Optimization of Physicochemical Parameters during the Electrocoagulation Cadmium Elimination

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1.Introduction

Heavy metals have recently become one of the major environmental problems for decision makers. Indeed, the demographic evolution in the world was so dazzling that the need to search for more efficient means of production had become paramount. However, this has generated a huge amount of byproducts and more or less harmful waste for human health in the first place and for the environment in general [1–3].

As an example, we can cite the increasing use of industrial fertilizers in agriculture to optimize harvests. These fertilizers are generally obtained from phosphate deposits containing a large proportion of heavy metals [4]. The latter are thus found widespread on the agricultural land and are transported, by leaching effect, towards aquatic resources.

The danger represented by these heavy metals is mainly due to their high bioaccumulation level in living organisms and their nonbiodegradability [5, 6]. The cleanup usually requires their removal. Several decontamination techniques have been developed in research laboratories and industrial sites in order to eradicate this pollution or at least to minimize their effects. These techniques have been tested by researchers around the world more or less effectively. Mention may be made of, for example, extractions by the chelating agent [7], ozonation process [8], precipitation [9, 10], electrodeposition [11], membrane processes, phytoremediation, and adsorption on the nanostructure [12, 13].

The increased use of fertilizers from phosphates in agriculture generates water pollution by heavy metals contained in these phosphates at levels higher than the standards. In our study, we used a cadmium nitrate Cd(NO3)2 solution to simulate artificially polluted water, whose decontamination efficiency will be evaluated by an electrocoagulation/flotation process. During this work, we aimed to optimize the electrocoagulation process according to the following factors: initial pH of the solution, density of the electrolysis current, cell time, and nature of the supporting electrolyte and its concentration. The criteria adopted during the optimization of the process are relatively different from those used in similar studies. Indeed, we have tried to achieve maximum efficiency and also seeking to minimize costs and facilitate implementation. We achieved a 98% Cd removal efficiency from the solution at pH 7, J = 6.25 A/m2, t = 10 min, and [K2SO4] = 0.01 M. In addition, during the characterization of the flocs obtained as a supernatant, we first highlighted the presence of Cd in this gelatinous body and then the relatively easy volatility of Cd as well as that of aluminum oxide (Al2O3).
Cadmium is one of the most harmful heavy metals for human health in particular and for the environment in general. One source of provenance for this element in the environment is actually the use of chemical phosphate fertilizers [4]. This element is carcinogenic and accumulates in the kidneys [5].

The work presented in this manuscript aimed to treat wastewater, mainly the elimination of cadmium ions by the electrocoagulation process, using two aluminum recovery electrodes. Electrocoagulation is an electrochemical dissolution of a sacrificial anode in order to generate, within the solution, coagulants [14–16]. For an aluminum electrode, electrolysis generates Al3+ ions at the anode, which, depending on the pH of the medium, hydrolyze and form aluminum hydroxides [17]. The latter contributes to the destabilization of the ions in solutions (as heavy metal cations) and push them to aggregate around these coagulants to form larger and separable agglomerates. These flocs could either precipitate by the gravitational effect or be brought to the surface by a flotation process. The production of oxygen and especially hydrogen bubbles by electrolysis, according to reactions (1) and (2), favored the flotation phenomenon when using a sacrificial aluminum electrode [18–20]. These reactions can occur regardless of the pH of the medium. At alkaline pH, the production of gas bubbles was done according to the following:

At the cathode,

\[
2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2(g) \quad (1)
\]

At the anode,

\[
4\text{HO}^- \rightarrow \text{O}_2(g) + 2\text{H}_2\text{O} + 4e^- \quad (2)
\]

By filtering, this pasty supernatant can therefore be removed from the contaminated solutions [21].

During this study, we tried to optimize the physicochemical factors that control the electrocoagulation process, namely, the initial pH of the samples, the density of the electrolysis current, the electrolysis time, and the concentration and nature of the carrier electrolyte used [22, 23]. We also did emphasize the behavior of chloride ions relatively to sulfates during the Cd removal process. EDX and SEM analysis were used to confirm the presence of Cd ions in the flocs.

2. Materials and Methods

The experimental part of our study consisted in determining the effects of each physicochemical parameter, mentioned in the introduction, on the efficiency of the elimination of cadmium from the artificially contaminated water by electrocoagulation proceeding. The common conditions of experimentation during all the tests were

(i) Magnetic stirring speed of 110 rpm. This speed made it possible to homogenize the solution while protecting the consistency of the aggregates formed during the coagulation process.

(ii) Temperature controlled by a thermostatic bath at 25°C.

(iii) The settling time of the solution was 10 min. Two preliminary tests were carried out at 20 and 30 min. The results did not differ from those obtained after 10 min.

2.1. Parameters. The physicochemical parameters controlling the electrocoagulation process are

(i) Initial pH of the Solution. Various studies have shown that the electrocoagulation process is highly dependent on the pH [24–26]. It is, above all, the parameter which determines the speciation of metals in a solution and conditions the formation of the coagulant [27].

(ii) Current Density J. It would determine the speed of the electrochemical reaction(s) during the electrocoagulation process, including bubble production [24].

(iii) Electrolysis Time t. With the density of current J, time will determine the quantity of reactants involved in the process: Al3+ and HO− as the constituents of the coagulant and H2 and O2 as the flotation initiators. Faraday’s law [26, 27] (equation (1)) gives \( u = \frac{m}{S} = \frac{M(\text{Al})}{nF} \ast J \ast t \),

\[
(3)
\]

where \( n \) is the number of electrons transferred per Al atom and F is the Faraday constant.

(iv) The supporting electrolyte was reported to play an important role in the electrocoagulation process [24, 28]: on the one hand, it increases the value of the conductivity of the solution which reduces energy consumption, and on the other hand, it avoids the effect of ion migration, and, thirdly, it can influence the kinetics of certain electrochemical reactions that take place during the electrocoagulation process.

(v) Concentration of the Supporting Electrolyte. The increase in the concentration of ions, resulting from the dissolution of the support electrolyte, will increase the conductivity of the solution and also increase the speed of the processes involving these ions.

Each factor was varied within an interval that we had already set according to preliminary tests and to the literature. Table 1 summarizes the range of variation of the studied factors.

2.2. Chemical Preparation. All reagents used were of analytical quality. We prepared an artificial solution of Cd
(10 ppm) by dissolving the corresponding mass of cadmium nitrate in double distilled water. We added the supporting electrolyte used, either KCl or K₂SO₄, by dissolving the appropriate mass of the product in the artificial solution containing the Cd²⁺ ions. We also prepared a concentrated appropriate mass of the product in the artificial solution following stages:

2.4. Electrocoagulation. The work carried out included the following stages:

2.5. Cadmium Dosage. We determined the initial concentration of cadmium and that remaining in the filtrate by an assay by atomic absorption spectrometry (AAS), of Thermo Scientific brand 3000A, previously calibrated by high-purity Cd standard solutions.

2.6. Electrocoagulation Efficiency. The efficiency, of the electrocoagulation process during the treatment of the solution, was evaluated by the percentage of cadmium reduction. We calculated this efficiency by the following relation:

\[
E(\%) = \left( \frac{C_i - C_f}{C_i} \right) \times 100,
\]

where \(C_i\) is the concentration of Cd in the initial solution and \(C_f\) is the concentration of Cd in the final solution after electrolysis and filtration.

| Factor                                      | Range of variation |
|---------------------------------------------|--------------------|
| pH initial                                  | 4, 7, and 10       |
| Electrolysis time (min)                     | 5, 10, and 20      |
| Current density (A/m²)                      | 3.125, 6.25, 12, 18.75, 37.5, 50, 70, and 100 |
| Supporting electrolyte                      | KCl and K₂SO₄      |
| Supporting electrolyte’s concentration (M)  | 0.01, 0.05, and 0.1 |

### Table 1: Interval of variation of the factors studied.

The methodology adopted consisted in studying the effect of each parameter considered in order to determine the optimal conditions for eliminating Cd, while keeping the other factors constant.
3.1. Initial pH Effect. The electrocoagulation process strongly depends on solution’s pH. It affects Al’s speciation, which has a significant influence on the treatment mechanism [31]. It is considered to be a critical factor for the formation of amphoteric hydroxide \( \text{Al(OH)}_3 \), responsible for the formation of flocs [29]. To evaluate the effect of the initial pH on the efficiency of process and to determine the optimal pH thereof, we carried out a series of tests with three pH values: 4, 7, and 10. The pH was adjusted before the start of each test with NaOH and HCl solutions, while keeping the other operating conditions constant:

(i) \( f = 6.25 \text{ A/m}^2 \) (I = 10 mA)

(ii) \( t = 10 \text{ min} \)

(iii) Supporting electrolyte: potassium chloride with \([\text{KCl}] = 0.01\ \text{M}\)

Also, the final pH and conductance \( G \) values were noted for each test carried out (A, B, and C); the results obtained are collated in Tables 2 and 3.

As noted in Figure 1, pH had a real effect on the efficiency of Cd extraction from the artificially contaminated solution. Indeed, the variation of the initial pH of the solution from 4 to 10 led to a variation of this efficiency from 40% to 95.5%. Between pH 4 and 7, the elimination efficiency increased greatly with pH; however, beyond pH 7, a certain stability of the latter was noted. This phenomenon can be attributed to the formation of aluminum hydroxide from the \( \text{Al}^{3+} \) ions [26] formed at the anode (reaction (5)–(7)) and the \( \text{HO}^- \) ions in the solution (reaction (1)):

At the anode,

\[
\text{Al} \rightarrow \text{Al}^{3+} + 3e^- \quad (5)
\]

In the bulk of the solution,

\[
\text{Al}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_3 + 3\text{H}^+ \quad (6)
\]

The overall:

\[
\text{Al} + 3\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_3 + 3\text{H}^+ + 3e^- \quad (7)
\]

For pH below 7, \( \text{HO}^- \) ions were the limiting reagents and therefore the efficiency increased significantly with pH. This finding was supported by the fact that the pH at the end of tests A and B was higher than the initial pH. On the other hand, beyond pH 7, the efficiency of elimination of Cd\(^{2+}\) ions from the solution was practically constant and maximal. This led us to suppose that the hydroxides formed were sufficient for Cd\(^{2+}\) ions’ elimination. This could also be in agreement with the decrease in the final pH in experiment C. In fact, the pH of the solution was buffered by the two reactions (7) and (6) which took place in the solution: the hydronium ions, produced by reaction (7), were offset [32] by the hydroxide ions produced in reaction (1). The balance of the two reactions is as follows:

\[
2\text{Al} + 6\text{H}_2\text{O} \rightleftharpoons 2\text{Al(OH)}_3 + 3\text{H}_2 \quad (8)
\]

Some authors had reported that electrocoagulation process, using aluminum electrodes, exhibits a buffering capacity, especially at alkaline conditions [33]. We could also oppose the formation of complex ions \( \text{Al(OH)}_3^- \) according to reaction (9), to explain the decrease in pH in test C at pH 10, in accordance with Al’s Pourbaix diagram [34]:

\[
\text{Al(OH)}_3^- + \text{HO}^- \rightleftharpoons \text{Al(OH)}_4^- \quad (9)
\]

The latter takes place at a relatively basic pH. Besides, reaction (9) explains the reduction of pH during experiment C (pH 10). However, depending on the pH of the aqueous medium, \( \text{Al}^{3+} \) and \( \text{HO}^- \) react to form various monomeric species [14, 17, 35] such as \( \text{Al(OH)}_3^- \), \( \text{Al(OH)}_2^- \), and \( \text{Al(OH)}_4^- \) and polymeric species \( \text{Al}_n(\text{OH})_{3n} \). This latter structure contributed to the formation of the gelatinous supernatant above the solution.

As shown in Table 3, the conductance of the solution varied very little during the electrocoagulation process. This means that the ions from the support electrolyte were sufficient to ensure electrical conduction in the solution while avoiding the phenomenon of ion migration. As the quantity used was sufficient, we verified, during the study of the effect of the support electrolyte, if it could be reduced without loss of performance of the whole process.
In conclusion, the optimal pH [36] was around 10, but we noticed that a neutral pH could be appropriate because it was close to the common wastewater’s pH value. In addition, even if the efficiency (88.25%) was lower than that at pH 10 (95.5%), we could hope to improve this efficiency when optimizing the other factors. Hence, the following experiments were carried out at pH 7.

3.2. Effect of Electrolysis Time. One of the most important parameters in this study was the electrolysis time t [37]. To study its effect on the efficiency of this process, we examined a series of treatment trials: the first lasting 5 min, the second 10 min, and the last 20 min, while keeping the other operating parameters constant (pH = 7, \( J = 6.25 \text{ A/m}^2 \), and [KCl] = 0.01 M).

The results obtained are expressed graphically in Figure 2.

The results corresponding to the evolution of the initial pH and of the conductance \( G \) of the solution, during the experiment, are presented, respectively, in Tables 4 and 5.

As we can see in Figure 2, the efficiency of cadmium removal increased significantly over time (from test A to test B) and then stabilized around 87% beyond 10 min with a slight downward trend (88.75 in test B to 86% in test C). This dependence on time led us to kinetic considerations where we identified two phases:

(i) A first phase (between A and B), where the increase was proportional to time, which made us suggest that the limiting parameter was brought in as time was increased: it was probably a product of electrolysis and which participated in the formation of flocs. It was either the Al\(^{3+}\) ions or the hydroxide ions or both.

(ii) A second period (between B and C) where time has practically no effect on the efficiency of the removal of Cd\(^{2+}\) ions from the artificial solution. This led us to suppose that it was the transformation (the formation of coagulants and then flocs) itself which was limiting in this second phase: all the reagents were therefore present in more than sufficient quantity, and thus the elimination efficiency was controlled by the transformations that would operate on the reactants.

The evolution of the conductance of the solution is presented in Table 5. The variation was less than 2% in the three experiments. This confirmed that the supporting electrolyte was in enough quantity so as to minimize ion’s migration.

The examination of the evolution of the initial pH (Table 4) which increased slightly at the end of the process for the three tests (A, B, and C) showed that the contribution of the hydroxide ions was made almost in the same way during the three tests, and then it was the contribution of Al\(^{3+}\) ions which was probably responsible for the efficiency evolution in the first phase (from A to B). The amplitude of the pH’s variation revealed that the solution was still buffered by reaction (8) mentioned above.

Some authors have suggested that aluminum hydroxides, freshly formed, were best suited to form aggregates by adsorption of soluble ions and/or trap colloidal particles in suspension in the solution [24, 27, 28]. This property was due to their small size and consequently their large specific surface. Indeed, at the beginning of the experiment, the aluminum hydroxides formed find Cd\(^{2+}\) ions very close to the electrode: the time between their formation and that of the interaction with the pollutants is very short and therefore their activity is maximum. But as time passed, the concentration of Cd\(^{2+}\) ions around the electrode decreased and it took time, so that these two entities might diffuse towards each other to interact. Hence, the hydroxides were no longer fresh, and therefore their activity was decreased. As a result, the efficiency of removing Cd ions decreased as the electrolysis time increased [17]. The optimal time corresponding to the maximum removal efficiency of the pollutant was very dependent on the distance between the electrodes. The lower the latter, the shorter the time to reach the maximum efficiency.

Thus, the optimal electrolysis time was around 10 min. As time was closely linked to the cost of the process, it was wise to choose the shortest acceptable time.

3.3. Effect of Current Density \( J \). Current density was a critical parameter in the electrocoagulation process since it could be controlled directly and determine the rate of the electro-chemical reactions.

We studied the influence of the intensity of the current on the elimination efficiency of cadmium. For this, we
carried out a series of tests by applying current intensities of 5.10, 20.30, 40, 60, 80, 112, and 160 mA. Knowing the surface of the electrode, worth $S = 16 \text{ cm}^2$, the current densities $J$ corresponded, respectively, to 3.125, 6.25, 12, 18.75, 37.5, 50, 70, and 100 $\text{A/m}^2$ (while always keeping the other operating conditions constant: $\text{pH} = 7$, $t = 10 \text{ min}$, and $[\text{KCl}] = 0.01 \text{ M}$). Tests B, G, and I were repeated in order to evaluate the passivation effect.

The results in Table 6 are illustrated in Figure 3.

Tables 7 and 8 present the initial and final pH and the conductance value during electrolysis for each test carried out.

The evolution of the $\text{Cd}^{2+}$ ions’ elimination efficiency, by the electrocoagulation process, as a function of the density of the current, presented a very uneven form:

(i) Increasing phases relatively to $J$ between A and B, D, and E and finally F and H
(ii) Stationary phase between E and F
(iii) Decreasing phase between B and D, as well as H and I

This led us to suppose that the studied system undergoes a structural transformation during this operation. This modification was strongly dependent on the density of the current and consequently would concern the state of the metal/solution’s interphase. This irregular development was later verified during the study of the supporting electrolyte’s chloride ions which contribute to the degradation of this layer of alumina by their pitting [22, 42, 43] corrosive power. This was later verified during the study of the supporting electrolyte effect on the electrocoagulation process.

In order to reduce the phenomenon of passivation of the electrodes, several precautions have been taken:

(i) Permutation of the roles of the electrodes, especially during redone experiments (tests B, G, and I);
(ii) Mechanical cleaning of electrodes, between two experiments, by rubbing them with the sandpaper, followed by abundant washing with distilled water. This last operation is cited by authors as the most effective method for preserving electrodes [44].

The pH evolution during the electrocoagulation process, as reported in Table 7, was very small (max around 8%). At pH 7, the buffer effect is mainly due to reaction (7) which leads to aluminum hydroxide formation. Also, the solution’s conductance remains relatively stable during the process: the electrocoagulation process does not change the electrolyte consistency of the solution.

The reasonable choice of the current density therefore had to meet the two criteria: cost and efficiency. We had chosen the value of 6.25 $\text{A/m}^2$ for this purpose and above all to avoid the area where we had observed the reduction of the efficiency of removing Cd ions.

3.4. Supporting Electrolyte Effect. To study the effect of supporting electrolyte on the elimination of cadmium by the electrocoagulation process, we used two salts: potassium chloride KCl, whose chloride ions are suspected to have a disruptive effect, and potassium sulfate $\text{K}_2\text{SO}_4$, which is free from chloride ions.

3.5. Potassium Chloride KCl. The presence of chloride ions in the solution has been reported to decrease passivation of the electrode surface and thereby increase the efficiency of the electrocoagulation processes [45]. To study their effect, we carried out a series of tests with different KCl concentrations (0.01, 0.05, and 0.1 M), while keeping the other parameters constant ($\text{pH} = 7$, $t = 10 \text{ min}$, and $J = 6.25 \text{ A/m}^2$). Figure 4 represents the results obtained.

Tables 9 and 10 group together the initial and final values of the pH and the conductance G of the electrolytic solution.

The concentration of KCl, the supporting electrolyte, has a great influence on the efficiency of elimination of the $\text{Cd}^{2+}$ ions contained in the solution. These two quantities are inversely proportional. Indeed the latter varies from 95% for [KCl] = 0.01 M to 42% for 0.1 M. This allowed us to suggest that in addition to their role in the electrical conduction of the solution, the ions of the supporting electrolyte had an active role during the electrocoagulation process. In addition, this role is in competition with the extraction of Cd ions because a decrease in the efficiency of their elimination was observed when the concentration of the electrolyte increased. Several authors [29] have attributed this reduction to the complexation of $\text{Al}^{3+}$ ions (reaction (10)) or their hydrates (reaction (11)) by ligands L, including the chloride ions as [32]

\[
\text{Al}^{3+} + n \text{Cl}^- \rightleftharpoons [\text{Al(Cl)}_n]^{(3-n)^+}
\]

\[
\text{Al(H}_2\text{O)}_m(\text{aq})^{3+} + n \text{Cl}^-_{(aq)} = [\text{Al(H}_2\text{O)}_m\text{Cl}_n]^{(3-n)^+} + n\text{H}_2\text{O}_{(aq)}
\]

These cations will not be available to participate in the electrocoagulation process and therefore contribute to reducing the efficiency of elimination. Besides that, other authors have highlighted the formation in the aqueous solution of cadmium complexes with the ligands Cl$^-$ according to the global reaction (12) [46–48]:

\[
\text{Cd}^{2+} + n\text{Cl}^- \rightleftharpoons \text{Cd(Cl)}_n^{(2-n)^+}, \quad \text{where } n = 1, 2, 3, \text{ and } 4.
\]

Stability constants $K_n$ for $\text{Cd}^{2+}$-chloride systems in water were calculated [47] and are, respectively, 22.3, 60, 26, and $10^{-0.2}$. On the other hand, the variation in conductance, although small, increases from test A to test C. This allowed us to assume that the electrolyte ions are actually engaged
during the process, in agreement with the two preceding reactions (10) and (11).

This observation is supported by the slight increase in pH at the end of experiments A, B, and C. Indeed a number of HO\(^{-}\) had gone into the solution instead of forming aluminum hydroxides, and thus contribute to the rising of pH and reducing the elimination efficiency. But, this proportion of HO\(^{-}\) involved cannot explain this significant drop in the Cd ions’ removal efficiency from the solution. Hence, the magnitude of the variation in the efficiency of elimination of Cd ions from the solution, which decreased from 92.31\% to 41.22\%, suggested that it is rather the complexation of Cd ions by chlorides that predominates in determining the extraction efficiency of pollutants.

3.6. Potassium Sulfate K\(_2\)SO\(_4\) We carried out a series of tests with three different concentrations of K\(_2\)SO\(_4\) (0.01, 0.05, and 0.1 M), while keeping the other parameters constant (pH = 7, t = 10 min, and J = 6.25 A/m\(^2\)).

Figure 5 represents the percentage of removed Cd, relative to its initial value, after treatment of the solution, as a function of the current density of the supporting electrolyte. Tables 11 and 12 group together the initial and final values of the pH and of the conductance G of the electrolytic solution in the case of K\(_2\)SO\(_4\) as the supporting electrolyte.

The use of K\(_2\)SO\(_4\) as a supporting electrolyte slightly influenced the efficiency of elimination of Cd\(^{2+}\) ions, as depicted in Figure 5. This effect is negative because a
Figure 4: Effect of potassium chloride KCl on electrocoagulation.

Table 9: Initial and final pH of the solution (case of the KCl supporting electrolyte).

|       | A      | B      | C      |
|-------|--------|--------|--------|
| pH initial | 7.06   | 7.03   | 7.04   |
| pH final   | 7.65   | 7.33   | 7.37   |
| ΔpH        | 0.59   | 0.3    | 0.33   |

Table 10: The initial and final values of the conductance of the solution (case of KCl).

|       | A       | B       | C       |
|-------|---------|---------|---------|
| G initial (mS) | 1.77   | 7.15   | 13.05  |
| G final (mS)    | 1.73   | 7.05   | 12.89  |
| ΔG (mS)        | −0.04  | −0.1   | −0.16  |

Figure 5: Cd removal efficiency depending on the concentration of the supporting electrolyte.

Figure 6: Cd removal efficiency depending on the concentration of K₂SO₄.

Table 12: Variation of the conductance of the solution (case of K₂SO₄).

|       | A       | B       | C       |
|-------|---------|---------|---------|
| G initial (mS) | 2.77   | 11.19  | 21.7   |
| G final (mS)    | 2.74   | 10.97  | 21.2   |
| ΔG (mS)        | −0.03  | −0.22  | −0.5   |

decrease in this effectiveness was observed from 97% to 81% when the concentration increased from 0.01 to 0.1 M.

The linearity shape, between the percentage of Cd elimination and the concentration of the supporting electrolyte K₂SO₄ (Figure 5), suggested that only one phenomenon, linked to the SO₄²⁻ ions, took place during the electrocoagulation process. It was a phenomenon in competition with the elimination of Cd²⁺ ions as revealed by the decrease in the latter. As some authors have mentioned that the Cd²⁺ ions form complexes with sulfate ions [48] in addition to the CdSO₄ precipitate.

The presence of sulfate ions was less inhibiting than that of chloride ones on the decontamination efficiency of the simulated effluent. To illustrate this statement, we have compared the cadmium elimination efficiency as a function of the current density \( J \) during treatment in a medium containing potassium sulfates as the supporting electrolyte and those obtained previously in the case of potassium chloride. We had worked under unfavorable conditions to visualize the reducing effect of the efficiency of removal of Cd ions from the solution.

In view of the results obtained, we opted for K₂SO₄ as a supporting electrolyte at a concentration of 0.01 M.

In conclusion, the optimal conditions for the removal of Cd²⁺ ions from the artificially contaminated solution, by electrocoagulation process, were

(i) pH = 7
(ii) \( T = 10 \) min
(iii) \( J = 6.25 \) A/m²
(iv) K₂SO₄ supporting electrolyte at 0.01 M

Under these conditions, an elimination efficiency of 97.31% was obtained.

As can be seen in Table 13, compared to similar works, we have achieved a relatively effective elimination, but with a shorter treatment time and a lower current density. These two objectives were among our optimization criteria.
3.7. Characterization of Flocs. To reveal the presence of chloride and the sulfate ions in the flocs resulting from the electrocoagulation, we had carried out an analysis of the latter by scanning microscopy (SEM) of the gel obtained at the end of the electrolysis on the surface of the solution and also that of the solid obtained during the drying of this gel by moderately heating it.

Two experiments were carried out under optimal conditions (pH = 7, \( T = 10 \text{ min} \), \( J = 6.25 \text{ A/m}^2 \), and \( C = 0.01 \text{ M} \)), each with a supporting electrolyte (KCl or K\(_2\)SO\(_4\)). We thus, recovered four samples: two gelatinous and two in the solid state.

The four samples were then analyzed, by MEB and EDX, to determine their structure and composition. In Table 14, we have reported all the results obtained (photo, spectrum, and composition).

(i) First, we noticed that all the samples had an amorphous structure.

(ii) The two gelatinous samples 1 and 2 consist mainly of aluminum and oxygen, as shown by their atomic composition (68% in oxygen and 25% in aluminum for the first and 70% in O and 70% in Al for the second).

(iii) For the two solid samples 3 and 4, obtained by drying the electrolyzed solution on a hot plate, the main remark was the absence of Cd and the reduction of the Al and O content. This suggested that these structures are likely to evaporate at a relatively high temperature (about 120°C in our study). We could advance as the first conclusion that the interactions in the process of electrocoagulation flocculation were of the physical type since even at this “low” temperature, these interactions were broken. On the other hand, as has been demonstrated by other authors, cadmium was volatile [52, 53], and its transfer could take place by air (propagation of the pollution around the garbage incinerators) [54].

(iv) We also observed that the amount of K and Cl increased sharply in sample 3 and that of K and S in sample 4. This was due to the recovery of the ions in the solution in the form of a solid, namely, KCl and K\(_2\)SO\(_4\).

(v) For Cd ions, on the other hand, they were absent in the analysis: they were not recovered after evaporation of the solution.

(vi) The amount of cadmium removal by the aluminum atom was to the advantage of the medium containing the chloride compared to the sulfates. Indeed, the ratio of atomic percentages %Cd/%Al was equal to 0.0075 for Cl\(^-\) and 0.0050 for SO\(_4^{2-}\).

Based on these results, we could not explain the reduction in the efficiency of elimination of Cd\(^{2+}\) as a function of the concentration of Cl\(^-\): there must be other phenomena linked to the presence of chlorides. Some authors have reported the formation of cadmium complexes with chlorides as ligands [48]: CdCl\(_2^+\), CdCl\(_2\), CdCl\(_3^-\), and CdCl\(_4^{2-}\).

### Table 13: Cd removal efficiency and operating conditions in the EC process (similar works).

| Electrode | Interelectrode distance (cm) | \( J \) current density | \( pH \) | \( T \) (min) | Removal efficiency (%) | Reference |
|-----------|-----------------------------|-------------------------|-------|---------|----------------------|-----------|
| Vasudevan et al. | Al | 0.5 | 10 A/m\(^2\) | 7 | 5 | 92.4 | [49] |
| | | | 50 A/m\(^2\) | | | 97.9 | |
| Chien et al. | Al | 0.5 | 20 A/m\(^2\) | 7 | 30 | 96.8 | [50] |
| Yilmaz et al. | Al | 0.5 | 15 A/m\(^2\) | 6 | 30 | 99 | [20] |
| Hung et al. | Al-Cgr | 1 | 22 A/m\(^2\) | 11 | 10 | 99.5 | [50] |
| Koby et al. | Fe | 1 | 30 A/m\(^2\) | 8–10 | 80 | 99.4 | [51] |
| Aityoub et al. | Al | 1 | 10 A/m\(^2\) | 7 | 10 | 97.31 | This work |

Figure 6: Comparison between the effects of the two supporting electrolytes.
The speciation of Cd in the seawater was reported by Robert P. Mason [46, 48] as 2.9% for Cd\(^{2+}\), 39.8% for CdCl\(^+\), 28.9% for CdCl\(^2-\), 15.1% for CdCl\(^{-3}\), and 3.3% for CdCl\(^{-4}\). We could therefore assume that it was perhaps the formation of these complexes which entered into competition with electrocoagulation and caused the efficiency to be very reduced in a medium relatively rich in chlorides. Indeed, the latter went from [48] 92.31% in the middle 0.01 M in Cl\(^{-}\) to 41.22% for [Cl\(^{-}\)] \(\geq\) 0.1 M.

4. Conclusion

An aqueous solution of Cd (NO\(_3\))\(_2\) was used to simulate an artificially contaminated effluent. The decontamination by electrocoagulation/flocculation enabled us to achieve an elimination at 97.31%.

The water reduction reaction generated the hydrogen bubbles, which contributed to the flotation of the formed flocs. The quest for this result was made through the study of the effects of the factors pH, time, current density, concentration, and supporting electrolyte’s nature.

The use of a supporting electrolyte has reduced the effectiveness of decontamination. This negative effect was due, among other causes, to parasitic reactions which compete with decontamination by forming complexes with Cd ions and hence keeps them in the solution and therefore reduces the efficiency of their elimination. However, its use was necessary in order to prevent the Al\(^{3+}\) ions from being engaged to ensure electrical conduction in the solution (minimum concentration).

Chloride ions were more unfavorable than sulfate ions for decontamination by electrocoagulation. The optimization of this decontamination obeyed the three criteria: the cost of the operation (minimum time and minimum \(J\)), the ease of startup (neutral pH), and the efficiency (maximum elimination).

We were able to reach an efficiency of 97.31% under conditions which were not very drastic: pH \(\geq\) 7, \(T\) = 10 min, \(J\) = 6.25 A/m\(^2\), and C = 0.01 M of K\(_2\)SO\(_4\).

We achieved an efficiency of 99.89% but under non-optimal conditions (experience of comparison between KCl and K\(_2\)SO\(_4\)).

SEM and EDX analysis of the supernatant confirmed the presence of Cd ions in this gelatinous compound. Lastly, we also highlighted the volatility of aluminum oxide (Al\(_2\)O\(_3\)) as well as of the Cd ions linked to it, at temperatures approaching 120°C.

Data Availability

All the data are in the possession of the authors and would be provided if requested.

Conflicts of Interest

The authors declare that they have no conflicts of interest.
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