

Comparative study of the efficiency of wastewater treatment by chemical coagulation and electrocoagulation: impact of a pretreatment step

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Abstract

Refinery effluents were treated by electrocoagulation and chemical coagulation. The application of electrocoagulation to the refinery effluent allowed to achieve abatement rates of 99%, dissolved oxygen of 88 %, turbidity of 96% and a reduction of the quantity of suspended solids to 40%.

A comparative study based on physicochemical parameters (COD, dissolved oxygen, turbidity) was carried out by treating the discharge water by chemical coagulation and electrocoagulation. The results obtained show reductions of 96% for turbidity and 99% for COD during treatment by electrocoagulation and reductions of 92% for turbidity and 96% for COD during treatment by chemical coagulation.

The efficiency of the electrocoagulation process was also evaluated on domestic wastewater from a treatment plant. The effect of the different pretreatment phases on COD reduction and microbial load was studied.

Keywords: electrocoagulation , coagulation, treatment, microorganisms

I- INTRODUCTION

Water plays a vital role in the various operations of an oil refinery. On average, one barrel of fresh water is required to process two barrels of crude oil. The effluents discharged are divided into several categories: wastewater from refining processes, water from ancillary activities and storm water. Process waters are directly exposed to substances treated during the separation, conversion and upgrading of petroleum products, including desalting water, distillation condensates, sour water, steam cracking rejects, catalytic alkylation water and bitumen blowing water. These effluents contain hydrocarbons, nitrogen, sulphur and oxygen compounds, naturally present in oil, as well as various chemical products used in the processes (solvents, soda, acids, amines, detergents, corrosion inhibitors) and by-products from thermal and chemical reactions (phenols, ammonia) or from the corrosion of equipment (metal oxides, suspended matter).

Ancillary activities also generate wastewater: floor washing water, boiler purges, ion exchanger regeneration residues, laboratory effluents and domestic water. Apart from the latter, which is treated and discharged into the sanitation network, many effluents are contaminated and require on-site treatment before being discharged.

The main pollutants in process waters include hydrocarbons (oils and greases), phenolic compounds, sulfides, ammoniacal nitrogen and suspended solids. Other contaminants, present at lower concentrations, include mineral salts, metals (iron, arsenic, chromium, vanadium, nickel) and chemical additives (caustic soda, sulfuric and phosphoric acids, solvents, detergents) [1].

After having shown the efficiency of the electrocoagulation process on different types of industrial effluent while maintaining the same operating parameters [2], this study makes a comparison between the treatment by chemical coagulation using respectively elumoin sulfate and Mohr's salt and the treatment by electrocoagulation. Furthermore, electrocoagulation is generally recommended for discharge volumes around $200 \text{ m}^3/\text{day}$ which limits its use in the treatment of domestic wastewater. This study focused on the use of the method in post-treatment in treatment plants, particularly its impact on the microbial organic load.

II- MATERIALS AND METHODS

II-1 Characterization of effluents

The effluents used in this study were collected from the waste storage basin of a refinery located in Dakar. The physicochemical characteristics are presented in Table 1:

TABLE 1. PHYSICOCHEMICAL CHARACTERISTICS OF RAW REFINING WATERS

Settings	Conductivity (mS /cm)	DBO ₅	COD (mg/L)	MES (mg/L)	Dissolved oxygen (mg/L)	pH	Turbidity (NTU)
Results	1,971	-	444	1,828	1.8	7.95	100

The effluents from the treatment plant underwent various pre-treatment phases, including:

- A de-sanding and de-oiling step;
- A decantation stage;
- A clarification step;
- A chlorine disinfection step.

II-2 Chemical coagulation

Hydrolysable metal salts, such as aluminum or iron chlorides and sulfates (Hydrated *Aluminum Sulfate* $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and *Mohr's salt hydrated* $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$), are commonly used as coagulating agents in water treatment. Their coagulation efficiency depends on the hydrolysis reactions in solution, as well as the nature and quantity of the products formed during this process.

Coagulation tests are first carried out using the Jar test to determine the appropriate dose of coagulant.



Fig. 1 Chemical Coagulation

II-3 Electrocoagulation

Electrocoagulation is a water treatment process based on the electrochemical dissolution of a sacrificial metal. Once released into the effluent, the metal ions resulting from this dissolution, combined with associated reactions such as

water electrolysis, form metal hydroxide complexes. The latter promotes the adsorption and flocculation of particles and dissolved pollutants [3]. This process is perceived as complex due to the synergy between multiple mechanisms contributing to purification. Electrocoagulation is based on three main mechanisms [4]:

- electrochemical reactions ,
- coagulation ,
- and hydrodynamics.

Applying an electric field to wastewater creates optimal conditions for coagulation-flocculation. This field generates a velocity gradient that influences all charged particles, such as ions and colloids, thus facilitating their agglomeration. In addition, the use of iron and aluminum anodes allows controlled quantities of metal ions to be released, which are essential for the formation of flocs of adequate size. The separation of the purified water is then carried out by flotation or decantation. [3].

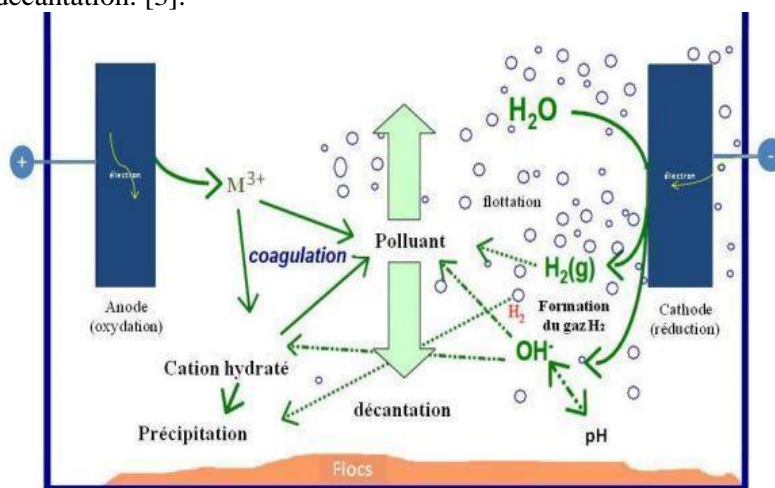


Fig2: Principle of the electrocoagulation process[5]



Fig. 3 Operation of the Electrocoagulation process

The electrocoagulation cell *Figure 3* , with a volume of 250 ml, has three electrodes, one of which is made of stainless steel serving as the cathode and two others made of aluminum serving as the anode. The electrodes used (anodes and cathodes) are metal plates measuring 2 cm (width) x 7 cm (length). The electrodes, two in number, have an active surface area of 28 cm² and the space between them is 1 cm. The electrode connected to the cathode is made of stainless steel and the one connected to the anode is made of aluminum. A Galvanostat is used to impose the current and the electric potential.

For refinery water the treatment conditions are as follows:

- Wastewater sample volume: 250 ml;
- Inter-electrode distance: 1 cm;

- Current intensity: 0.66 Ampere;
- Processing time: 60 min.

For the water from the treatment plant, a volume of 250 ml is placed in a reactor with an electrolyte concentration (NaCl) of 1 g/L. Two electrodes with an inter-electrode distance of 1 cm, one of which is made of stainless steel and the other of aluminum. These two electrodes are connected to a galvanometer whose intensity is set at 0.30 A. The device is kept under tension for a period of 25 min.

II-3 Microbiological analysis

Microbiological analyses are carried out on water samples from the treatment plant, taken in 250 mL glass bottles, previously sterilized in an autoclave at 120 °C for 15 minutes. They concern both raw samples and samples treated by electrocoagulation and cover total germs (GT), total coliforms (CT) and fecal coliforms (CF), fecal streptococci (SF), sulfite-reducing Clostridium and staphylococci. The results are expressed in CFU (Colony Forming Units) per 100 mL. The effect of the imposed voltage on microbiological quality was monitored.

II-4 Pretreatment by adsorption

The pretreatment is done with activated carbon based on moringa cakes. A mass of four grams (4g) of adsorbent is dissolved in 250 ml of desanded water. This solution is stirred for one hour (1h) using a magnetic stirrer.

After 1 hour of stirring, the solution is allowed to settle before filtering and finally undergoing electrocoagulation.

III- RESULTS

III-1 Test on refinery effluents

Electrocoagulation treatment

The results obtained after electrocoagulation treatment of refining water showed the following results:

TABLE II
PHYSICOCHEMICAL PARAMETERS BEFORE AND AFTER ELECTROCOAGULATION TREATMENT

Settings	Refinery effluent	
	Before treatment	After treatment
Conductivity (mS/cm)	1,971	4,287
BOD5 (mg/L)	-	50
COD (mg/L)	444	4
MES (mg/L)	1,828	1,074
Oxygen dissolved (mg/L)	1.8	0.1
pH	7.95	7.9
Turbidity (NTU)	100	23

Conductivity increased from 1.971 mS /cm to 4.287 mS /cm. This increase may be due to the presence of Al^{3+} ions released during electrocoagulation.

The BOD5 value gave a value of 50 mg/L, which can be explained by the fact that, being heavily loaded with organic compounds, the wastewater sample was an environment that did not allow microbiological growth, hence a low or even non-existent BOD5, whereas after treatment, there was a reduction or elimination of organic or mineral matter, which led to the BOD 5 value obtained.

Chemical coagulation treatment

Chemical coagulants such as Aluminum sulfate and Mohr's salt were used for the treatment of wastewater loaded with organic matter to reduce the physicochemical parameters such as COD, turbidity and dissolved oxygen. The Jar test made it possible to optimize the amount of coagulants required to obtain a satisfactory treatment yield. The results obtained showed that a mass of 3 g of aluminum sulfate gave a better yield with a reduction rate of 96%.

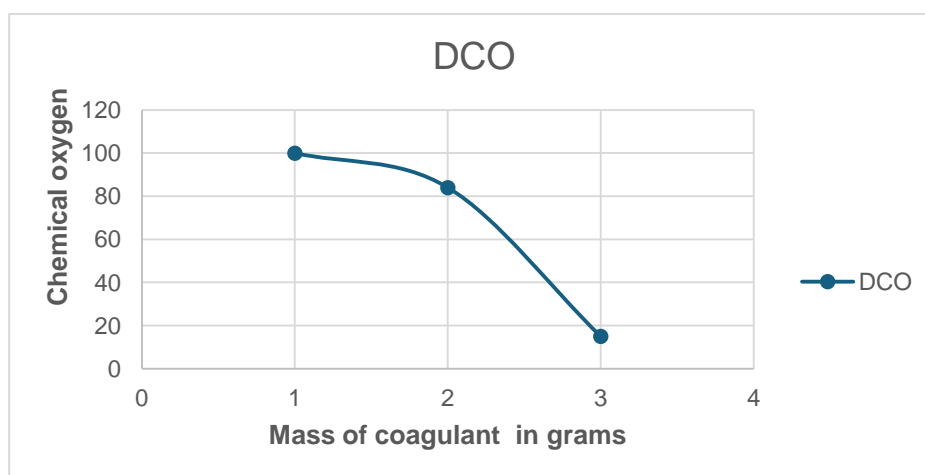


Fig4: Evolution of COD as a function of the mass of aluminum sulfate

The effect of the coagulant type was studied through a comparison between aluminum sulfate and Mohr's salt. The results showed a COD reduction rate of 88% for Mohr's salt versus 96% for aluminum sulfate. This same trend is noted on turbidity and dissolved oxygen.

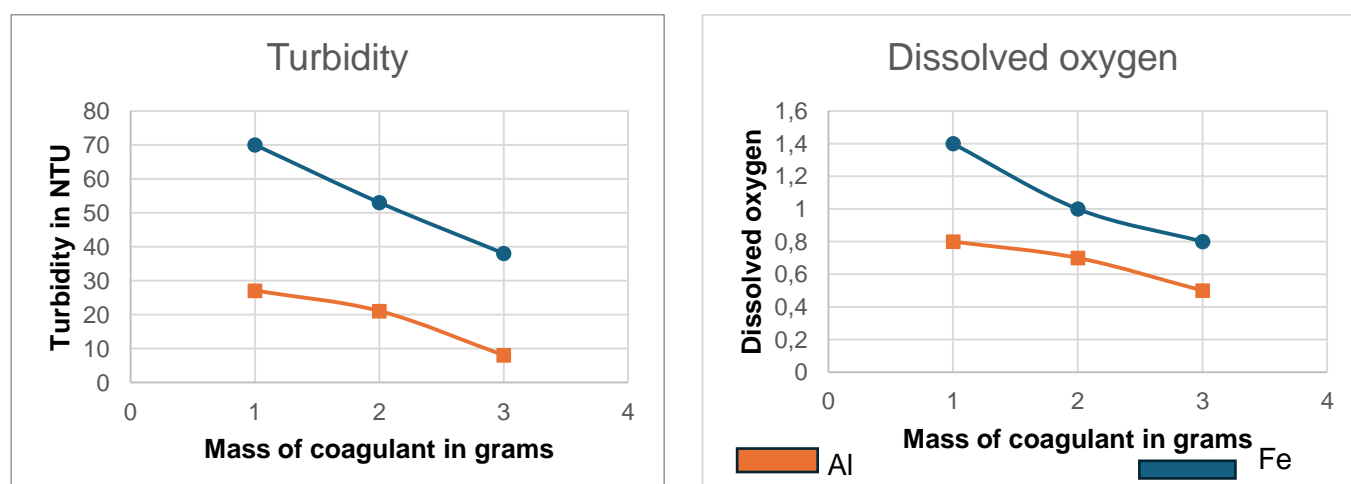


Fig 5: Evolution of turbidity and dissolved oxygen as a function of the type and mass of coagulant

A decrease in turbidity is observed as a function of the mass of the coagulant added. This reflects a decrease in suspended matters. The results obtained allow us to say that the treatment with Aluminum sulfate gave a good yield, i.e. 8 NTU against 38 NTU for Mohr's Salt. Indeed, iron can serve as a substrate for microorganisms present in the environment, which slows down their elimination. These results are confirmed by those of Zouaghi and Hamdane (2016) [6].

The results obtained by these two processes give a treatment efficiency greater than 90% for a consumption of coagulant (Al^{3+}) of 3g for chemical coagulation and 0.7g for EC. In the case of chemical coagulation, the quantity of Al^{3+} ions is released in a quantity proportional to the quantity of salt ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) introduced into the effluent. For electrocoagulation, the production of Al^{3+} ions is proportional to the current density applied to the electrodes. The production of hydrogen bubbles, necessary for the formation of aluminum hydroxide flocs, also depends on this current density. Whatever the process, the Al^{3+} ion production reaction is optimal at a pH between 6 and 7.5.

These results are consistent with those of the work of Daouda et al, (2016)[7] as well as Tchamango et al. (2019) [8]. The effectiveness of electrocoagulation is related to the amount of coagulant produced in situ.

III-2 Test on effluents from the treatment plant

In the first tests the objective is to determine the efficiency and performance of electrocoagulation according to the degree of water pollution. Thus, in this part the reductions in COD and turbidity are determined.

As for the second tests, the main objective is to see among the adsorbents used in pretreatment of desanded raw water, those which give both the lowest COD and turbidity rates after treatment by electrocoagulation.

And finally, a comparison is made on the effectiveness of electrocoagulation depending on whether there is pretreatment or not using desanded raw water as a sample.

The results for water treatment by electrocoagulation without pretreatment are presented in Table III.

TABLE III: CHEMICAL OXYGEN DEMAND OF WATER FROM THE DIFFERENT PHASES OF PHYSICOCHEMICAL TREATMENT OF THE TREATMENT PLANT AFTER TREATMENT BY ELECTROCOAGULATION

Water type	desanded raw water	decanted water	clarified water	chlorinated water
COD before treatment (mg/l)	1193	414	310	450
COD after electrocoagulation (mg/l)	113	63	54	20
Rate of abatement in COD (%)	90.53	84.78	82.58	95.56

These results show that the pretreatment phase improves the performance of the electrocoagulation process, particularly when the effluent has undergone all the stages of physicochemical treatment.

At this level it is important to note that the water coming from the treatment plant, even after the tertiary treatment stage, has a COD value higher than that permitted by the Senegalese standard NS05-061 [9].

The desanded raw water was mixed with activated carbon made from moringa seed and activated with acid to always evaluate the impact of a pretreatment step on the performance of the electrocoagulation system.

TABLE IV: IMPACT OF ADSORPTION PRETREATMENT ON ELECTROCOAGULATION PERFORMANCE

Adsorbent	COD after pretreatment (mg/l)	COD after electrocoagulation (mg/l)
activated moringa	710	63
Rate of abatement in DCO	40	91

The pre-treatment step with activated carbon (acid activation) allows to reduce the initial organic matter load by 40% before electrocoagulation treatment.

III-3 Microbiological Analysis

Microbiological analyses, after 25 minutes of variable voltage treatment, showed a reduction rate of over 99% for coliforms and clostridia.

TABLE V: MICROORGANISMS ENUMERATION AND DISCOUNT RATE

Tension applied		5V	10V	5V	10V
Microorganisms (CFU/100mL)	Desanded raw water	enumeration	enumeration	Discount rate	Discount rate
Germes totals	$15.22.10^8$	42.10^6	50.10^5	97.2%	99.97%
Coliforms totals	$7.33.10^7$	21.10^5	$7.15.10^4$	97.13%	99.9%
Coliforms fecal	$4.12.10^6$	$1.65.10^5$	$16.65.10^4$	96%	96%
Clostridium	$33.4.10^4$	$6.32.10^3$	$1.22.10^2$	98.1%	99.9%
Staphylococci	$22.66.10^6$	$14.25.10^5$	$6.42.10^5$	94%	97.1%
Streptococci fecal	$2.75.10^6$	$1.42.10^5$	$11.32.10^4$	95%	96%
Salmonella	absence				

A linear variation in the reduction of microorganisms as a function of the imposed voltage is observed. This decrease in the microbial load may be due to two factors, namely the bactericidal effect induced by the electric field or the formation of hypochlorous derivatives from the chloride ions present in the medium. Paternaraki et al. (1990) [10], using titanium electrodes, confirmed the bactericidal action of the electric field without observing the formation of hypochlorous derivatives or other chlorinated compounds.

Some studies have compared electrocoagulation to a physicochemical process based on the addition of chemical coagulants such as aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) and ferric chloride (FeCl_3). They have thus confirmed the impact of the electric field on the elimination of bacterial flora. Persin et al. (1989)[11] also highlighted the importance of the electric field in the destruction of certain bacterial strains.

Further comparative research between electrocoagulation and chemical coagulation reinforced these findings, revealing a higher rate of elimination of bacteria and viruses using the electric field compared to chemical treatment [12].

In addition, during the electrocoagulation process, some oxidants such as hydrogen peroxide and hypochlorous acids can be formed by oxidation of chlorides naturally present in domestic effluents. These oxidants are powerful bactericidal agents, often present in detergents.

Unlike the hypochlorite ion (ClO^-), hypochlorous acid, which has no electrical charge, more easily crosses the cytoplasmic membrane of bacteria, leading to their destruction by disrupting certain metabolic processes. However, the mechanisms of active chlorine action are not yet fully elucidated.

Conclusions

In this study, the aim was to treat water from a refining company that was loaded with organic matter. For this purpose, electrocoagulation and chemical coagulation techniques were applied to this water.

The results of the various physicochemical pollution parameters obtained after electrocoagulation treatment show reductions of 96% for turbidity and 99% for COD. As for chemical coagulation, reductions of 92% and 96% respectively for turbidity and COD.

The study showed that the electrocoagulation process gives better performance when it is preceded by a pretreatment phase to reduce turbidity and organic load. Similarly, electrocoagulation allows a reduction of the microbial load of more than 99% on different bacteria.

This study confirmed the effectiveness of electrocoagulation treatment on different types of effluents compared to chemical coagulation. The study prospects are therefore turning towards the recovery of sludge from the treatment process with a view to having a system that does not generate any waste.

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