ_c, the cathodic overvoltage, can vary because the change of the pH of the solution; decreasing the pH allows to the H^+ reduction to take place; conversely for slightly acidic solutions (pH>4), the rate of the reduction of H^+ is negligible, water reduction involves and the overvoltage is higher ($\Delta_{cH_2O/H_2}| > \Delta_{cH^+/H_2}|$), implies lowering the current for constant voltage operations. Nevertheless, changes in the pH only arise at the beginning of the electrolysis, rapidly it stabilizes and solution becomes buffered, so Δ_c can be assumed as constant,

➢ RI, the ohmic drop, can vary for various reasons:
➢ In the case of acidic solutions (pH<4) reduction of H^+ causes the conductivity of the cathodic part of the solution to decreases; for constant voltage operations this implies a decrease in the current and consequently in the floculant produced flux.
➢ The aluminum oxidation produces Al(III), a part of which can deposites on the aluminum surface. If this deposit was no removed from the electrode, it can causes its passivation and consequently the increase of the corresponding overvoltage and the decrease of the current. In fact, oxidation of aluminum continuously destroys the deposit and allows its ease dispersion in the bulk to react with the dye.
Note that these effects influence the system in the begin of the electrolysis, indeed, as explained in previous sessions the global reaction (5-c) does not modify the overall H^+ or OH^- concentration.

Theapplied voltage (ΔV) directly influence the electrical power and energy consumption, so the most important part of the operating cost for the process the removal of pollutants [22].
In order to examine this effect of the applied voltage on the color and COD removal efficiency, experiments were carried out in the range from 1.4 to 2.0 V (kind of ΔV_2 curves 5 and 3 of the plot in Fig.9), all other parameters kept constants. Results, present in **Figure 6**, in terms of dye decolorization and the COD abatement as functions of the applied voltage, indicate that decolorization of solution is complete (99%) and the COD abatement stay close to 98%. Moreover it seems that the voltage has no effect on both parameters.

An explanation of this evolution is thatthe applied voltage is so much larger in comparison with the minimum voltage required (<1V). Choice of values of voltage higher than 1.5V is justified by the fact that at pH 5.5, it is necessary to overcome an eventual passivation of the anode by deposit of $Al(OH)_3$; indeed maintaining high anodic potentials allows to significant rates of oxidation of the aluminum, that causes delaminating any deposit which can appear in the aluminum plate. Note that dye adsorption on $Al(OH)_3$, could facilitates delaminating of the anode. To sum, it could be possible to operate with voltages of 1.5V, and vigorous stirring of suspension could contributes to reduce this value, in order to save electrical power consumption.
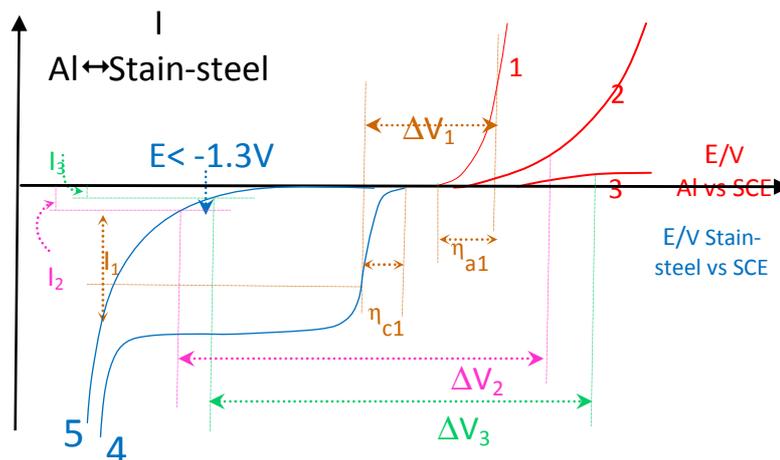

Figure 8: Schematic current-potential curves allow understanding the constant voltage operation of electrofloculation. Curves 1 to 3: oxidation of Al to Al(III) at pH 1.5, 3 and 6 respectively. Curve 4 reduction on stainlesssteel of free H^+ (diffusion limited plateau) to H_2, followed by reduction of water to H_2 (exponential part). Curve 5 reduction on stainlesssteelof water to H_2 (exponential part). ΔV_1 applied voltage and respective flowing current between Al anode and stainlesssteelcathode, at pH 1.5. ΔV_2 applied voltage and respective flowing currents between Al anode and stainlesssteelcathode, at pH 3 and 6 respectively. Curves plotted in absence of dissolved O_2; in real treatment oxygen is present and allows decrease the ΔV_{min}, but leads to currant consumption and decreases the faradic yield.
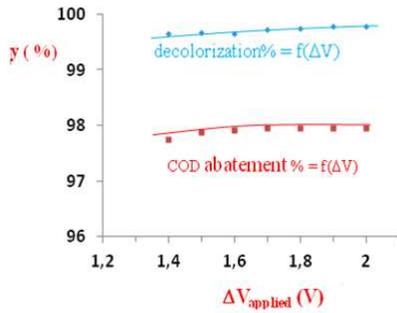
Figure 9: Applied voltage dependence of the dye decolorization and the COD abatement of the solution. Crystal violet at 100 mg/L,NaCl at 1g/L, initial pH=5.43, electrocoagulation duration 1 hour.

3.2.3 Parametric studies: effect of the various parameters (current density, conductivity, initial concentration, inter-electrode distance) on the CV's recovery ratio

Here were examined the effect of various operating parameters that can affect the rate and the ratio of the crystal violet recovery by electrocoagulation and **Figures10, 11, 12** summarizes all the experimental results.
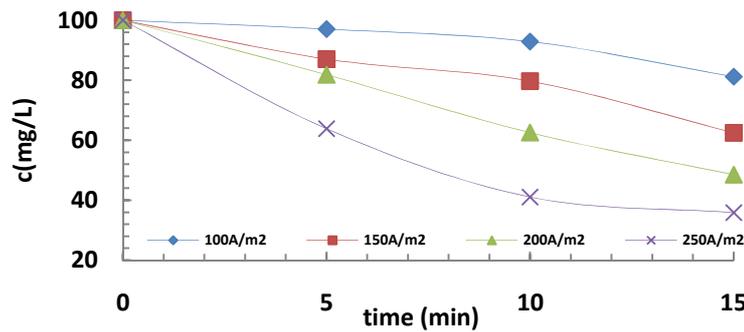

Figure 10: Evolution of crystal violet concentration over time with different current density; ied = 0.5 cm; conductivity = 4.27mS/cm; initial concentration=100mg/L; pH=5.43
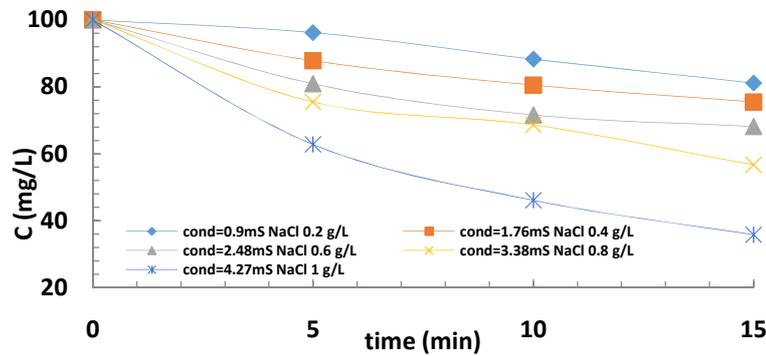

Figure 11: Evolution of crystal violet concentration over time with different initial conductivity;i = 250A/m^2; ied = 0.5 cm; initial concentration=100mg/L; pH=5.43
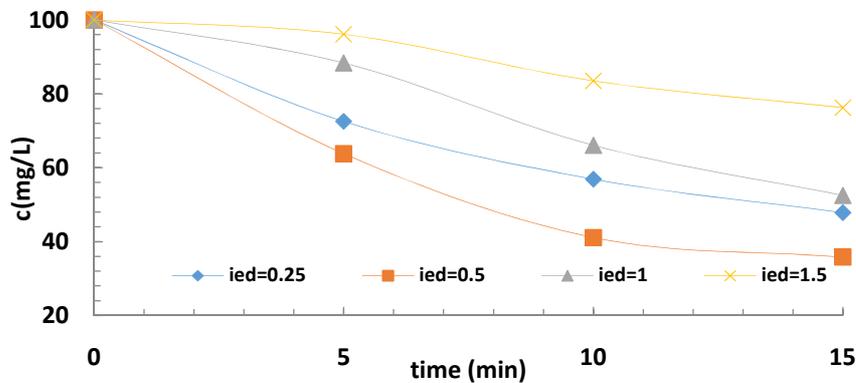

Figure 12: Evolution of crystal violet concentration over time with different inter electrode distance;i = 250A/m^2; pH = 5.43; conductivity = 4.27mS/cm; initial concentration=100mg/L

First parameter studied is the applied current density in the range of 100 to 250 A/m² (Fig.10). Results indicate that increasing the current density leads to an increase of both the rate of decolorization as well as the ratio of the CV electrocoagulated.

Aluminum oxidation takes place under activation limitation; which implies that all the applied current is used to oxidize the Al and the proportion of other reactions (oxidation of water or chloride or CV) is insignificant at the chosen operating conditions (neutral or slightly acidic solutions [21]). Moreover these results indicates that the product of the Al oxidation (e.g. Al$^{(III)}$ does not remains at the anode but leaves the electrode to react with the CV at the bulk. Consequently, at the least at the begin of the electrolyses (constant pH), current density must be proportional to the rate of electrochemical oxidation of the Aluminum, and as the function of the mechanism of electrocoagulation, directly correlated with the rate of the CV reaction with the solid Al(OH)$_3$.

The conductivity of the solution in the interelectrodes space (directly correlated with the amount of NaCl added) affects the cell voltage 5V. Typically decreasing conductivity from 4.43 to 0.09 mS /cm causes operating voltage 5V to increase from 5V to 12V, and leads to slightly heat the media (14.10^{-4}m²×250A/m²×12V=4.2W for 100cm³ of solution). Results of the electrolyses achieved under various conductivities (**figure 11**) does not indicate significant changes on the temporal evolution of the residual concentration of the CV. A slight difference appears in the residual concentration of CV after 5 min of electrolyses: increasing the conductivity seams to increases the electrocoagulation rate, the observed residual concentration of CV decreases (0.09→4.43 mS/cm corresponds to 30→70 mg/L of CV); nevertheless for longer electrolysis durations no differences wereobserved. This 'initial' observed effect is probably caused by the production of OH$^-$ at the cathode which modifies the pH, and disappears simultaneously to the stabilization of this pH at around 9.

The effect of the inter-electrode distance on the CV recovery was examined and results are presented in Fig.12. Even if the shape of the obtained curves appears to be the same, the rate of the CV recovery rate changes with the interelectrode distance. Nevertheless, a no clear evolution of the CV residual concentration is observed versus time. The interelectrode distance affects two parameters: i) the resistance of the electrolyte between the electrodes (e.g. the cell voltage by the ohmic drop), so the power loosed under joule effect, and ii) the stirring

of the solution present between the electrodes, and consequently the rooting up of the solid from the electrode surface.

Indeed, increasing the inelectrodes gap from0.5 to 2 cm cause decrease in the electrofloculation performances (decolorization yield and COD abatement decrease from 99 to 85% and to 98 to 66% respectively) Fig.13.

An explanation could be the higher ohmic drop: indeed, keeping all other parameters constants, the increase of the interelectrod gap, cause RI to increase and consequently both the anodic and cathodic (absolute value) overvoltages decrease. At constant voltage the resulting current is lower (ΔV_2, I_2,), and consequently the electrofloculation performances too.

At the chosen conditions the best result was obtained for 0.5 cm of interelectrodes gap; nevertheless to overcome this limitation (e.g. to maintain higher interelectrode distance in order to have vigorous stirring and dispersion of the produced flocculent) one possibility is to increase the applied voltage, at the expense of the consumed electrical power.
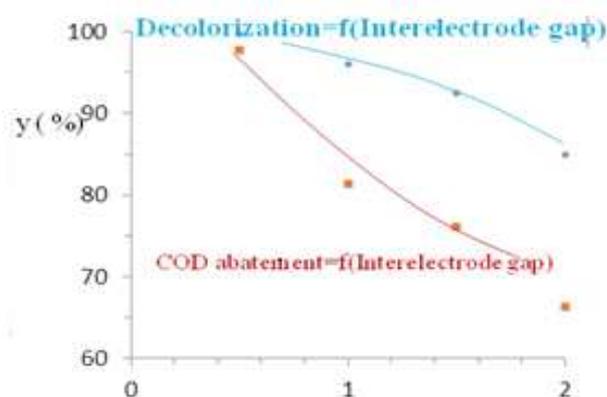

Figure 13: Interelectrode gap dependence of the dye decolorization and the COD abatement of the solution. Crystal violet at 100 mg/L, NaCl at 1g/L, initial pH=5.43, current density 250A/m²,electrocoagulation duration 1 hour.
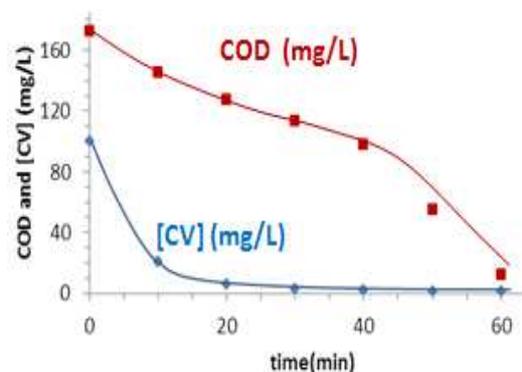

Figure 14: Temporal evolution of both COD abatment and dye decolorization, during electrocoagulation process. [CV]° = 100mg/L; [NaCl]= 1g/L; pH$_{t=0}$=5.43, i=250A/m². Anode: Al 14 cm²/face; cathode stainless steel 14cm²/face; electrolyzed volume = 100cm³; pH$_{t=0}$=5.43; κ=4.27mS/cm; Inter-electrode distance0.5cm.

To confirm the previous results the chemical oxygen demand was estimated [23] during the electrocoagulation of the CV dye. This is important in order to get an idea about the presence of other eventual organic products (for this study, only the CV dye is used), or the presence of sub products arising from the CV electrochemical transformation. Results (Fig.9) indicates that the residual concentration of CV decreases ~30% during the first 10 min of electrolysis; simultaneously, the curve COD=f(t) indicates a relatively high concentration of organics dissolved in the solution (COD=145 mg O_2/L; for an initial COD of 175, so 17% of lowering). This means that there are organic colorless (at 592 nm) products in the solution, probably some ionic forms of CV which does not adsorbs at the corresponding pH. An one hour duration of electrolyses is required to completely recovery the CV (COD and [CV] lower than ~5% of their initial values) from the solution.

3.3 Removal mechanism of crystal violet

When current flows in the cell two reactions are in competition:

✓ Al^{3+} released in solution can react with the OH^- ions forming $Al(OH)_3$;
✓ the Al^{3+} released in solution can react with the crystal violet by complexing.

In its structure, crystal violet has three nitrogens bearing free doublets that can act as donor; it is tridentate and will be symbolized by $AN_3^+Cl^-$.The study of the rate of crystal violet discolorationshowed that the kinetics is second order with respect to crystal violet (**Figure 3** II (b)). In the following reaction mechanisms, it is assumed that one molecule of Al $(OH)_3$ reacts with two molecules of crystal violet.

The buffer electrocoagulation process effect is observed after 3 minutes of treatment (pH stabilizes around 8 and remains constant throughout the electrolysis). The absorbance measurement shows a reduction of 10% color. The COD measurement showed that there was no decrease on the initial COD.

The sample is filtered and remarks that are no sludge formation. During the first 3 minutes of treatment, the discoloration would be observed due to complexation of crystal violet by metal cations Al^{3+} in solution.

This first reaction is :

$$2nAN_3^+Cl^- + (Al^{3+})n_{(aq)} \rightarrow (Al(AN_3^+Cl^-)_{2n})_n^+ \qquad (8)$$
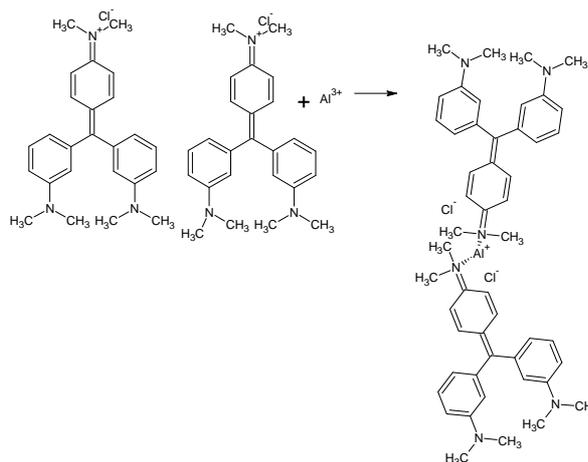
The predominant form of the aluminum hydroxide is formed in the polymer solution $(Al(OH)_3)_n$, whose structure is:
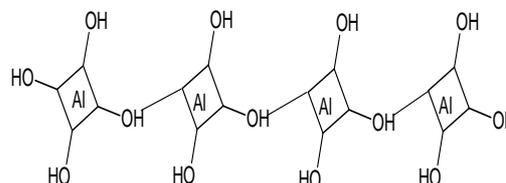

Figure 15: Aluminum hydroxide structure

This is an endless linked chain square planar in pairs by their two free OH giving top and two other bridging.

After electrolysis, the sample was filtered and complexation tests are made on the sludge and the filtrate recovered. The acid Ethylene Diamine Tetra Acetic Acid is used as complexing agent. Its usefulness arises because of its role as a hexadentate ("six-toothed") ligand and chelatingagent, i.e. its ability to "sequester" metal ions such as Al^{3+} and Fe^{3+}. After being bound by EDTA, metal ions remain in solution but exhibit diminished reactivity.

The EDTA structure is shown in **Figure 16**.For tests complexing the mass of EDTA used is 5mg and the sludge is diluted to 1/10. Complexation occurs with heating and stirring the sample. **Figure 17** and **18** shows the results obtained.
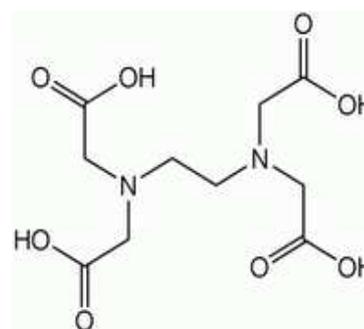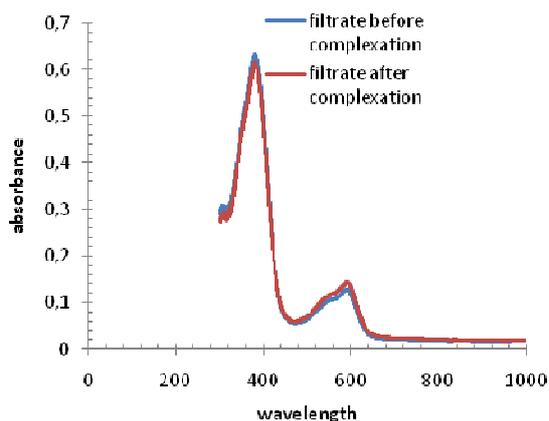

Figure 16: EDTA structure

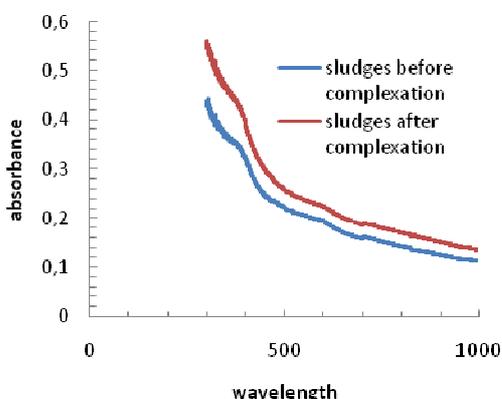**Figure 17:** Spectral scan; Evolution of the absorbance versus wavelength on filtrate before and after complexation


Figure 18: Spectral scan; Evolution of the absorbance versus wavelength on sludge before and after complexation

Figure 17 and **18** shows that after complexation there has increase in absorbance at 592 nm.

The filtrate and sludge that had colorless to the end of treatment, found a slight coloration after complexation.
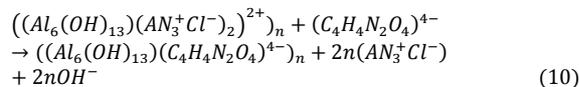
After treatment, the measurement of the absorbance of the filtrate indicated a purification yield of 99.75%. This shows that there is a portion of crystal violet solution even if the filtrate is visibly colorless. The increase in absorbance of the filtrate after complexation with EDTA indicating that the crystal violet solution is also in a form bound with the aluminum hydroxide in solution (oligomeric species such as $Al_6(OH)_{15}^{3+}$ $Al_7(OH)_{17}^{4+}$, $Al_{13}(OH)_{34}^{5+}$). This complex is colorless can not be detected at 592 nm. The reaction is as follows

$$2n(AN_3^+Cl^-) + (Al_6(OH)_{15}^{3+})_{n(aq)} \rightarrow ((Al_6(OH)_{13})(AN_3^+Cl^-)_2)^{2+}{}_n + 2nOH^- \quad (9)$$
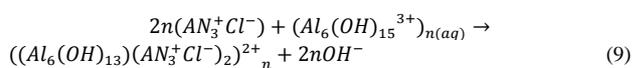
Indeed, because of its higher than crystal violet ligand power, EDTA releases it in solution to bind to the bonding area with aluminum hydroxide present in solution.

The reaction is as follows

$$((Al_6(OH)_{13})(AN_3^+Cl^-)_2)^{2+})_n + (C_4H_4N_2O_4)^{4-}$$
$$\rightarrow ((Al_6(OH)_{13})(C_4H_4N_2O_4)^{4-})_n + 2n(AN_3^+Cl^-)$$
$$+ 2nOH^- \quad (10)$$

We therefore deduce that the crystal violet is present in the final solution in a free form ($AN_3^+Cl^-$) and in a complexed form like $((Al_6(OH)_{13})(AN_3^+Cl^-)_2)^{2+}{}_n$.

The same phenomenon is observed in the sludge.

The sludge is mainly composed of aluminum hydroxide ($Al(OH)_3$) associated with crystal violet. The complexing reaction is carried out with EDTA release with crystal violet solution.

However the absorbance obtained in the sludge after complexation (taking into account the dilution), shows that there is 97 mg of crystal violet in sludge.

The COD of the sample after treatment, and presence of sludge is 170 mg /L.

We deduce that almost 98% crystal violet initially introduced is completely complexed by aluminum hydroxides (if we take into account losses).

The crystal violet degradation is likely due to oxidation by the oxygen liberated at the anode.

The reaction between crystal violet and the aluminum hydroxide is effected in several steps:

Indeed the polymer after its formation $(Al(OH)_3)_n$ acts as coagulant. There will then adsorb crystal molecules which are in solution. This is due to the affinity between nitrogen atoms (doublets with giving them a free ligand power) and aluminum atoms are electropositive in this step discoloration cannot be observed because there is no reaction of crystal violet molecules are in the coordination sphere.

$$(Al(OH)_3)_n + 2n(AN_3^+Cl^-) \rightarrow (Al(OH)_3)_n(AN_3^+Cl^-)_{2n} \quad (11)$$
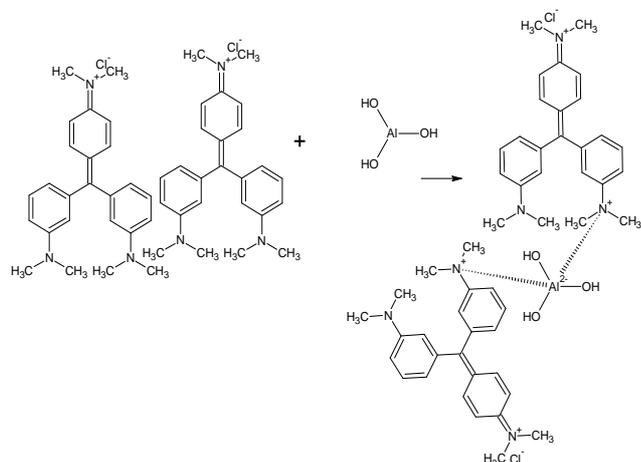
This physical adsorption is followed by a chemical adsorption (complexation) which was confirmed by the pseudo second order model.
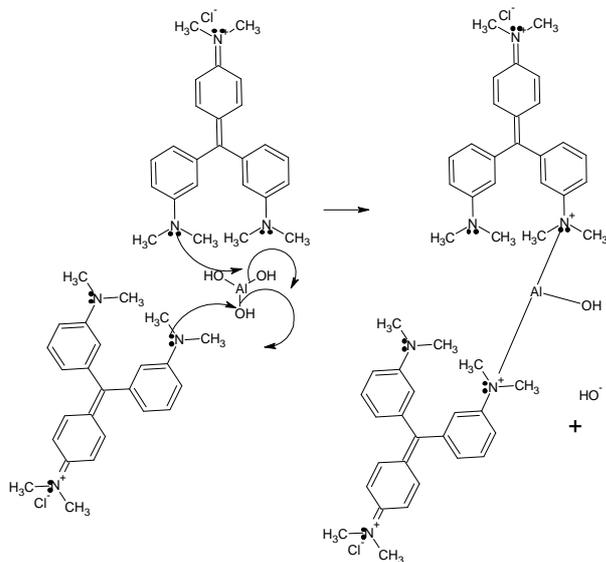
The overall reaction becomes:

$$(Al(OH)_3)_n + 2n(AN_3{}^+Cl^-) \rightarrow$$
$$(Al(OH)(AN_3{}^+Cl^-)_2)_n^{2+} + 2nOH^- \quad (12)$$
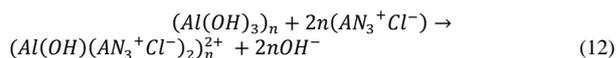
The sludge obtained has a structure of the form.The color return observed in the filtrate and the sludge by complexation with EDTA showed that the reactions which lead to discoloration are complexing reaction.

4. Conclusion

This study allowed us to test the effluent treatment electrochemically. Indeed the effectiveness of the method for electrocoagulation treatment of crystal violet solutions was demonstrated with a greater than 99 % for the reduction of color and about 98 % for the reduction of organic matter yield . The optimization of the system has shown that an inter-electrode distance of 0.5 cm, a current density of 250A/m^2 , an initial pH of about 5.43 and a
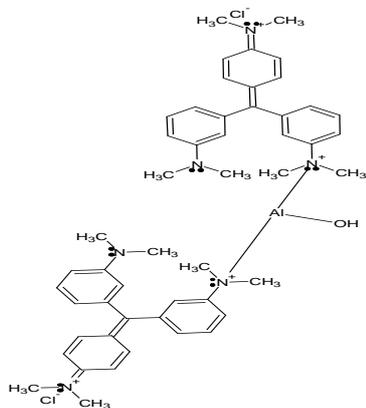
supporting electrolyte mass of NaCl 1 g / L, the yield could give after 1 hour treatment. The complexation tests allowed to see the different reaction mechanisms but also to confirm that electrocoagulation is essentially a complexing reaction.

Nomenclature

CV : Crystal Violet dye (CI 42555) $C_{25}H_{30}N_3Cl$
COD chemical oxygen demand
EC Electrocoagulation
Φ dye removal efficiency
C_0 and C are concentrations of crystal violet before and after electrocoagulation in mg/L.
α, β, γ partial reaction orders
a and b stichiometric coefficient of reaction
pHi : initial pH

Acknowledgment

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