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Influence of the anodic material on electrocoagulation performance

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ABSTRACT

The removal of organic pollutants from a highly complex industrial wastewater by aluminum, iron and aluminum + iron electrocoagulation systems was evaluated. Under optimal conditions of pH 8 and 45.45 A m^{-2} current density, the electrochemical method yields a very effective reduction of all organic pollutants. The optimal treatment (aluminum + iron) reduced chemical oxygen demand (COD) by 69%, biochemical oxygen demand (BOD_5) by 71%, color by 83%, turbidity by 80% and total coliforms by 99%. The raw and treated wastewater was characterized by UV–vis spectroscopy and cyclic voltammetry to confirm the increase in water quality. Finally, the sludge produced during electrocoagulation was characterized by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDS).

1. Introduction

Billions of liters of industrial wastewater are produced every day. The presence of dyes and organic substances constitute a substantial source of pollution which exhibits intense color, high chemical and biochemical oxygen demand and suspended particles. Colored wastewater can cause environmental problems by absorbing light and interfering with fundamental aquatic biological processes. Several kinds of treatments have been used to remove pollutants from these effluents; unfortunately, most are not very effective in the case of mixed industrial wastewater [1,2].

Electrocoagulation processes are a promising technology that can be used for the removal of both color and colloidal particles [2–8]. Electrocoagulation is an electrochemical method of treating polluted water whereby sacrificial anodes dissolve to produce active coagulant precursors (usually aluminum or iron cations) into solution. Additionally, electrolytic reactions evolve gas (usually as hydrogen bubbles) at the cathode that can enhance the process; this effect is known as electroflotation [9–14].

Electrochemical methods offer some advantages over traditional chemical treatment: less coagulant ion is required, less sludge is formed, and electrocoagulation equipment is very compact; thus, suitable for installation where the available space is rather limited. Furthermore, the convenience of dosing control only by adjusting current makes automation quite easy [15–17].

Usually, aluminum or iron plates are used as anodes in the electrocoagulation process. When a direct current voltage is applied, the anodes dissolve to produce Al^{3+} or Fe^{2+} ions. The electrochemically generated metallic ions are good coagulants. They can hydrolyze near the anodes to produce a series of activated intermediates that are able to destabilize the finely dispersed particles present in the wastewater. The destabilized particles then aggregate to form flocs. At the same time, hydrogen bubbles produced at the cathode can float most of the flocs. Thus, the aggregates formed can be removed by decantation or flotation from wastewater [18].

A number of electrocoagulation studies have been carried out by different types of wastewater using either iron or aluminum as anodes. However, it has been noted that iron electrodes introduce a green color into treated water which then turns yellow and turbid. This effect is due to the presence of Fe^{2+} ions which oxidize to Fe^{3+} in acidic or neutral conditions. The formation of $Fe(OH)_3$ as result of the reaction of Fe^{3+} with OH^- ions gives yellow color to the water and increases turbidity. This phenomenon is the reason for choosing aluminum electrodes for electrocoagulation processes [19]. However, in the case of arsenic removal and colored wastewater, iron electrodes are much more effective than aluminum. The reason for this special case is that the adsorption capacity of hydrous aluminum oxide for As(III) is higher than ferric oxides [16]. Therefore, for an evaluation of the best performance of electrocoagulation, a laboratory treatment of pollutants is required to obtain the best removal yields [20,21].

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Only a very few reports on the combined use of both aluminum and iron electrodes in the same cell has been published [22–25]. Aluminum has been used as sacrificial anode and stainless steel or iron as cathode for removal of carbon black, clay, and suspended solids without changing polarity of electrodes. The use of combination electrodes of dissimilar metals and the frequent change of their polarity has not yet been studied, which may provide an alternative method for efficient removal of both organic materials and heavy metals from water. Recently arsenic removal efficiency of the Al–Fe combination electrode system has been described [26]. However, the use of combined aluminum and iron anodes in the same electrolytic cell for industrial wastewater has not been reported. Thus, the goal of this research is to investigate the influence of anodic material on the electrocoagulation process for treating highly polluted industrial wastewater.

The anodic materials used in the electrocoagulation process were aluminum, iron and aluminum + iron plates. The effectiveness of aluminum, iron, and aluminum + iron electrocoagulation systems was evaluated and the influence of different operating parameters optimized. The physicochemical characteristics of the wastewater before and after applying the electrochemical treatments are presented.

2. Materials and methods

2.1. Wastewater samples

Samples of wastewater were collected from a treatment plant located at the end of an industrial park. This facility receives the industrial discharge of 144 different factories. All of the industrial effluents enter the wastewater treatment plant together [18]. The actual wastewater treatment plant consists of shredders, sand separators, oil and grease separators, primary clarifiers, biological activated sludge reactors, secondary clarifiers and a chlorine disinfecting unit. This treatment only achieves a 60% reduction in COD, which does not comply with environmental discharge standards. Thus, additional treatment steps are required to improve the quality of the water.

Wastewater samples were collected at the inlet of the biological activated sludge reactor in plastic containers and cooled to 4 °C, then transported to the laboratory for analysis and electrochemical treatments.

2.2. Electrochemical reactors

Three different electrochemical reactors were used in this study. The main difference among them is the anodic material. The aluminum and iron reactors have the same characteristics; both of them are batch monopolar electrochemical reactors which contain an array of 10 parallel electrodes. Each electrode has 0.11 m long and 0.06 m wide which gives an area of 0.0132 m^2 each and a total anodic area, A_a of 0.066 m^2. A 4 dm^3 recipient served as the supply vessel for the reactor. A dc power source supplied the system with 1–4 A at 8 V, corresponding to a current density of 15.15–60.60 A m^{-2}. The electrochemical reactor with aluminum–iron anodes contains an array of 12 parallel electrodes; 6 aluminum and 6 iron electrodes, alternating the aluminum and iron. Each electrode is 0.11 m long and 0.06 m wide for an area of 0.0132 m^2 each and a total anodic area, A_a of 0.0792 m^2. The volume of the reactor is 4 dm^3, the dc power source supplied the system with 1–4 A at 13 V, corresponding to a current density of 12.62–50.5 A m^{-2}. After various elapsed times, samples were taken. A schematic diagram of the electrochemical reactors is shown in Fig. 1.

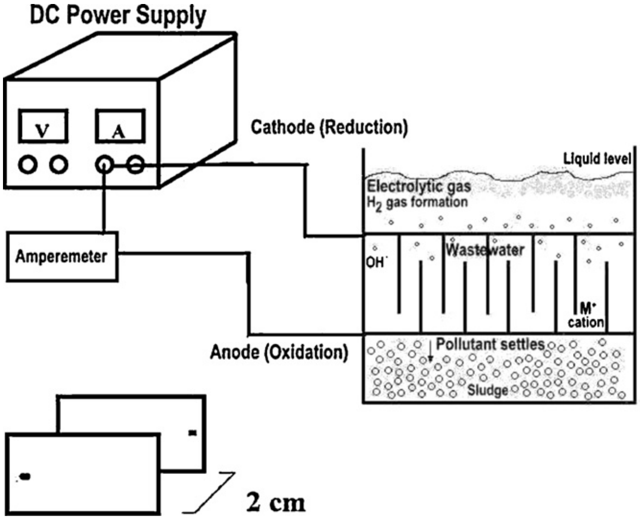

Fig. 1. A schematic diagram of the electrochemical reactors.

2.3. Methods of analysis

The initial evaluation of the electrochemical treatment was determined by analysis of the chemical oxygen demand (COD) and the color (465 nm, Pt/Co scale) at different time intervals. However, once the optimal conditions were found the raw and treated wastewater samples were analyzed for the BOD$_5$ and COD, color, pH, total coliforms, turbidity, iron and aluminum content, as indicated in the Standard Methods procedures [27].

2.3.1. Cyclic voltammetric measurements

Cyclic voltammetry of crude and treated wastewater was performed using a standard three-electrode cell. The waveforms were generated by a potentiostat model Epsilon-BAS The carbon paste electrodes (CPE) were circular with a surface area of about 3.5 mm^2. The CPE was prepared from a 1:1 mixture of 99.99% pure single crystal graphite (Alfa AESAR) and nujol oil (Fluka). The paste was transferred into a PVC tube and compacted to eliminate trapped air then a copper conductor was inserted before the paste set. The surface of the electrode was renovated after each potential scan [28]. The scan rate was 100 mV s^{-1}. The reference electrode was an Ag/AgCl saturated with KCl and the counter electrode was a platinum wire.

2.3.2. UV–vis spectrometry

UV–vis spectra were obtained from samples of raw and treated wastewater using a double beam PerkinElmer 25 spectrophotometer. The scan rate was 960 nm s^{-1} within the 200–700 nm wavelength range. The samples were scanned in quartz cells with a 1 cm optical path.

2.3.3. Thermodynamic analysis

The existence of aluminum and iron complexes in aqueous solution has been reported [29,30]. Using this information the distribution diagrams of chemical species were calculated using the MEDUSA program [31].

2.3.4. Sludge characterization

The sludge generated by the electrochemical technique was analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis (EDS). The analysis was performed on a Phillips XL-30 microscope to observe the composition and configuration of the structure. SEM provides images of rough material with resolu-

Table 1
Physicochemical characteristic of the raw industrial wastewater

Parameter	Value	Discharge limits in Mexico
COD (mg dm^{-3})	2000–2500	No value
BOD$_5$ (mg dm$^{-3)}$	900–1050	150
Color (Pt–Co U)	2500–4750	No value
Turbidity (NTU)	1400–1800	No value
pH	8	5–10
Fecal coliforms, MPN (mg dm^{-3})	110,000	No value
Total solids (mg dm^{-3})	5360	125

tion down to fractions of a micrometer, while energy disperse X-ray spectroscopy offers *in situ* elemental analysis.

3. Results and discussion

3.1. Wastewater characteristics

Table 1 shows the physicochemical characteristic of the raw industrial wastewater and the discharge limits indicated in the Mexican legislation.

3.2. Electrocoagulation using the aluminum anodes electrochemical reactor

Wastewater samples were taken from the inlet of the biological treatment tank, then electrochemically treated using the aluminum reactor, adjusting the pH (using NaOH or H_2SO_4) and applying 3 A of direct current with a treatment time of 60 min. The COD reduction as a function of treatment time at different initial wastewater pH values is shown in Fig. 2.

As shown in Fig. 2, the maximum COD reduction occurs in the pH range of 6–8 (46–50%). While the COD is reduced at all pH values, the least effective was at pH 12 (<37%).

It is important to note in Fig. 2 that the influence of the pH on the COD removal in the range of 4–8 is not significant. Chemical species associated with the aqueous pH are presented in Fig. 3. At a pH below 3.5 the aluminum ion is the predominant specie. However, at a pH 4–9.5 the predominant aluminum chemical specie is $Al(OH)_{3(s)}$. However, it is interesting to note that at pH greater than 10 a new aluminum complex forms: $Al(OH)_4{}^-$. This ion is soluble and directly affects the pollutant removal [3,5]. These results agree with previous research, which indicate that the maximum COD removal in wastewater is observed around pH 7 [4,32,33].

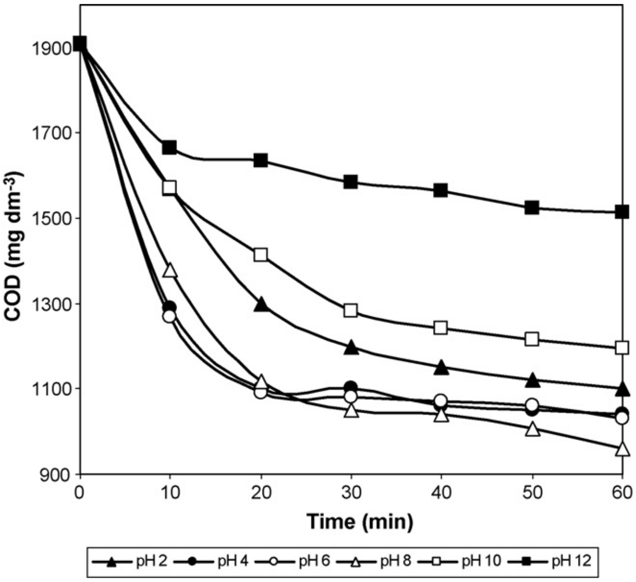

Fig. 2. Effect of pH on COD reduction by Al electrode reactor, applying 3 A of direct current with a treatment time of 60 min.

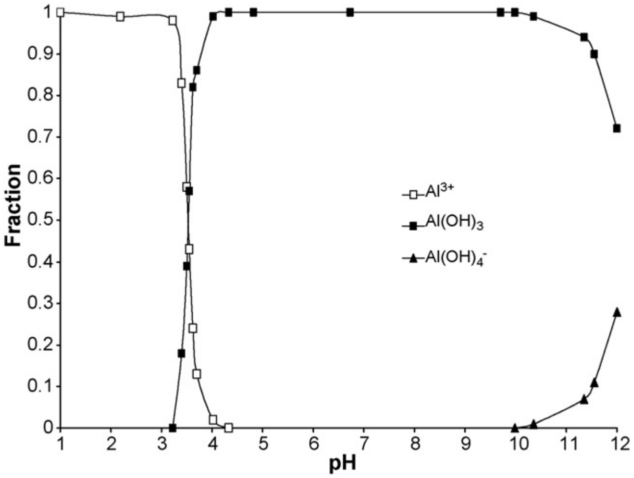

Fig. 3. Aluminum species distribution in wastewater as a function of pH. The concentration of aluminum is $[Al^{3+}]_{TOT} = 9.0$ mM.

COD removal is quite similar from pH 4 to 8. Since the actual initial pH of the wastewater is around 8, further experiments were performed at this condition.

The current density not only determines the coagulant dosage rate but also the bubble production rate and size of the flocs, which can influence the treatment efficiency of electrocoagulation [9,13]. Therefore, the effect of current on the pollutant removal was investigated. Fig. 4 shows the variation of the COD as a function of current density, note that the best removal rate is achieved under 45.45 A m^{-2} (50%) and no further increase in the COD removal is observed when the current density is increased to 60.6 A m^{-2} (50.6%).

Using the aluminum electrochemical treatment the total coliforms concentration was reduced by 99%, color was also reduced by 85% and an 83% reduction in turbidity was observed.

The Al concentration in the wastewater plays an important role in pollutant removal. Concentration and pH define the

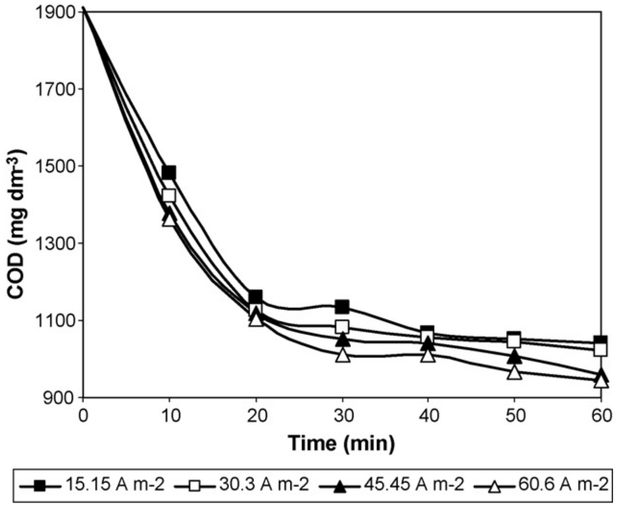

Fig. 4. COD removal from wastewater at different current densities by Al electrode reactor, wastewater pH of 8 and treatment time of 60 min.

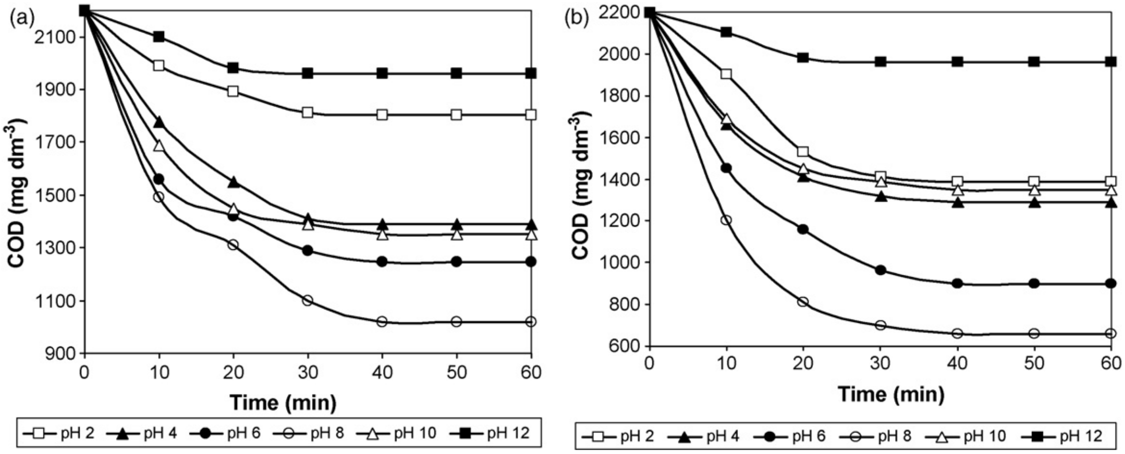

Fig. 5. COD reduction in wastewater as a function of treatment time by Fe electrode reactor at different initial pH, and applying 3 A of direct current with a treatment time of 60 min. Before (a) and after (b) precipitation of iron hydroxides with NaOH.

different possible Al chemical species present in aqueous solution.

The chemical dissolution process corresponds to the oxidation of the aluminum plates with the simultaneous reduction of water to form hydrogen [34], as shown in Eq. (1):

$$2Al_{(s)} + 6H_2O \rightarrow 2Al^{3+}{}_{(aq)} + 3H_{2(g)} + 6OH_{(aq)}{}^{-} \quad (1)$$

On the other hand, the electrochemical processes that occur on the anode and on the cathode surfaces are represented in Eqs. (2)–(4). On the anode, aluminum dissolution and oxygen evolution can compete. On the cathode, hydrogen evolution is the main expected reaction.

$$Al_{(s)} \rightarrow Al^{3+}{}_{(aq)} + 3e^{-} \quad (2)$$

$$2H_2O \rightarrow O_{2(g)} + 4H^{+}{}_{(aq)} + 4e^{-} \quad (3)$$

$$H_2O + e^{-} \rightarrow (1/2)H_{2(g)} + OH^{-}{}_{(aq)} \quad (4)$$

The cathode may also be chemically attacked by OH^- ions generated during H_2 evolution at high pH.

$$2Al + 6H_2O + 2\,OH^{-} \rightarrow 2Al(OH)_4{}^{-} + 3H_2 \quad (5)$$

The aluminum and hydroxide ions generated by electrode reactions react to form $Al(OH)_{3(s)}$.

Using Faraday's law to calculate the maximum amount of Al produced in the electrochemical process in Eq. (6) and with the experimental conditions of 3 A of current and 60 min of electrolysis along with the Faraday constant and the charge on the cation ($z = +3$), it is possible to calculate the maximum amount of Al, in this case 0.036 mol or 972 mg:

$$n = \frac{It}{zF} \quad (6)$$

The Al concentration in solution can be calculated using Eq. (7):

$$[M] = \frac{n}{V} \quad (7)$$

where n is the number of moles and V is the volume (4 dm^{-3}) of the reactor. The maximum expected Al concentration is thus 242 mg dm^{-3}. A particular effect that has been recently noted is the so-called "superfaradaic efficiencies". This term describes the difference between the theoretical amount of aluminum in aqueous solution and the actual Al detected. The detected Al concentration in aqueous solution in the mixed solution is 358 mg dm^{-3} (previous to settling). The theoretical calculation corresponds to 242 mg dm^{-3}, which implies that there is an excess of 50%. A possible explanation of this difference is that a chemical process takes place at the cathode promoting aluminum dissolution. The electrochemical oxidation and reduction of water can modify the pH on

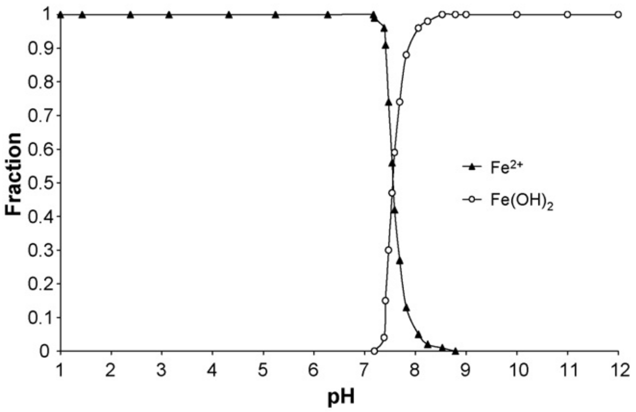

Fig. 6. Iron(II) species distribution diagram in wastewater as a function of pH. The concentration of iron is $[Fe^{2+}]_{TOT}$ = 18.0 mM.

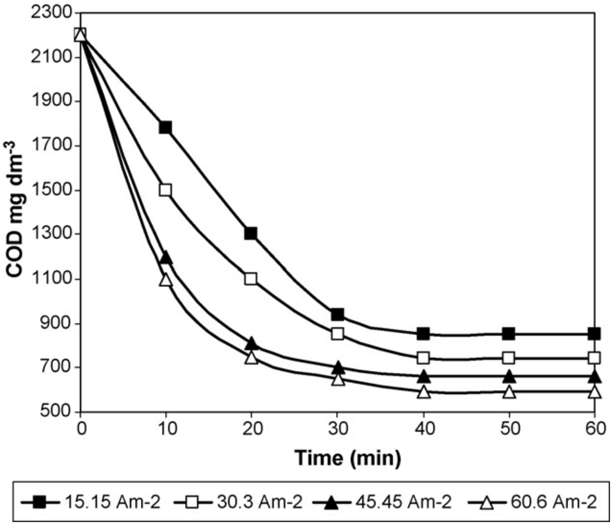

Fig. 7. COD removal from wastewater in time in Fe reactor at different current densities, wastewater pH of 8 and treatment time of 60 min.

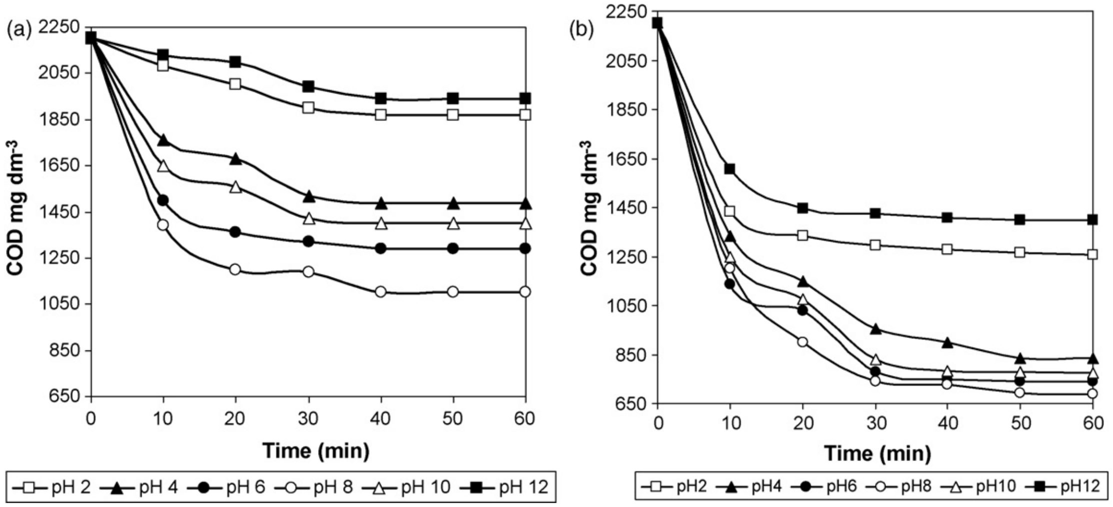

Fig. 8. COD reduction in wastewater in time by Al + Fe electrode reactor at different initial pH, and applying 3 A of direct current with a treatment time of 60 min. Before (a) and after (b) precipitation of iron hydroxides with NaOH.

the anode and cathode surfaces with respect to the bulk pH. This is especially important on the cathode, where the pH can become strongly alkaline. This can justify the important contribution of the aluminum chemical dissolution in the cathode to the total dissolution rate [6].

3.3. *Electrocoagulation using the iron anodes electrochemical reactor*

In the case of iron anodes, wastewater samples were taken at different treatment times, as shown in Fig. 5, the best conditions to obtain insoluble chemical specie starts at pH 9. Therefore, we present two figures to show how the COD removal rate can be modified if the final pH is adjusted.

Fig. 5a and b shows the COD removal as a function of treatment time at different initial wastewater pH values. After certain elapsed times, samples were taken and the supernatant (Fig. 5a) analyzed. At the same time, another set of samples were adjusted to final pH 9.5 using NaOH for precipitating iron hydroxides (Fig. 5b).

Fig. 5a shows that the maximum COD removal occurs at pH 8 (53%) and the lowest at pH 12. Fig. 5b shows that if pH is adjusted to 9.5, increasing precipitation, COD reduction increases, with the maximum reduction still at pH 8 (70%).

It is generally accepted that iron hydroxyl complexes form after the initial oxidation at the anode and the highly insoluble compound $Fe(OH)_2$ is the predominant specie over a wide pH range [35]. These results agree with previous research [36,37] that at pH 5–9, the majority of iron complexes (coagulants) are formed and this is the optimum pH range for carrying out electrocoagulation. The minimum COD reduction was at pH 2, since hydroxide ions generated at the cathode were neutralized by H^+ ions, limiting the formation of iron hydroxide complexes (Fig. 6).

As previously discussed, COD reduction is quite similar from pH 4 to 8. Since the actual pH of the wastewater is around 8, further experiments were performed in this condition but final pH is adjusted to 9.5, to improve the hydroxide precipitation.

Fig. 7 shows the variation of the COD as a function of current density, note that the best removal rate is achieved under 45.45 A m^{-2} (70%) and no significant increase in the COD removal is observed when the current density is increased to 60.6 A m^{-2} (73%).

The total coliforms, color and turbidity concentration were reduced by 99%, 81% and 80%, respectively.

The iron concentration in wastewater plays an important role in pollutant removal. Concentration and pH define the different possible iron chemical species present in aqueous solution. Using Faraday's law to calculate the maximum amount of Fe^{2+} produced in the electrochemical process in Eq. (6), with the experimental conditions of 3 A of current and 60 min of electrolysis along with the Faraday constant and the charge on the cation ($z = +2$), it is possible to calculate the maximum amount of Fe^{2+} to be 0.056 mol or 3.12 g.

The iron concentration in solution can be calculated using Eq. (7): where n is the number of moles and V is the volume (3 dm^{-3}) of the reactor. The maximum concentration is thus 1042 mg dm^{-3} Fe^{2+}. A particular effect that has been recently noted is the so-called "superfaradaic efficiencies". The detected Fe concentration in aqueous solution in the mixed solution is 1150 mg dm^{-3} (previous to settling). The theoretical calculation corresponds to mg dm^{-3}; this implies that there is an excess of 10%.

Electrocoagulation of wastewater using iron electrodes takes place according to the following reactions [38]:

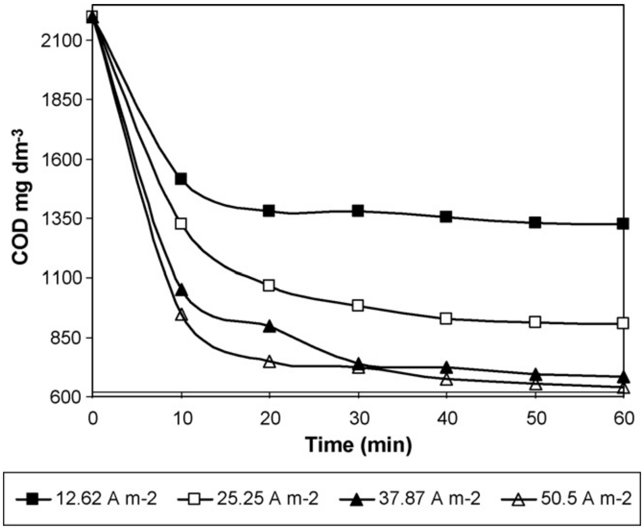

Fig. 9. COD reduction in wastewater in an Al + Fe reactor at different current densities, wastewater pH of 8 and treatment time of 60 min.

Anodic reaction:

$$Fe_{(s)} \rightarrow Fe^{2+}{}_{(aq)} + 2e^{-} \quad (8)$$

Cathodic reaction:

$$2H_2O_{(l)} + 2e^{-} \rightarrow 2OH^{-}{}_{(aq)} + H_{2(g)} \quad (9)$$

Solution reaction

$$Fe^{2+}{}_{(aq)} + 2OH^{-}{}_{(aq)} \rightarrow Fe(OH)_{2(s)} \quad (10)$$

Overall reaction:

$$Fe_{(s)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + H_{2(g)} \quad (11)$$

3.4. Electrocoagulation using the aluminum + iron anodes electrochemical reactor

In the cases of the reactor with both aluminum and iron anodes, wastewater samples were taken at specific treatment times as shown in Fig. 8. The best conditions for forming the insoluble iron complex starts at pH 9. Since final pH affects iron complex precipitation, analysis was done both straight out of reactor and after treatment with NaOH as shown in Fig. 8a and b.

As shown in Fig. 8, minimal COD reduction occurs when the initial pH is 2 or 12 and the maximum is at pH 8. In addition, post-treatment addition of NaOH to encourage precipitation of the iron hydroxides, increases the maximum COD removal from 50% to 69%.

The distribution diagram of aluminum and iron chemical species calculated from the MEDUSA program gives the same results as shown in Figs. 3 and 6. At low pH the aluminum ion is the predominat specie in solution, from pH 3.3 to 10.0 $Al(OH)_{3(s)}$ is the most abundant chemical specie in the solution; however, above pH of 10 the soluble $Al(OH)_4{}^{-1}$ appears in the solution causing the redisolution of sludge. The iron species are: Fe^{2+} dominates up to pH 7.5, after which $Fe(OH)_{2(s)}$ remain.

Since the COD reduction is quite similar from pH 4 to 8 and the actual pH of the wastewater is around 8, the experiments were performed at that pH, but afterwards adjusted to about 9–10 to improve the iron hydroxide precipitation.

The variation of the COD as a function of current density is shown in Fig. 9. The optimum reduction is achieved at 37.87 A m^{-2} (69%) with only a slight increase when the current density is increased to 50.5 A m^{-2} (71%).

The aluminum + iron combined electrochemical treatment reduces total coliforms, color and turbidity by 99%, 83% and 80%, respectively.

Using Faraday's law in Eq. (6), with the experimental conditions of 3 A of current and 60 min of electrolysis along with the Faraday constant and the charge on the cation (z = + 3), the calculated maximum amount of Al is 0.036 mol or 972 mg. The Al concentration in solution is calculated using Eq. (7) to be 242 mg dm^{-3}.

Likewise, the calculated maximum amount of Fe^{2+} is 0.056 mol or 3.12 g and the corresponding maximum concentration is 782 mg dm^{-3} Fe^{2+}.

The detected Fe and Al concentration in aqueous solution in the mixed solution were found to be quite similar to the expected theoretical values.

Table 2
COD reduction kinetics, using first- and second-order equations

Electrode	First-order model		Second-order model	
	K (min^{-1})	r^2	$K \times 10^{-5}$ (dm^3 mg min^{-1})	r^2
Aluminum	0.026	0.984	2	0.997
Iron	0.050	0.985	4	0.999
Aluminum + iron	0.044	0.958	3	0.991

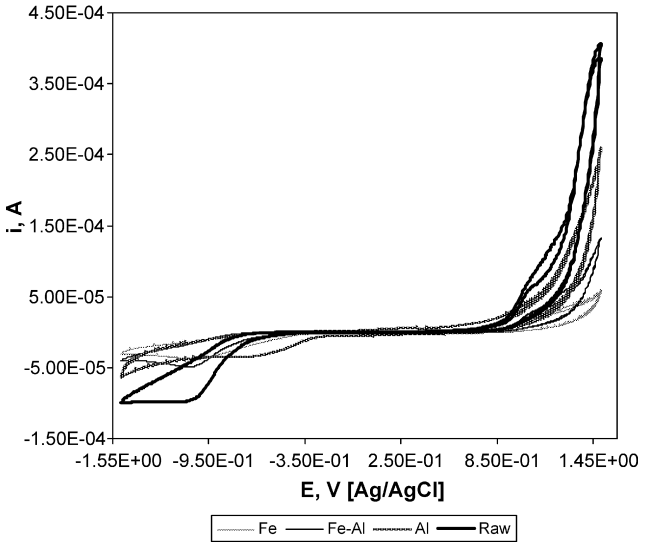

Fig. 10. Cyclic voltammograms recorded at the 3.5 mm^2 CPE over a potential window of −1.5 to 1.45 V of the raw, aluminum, iron, and aluminum + iron treated wastewater.

The reactions that are taking place are show below:

Anodic reactions:

$$Al_{(s)} \rightarrow Al^{3+}{}_{(aq)} + 3e^{-} \quad (12)$$

$$Fe_{(s)} \rightarrow Fe^{2+}{}_{(aq)} + 2e^{-} \quad (13)$$

Cathodic reaction:

$$2H_2O_{(l)} + 2e^{-} \rightarrow 2OH^{-}{}_{(aq)} + H_{2(g)} \quad (14)$$

Solution reactions:

$$Fe^{2+}{}_{(aq)} + 2OH^{-}{}_{(aq)} \rightarrow Fe(OH)_{2(s)} \quad (15)$$

$$Al^{3+}{}_{(aq)} + 3OH^{-}{}_{(aq)} \rightarrow Al(OH)_{3(s)} \quad (16)$$

Overall reaction:

$$Fe_{(s)} + Al_{(s)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + Al(OH)_{3(s)} + H_{2(g)} \quad (17)$$

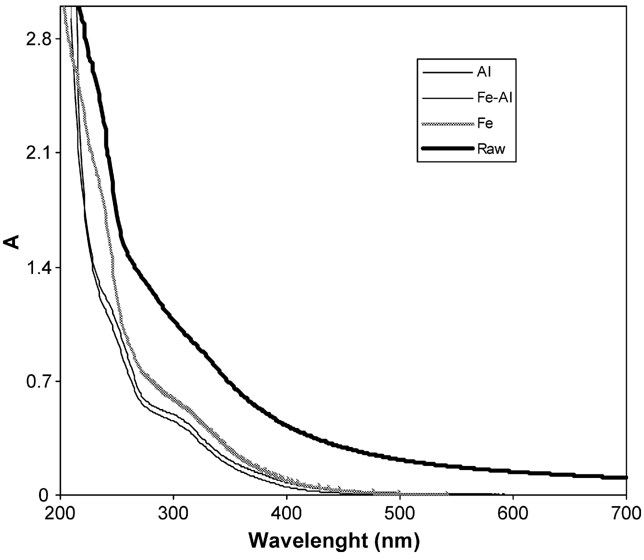

Fig. 11. UV–vis spectra of the raw, aluminum, iron, and aluminum + iron treated wastewater, The scan rate was 960 nm s^{-1} within the 200–700 nm wavelength range. The samples were scanned in quartz cells with a 1 cm optical path.

Table 3
A comparative results obtained by the three anodic experiments.

Parameter	Raw wastewater	Aluminum		Iron		Aluminum–iron	
		Concentration	% Removal	Concentration	% Removal	Concentration	% Removal
COD ($mg\,dm^{-3}$)	2202	1107	50	660	70	687	69
BOD_5 ($mg\,dm^{-3}$)	1030	552	46	315	70	300	71
Color (Pt–Co U)	3525	535	85	650	81	600	83
Turbidity (NTU)	1975	320	83	388	80	388	80
Total coliforms, MPN ($mg\,dm^{-3}$)	1.1×10^5	<3	>99	<3	>99	<3	>99
Sludge ($kg\,m^{-3}$)	NA	11	NA	20	NA	9.6	NA
Al and/or Fe ($mg\,dm^{-3}$)	<1.0	21.37	NA	0	NA	9.0	NA

3.5. COD reduction velocity

The COD reduction velocity can be obtained using a kinetic model. Recent research describes that the kinetic constant can be obtained using the drop of the pollutant and discarding the points that remain constant in wastewater [39]. The COD reduction kinetics was evaluated using the first and second-order equations (Table 2) through a final electrolysis time of 60 min, pH 8 and 3 A. The second-order model best fits the decrease in COD with time is (Eq. (18)):

$$\frac{dC_{COD}}{dt} = -k[C_{COD}]^2 \qquad (18)$$

where C_{COD} represents the COD ($mg\,dm^{-3}$), t represents the time, and k the rate constant or the velocity at which the pollutant is being removed from wastewater ($dm^3\,mg\,min^{-1}$).

Recent research indicates that this model represents the COD reduction kinetics for electrocoagulation treatment [33].

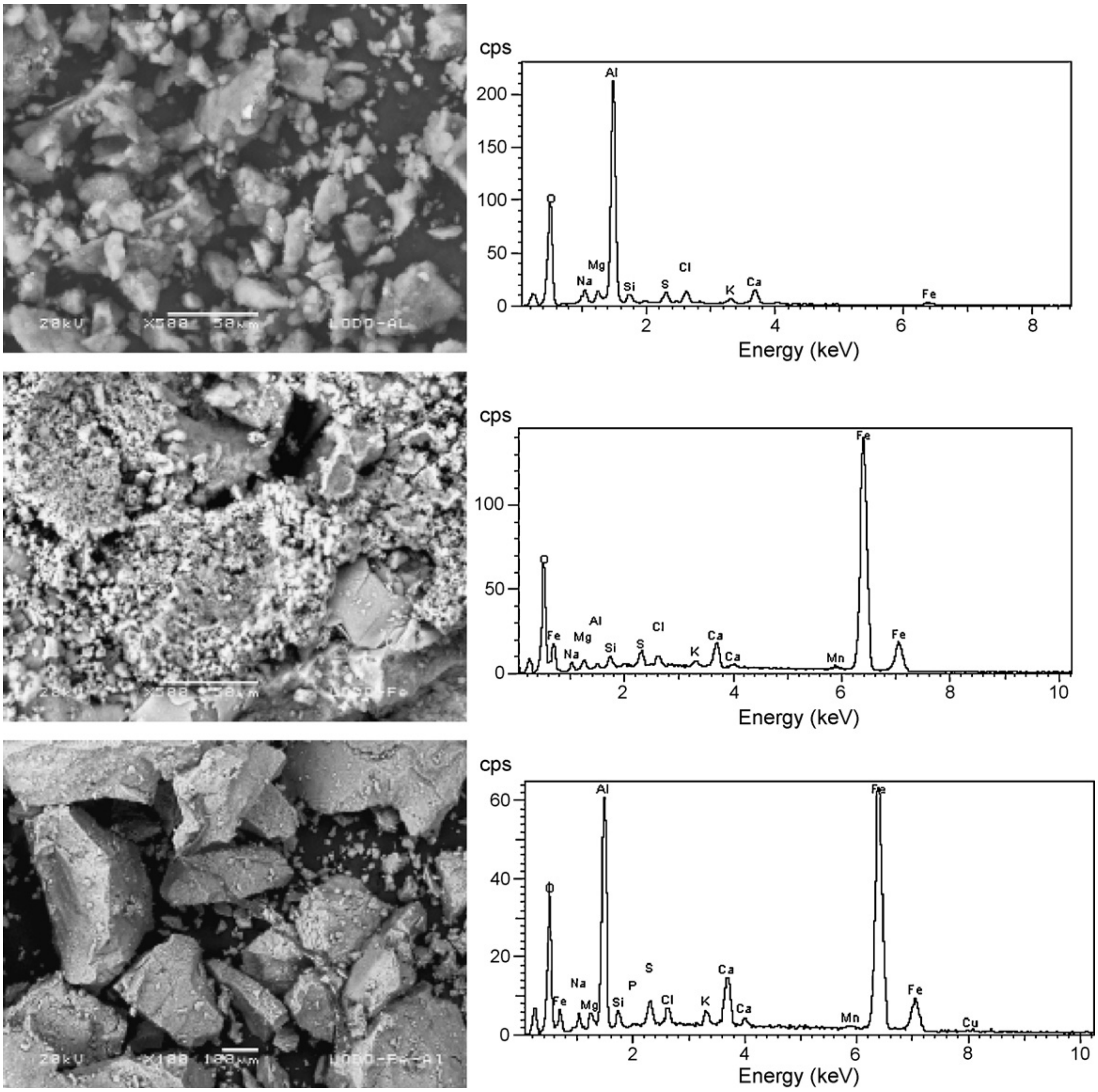

Fig. 12. Micrographs and elemental analysis of the sludge generated by aluminum (a), iron (b), and aluminum + iron and (c) electrocoagulation process.

3.6. Comparative results

Once the optimal conditions were found the raw and treated wastewater samples were analyzed using the BOD_5 and COD, total coliforms and turbidity. Table 3 shows the efficiencies obtained.

Both aluminum and iron are almost equally effective in reducing fecal coliforms and turbidity. However, aluminum was found to be more effective in removing color than iron.

However, aluminum was found to be more effective in removing color than iron and iron was more effective in reducing COD. The effluent treated with iron as the sacrificial anode appeared yellow, then turned brown. This behavior is attributed to the excess of iron ions generated during the electrolysis. The charge of Al (3^+) is greater than Fe (2^+), so the removal capability of Al is greater than Fe. COD is a measure of oxidizable components of solution including organics (dye, etc.) and inorganics (Fe (2^+), among others). So, the oxidation capability of Fe increases the COD removal value while for determination of correct COD removal value of the solution, the Fe must be removed from solution because Fe (2^+) was oxidized to Fe (3^+) and increases the COD removal value. Indeed, aluminum + iron was combined to gain the advantages of both.

3.7. Cyclic voltammetry measurements

Cyclic voltammetry of raw and treated wastewater was performed using a standard three-electrode cell. A chemically irreversible oxidation peak at a potential lower than that corresponding to oxygen evolution is seen in Fig. 10 indicating the reduction in COD.

3.8. UV–vis spectrometry

The UV–vis spectra of the raw, Al, Fe and Fe + Al electrochemically treated wastewater are shown in Fig. 11. There is a continuous signal curve in the region around 200–700 nm in the spectra corresponding to components of the wastewater. It is interesting that the intensity of the curves decrease by anodic effects. These results indicate that there is a significant color reduction of the raw wastewater when the electrochemical treatments are applied.

3.9. Sludge characterization

SEM and EDS provides information about the morphology and elemental composition of the sludge generated by aluminum, iron, and aluminum + iron electrocoagulation process. Fig. 12 shows different morphological images of the sludge. Fig. 12a shows the aluminum sludge flocs composed primarily of aluminum compounds. Fig. 12b shows the iron treatment sludge composed mainly of iron compounds. Fig. 12c shows the aluminum + iron treatment sludge with both aluminum and iron present in the structure.

Previous research indicates that when combined Fe and Al electrodes where used in a single electrochemical cell for As removal, the sludge seem to be amorphous/poorly crystalline phases for aluminum hydroxide/oxyhydroxides (bayerite ($Al(OH)_3$), diaspore ($AlO(OH)$)), and iron oxyhydroxides (lepidocrocite ($FeO(OH)$), magnetite (Fe_3O_4), iron oxide (FeO)) [26].

4. Conclusions

The use of iron or aluminum as sacrificial electrodes in the treatment of wastewater by electrocoagulation has been found to be dependent on both pH and current density. Under the same operational conditions aluminum and iron electrodes are almost equally effective in reducing fecal coliformes and turbidity. However, aluminum was found to be more effective in removing color, while iron was more effective in reducing COD, therefore the optimum practice is to combine aluminum + iron for obtaining high COD and color removal efficiencies.

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References

[1] J.G. Ibanez, M.M. Singh, Z. Szafran, Laboratory experiments on electrochemical remediation of environment. IV. Color removal of simulated wastewater by electrocoagulation–electroflotation, J. Chem. Educ. 75 (1998) 1040–1041.
[2] A.H. Essadki, M. Bennajah, B. Gourich, Ch. Vial, M. Azzi, H. Delmas, Electrocoagulation/electroflotation in an external-loop airlift reactor—Application to the decolorization of textile dye wastewater: a case study, Chem. Eng. Process. 47 (2008) 1211–1223.
[3] M. Bayramoglu, M. Eyvaz, M. Kobya, Treatment of the textile wastewater by electrocoagulation economical evaluation, Chem. Eng. J. 128 (2007) 155–161.
[4] M. Kobya, E. Demirbas, O.T. Can, M. Bayramoglu, Treatment of levafix orange textile dye solution by electrocoagulation, J. Hazard. Mater. 132 (2006) 183–188.
[5] N. Daneshvar, H. Ashassi Sorkhabi, M.B. Kasiri, Decolorization of dye solution containing acid red 14 by Electrocoagulation with a comparative investigation of different electrode connections, J. Hazard. Mater. 112 (2004) 55–62.
[6] P. Cañizares, F. Martínez, M. Carmona, J. Lobato, M.A. Rodrigo, Continuos electrocoagulation of synthetic colloid-polluted wastes, Ind. Eng. Chem. Res. 44 (2005) 8171–8177.
[7] C. Tsouris, D.W. DePaoli, J.T. Shor, M.Z.-C. Hu, T.-Y. Ying, Electrocoagulation for magnetic seeding of colloidal particles, Colloids Surf. 177 (2001) 223–233.
[8] S.S. Vaghela, A.D. Jethva, B.B. Mehta, S.P. Dave, S. Adimurthy, G. Ramachandraiah, Laboratory studies of electrochemical treatment of industrial azo dye effluent, Environ. Sci. Technol. 39 (2005) 2848–2855.
[9] P.K. Holt, G.W. Barton, C.A. Mitchell, The future of electrocoagulation as a localized water treatment technology, Chemosphere 59 (2005) 355–367.
[10] X. Chen, G. Chen, P.L. Yue, Investigation on the electrolysis voltage of electrocoagulation, Chem. Eng. Sci. 57 (2002) 2449–2455.
[11] M. Khemis, J.P. Leclerc, G. Tanguy, G. Valentin, F. Lapicque, Treatment of industrial liquid wastes by electrocoagulation: experimental investigations and an overall interpretation model, Chem. Eng. Sci. 61 (2006) 3602–3609.
[12] X. Chen, G. Chen, P.L. Yue, Separation of pollutants from restaurant wastewater by electrocoagulation, Separ. Purif. Technol. 19 (2000) 65–76.
[13] N. Adhoum, L. Monser, Decolourization and removal of phenolic compounds from olive mill wastewater by electrocoagulation, Chem. Eng. Process. 43 (2004) 1281–1287.
[14] G. Chen, Electrochemical technologies in wastewater treatment, Separ. Purif. Technol. 38 (2004) 11–41.
[15] J.Q. Jiang, N. Graham, C. André, G.H. Kelsall, N. Brandon, Laboratory study of electro-coagulation-flotation for water treatment, Water Res. 36 (2002) 4064–4078.
[16] P. Ratna Kumar, S. Chaudhari, K.C. Khilar, S.P. Majan, Removal of arsenic from water by electrocoagulation, Chemosphere 55 (2004) 1245–1252.
[17] C. Barrera-Díaz, M. Palomar-Pardavé, M. Romero-Romo, S. Martínez, Chemical and electrochemical considerations on the removal process of hexavalent chromium from aqueous media, J. Appl. Electrochem. 33 (2003) 61–71.
[18] I. Linares-Hernández, C. Barrera-Díaz, G. Roa-Morales, B. Bilyeu, F. Ureña-Nuñez, A combined electrocoagulation–sorption process applied to mixed industrial wastewater, J. Hazard. Mater. 144 (2007) 240–248.
[19] C. Barrera-Díaz, F. Ureña-Núñez, E. Campos, M. Palomar-Pardavé, M. Romero-Romo, A combined electrochemical-irradiation treatment of highly colored and polluted industrial wastewater, Rad. Phys. Chem. 67 (2003) 657–663.
[20] A. Vlyssides, E.M. Barampouti, S. Mai, Degradation of methylparathion in aqueous solution by electrochemical oxidation, Environ. Sci. Technol. 38 (2004) 6125–6131.
[21] Z. Zaroual, M. Azzi, N. Saib, E. Chainet, Contribution to the study of electrocoagulation mechanism in basic textile effluent, J. Hazard. Mater. 131 (2006) 73–78.
[22] D.P. Avetisyan, A.S. Tarkhanyan, L.N. Safaryan, Electrofloatationcoagulation removal of carbon black from acetylene production wastewaters, Sov. J. Water Chem. Technol. 6 (1984) 345–346.
[23] P.K. Holt, G.W. Barton, M. Wark, C.A. Mitchell, Aquantitative comparison between chemical dosing and electrocoagulation, Colloids Surf. A 211 (2002) 233–248.
[24] A.I. Ivanishvili, V.I. Przhegorlinskii, T.D. Kalinichenko, Comparative evaluation of the efficiency of electrocoagulation and reagent methods of clarifying waste water, Sov. J. Water Chem. Technol. 9 (1987) 468–469.
[25] V.K. Syrbu, R.V. Drondina, A.M. Romanov, A.I. Ershov, Combined electroflotocoagulation apparatus for water purification, Elektronnaya Obrabotka Materialov (Electron Treat. Met.) (1986) 57–59.

[26] A.G. Jewel, Gomesa, A Praveen Daida, a Mehmet Kesmez, A Michael Weir, H. Morenoa, R. Jose, B. Parga, C. George Irwin, D. Hylton McWhinney, D. Tony Grady, A. Eric Peterson, L. David, Cocke, Arsenic removal by electrocoagulation using combined Al–Fe electrode system and characterization of products, J. Hazard. Mater. B139 (2007) 220–231.

[27] APHA, AWWA, Standard Methods for the Examination of Water and Wastewater, 19th edition, American Public Health Association, Washington, DC, 1995.

[28] G. Roa-Morales, L. Galicia, M.T. Ramírez-Silva, Evidence of ternary inclusion complexes formation using factorial design and determination of constant, J. Incl. Phenom. 46 (2003) 139–145.

[29] M.R. Smith, A.E. Martell, Critical Stability Constants, Plenum Press, USA, 1974.

[30] C. Baes, R. Mesmer, The Hydrolysis of Cations, Robert E. Kriegeer, Malabar, FL, 1986.

[31] I. Puigdomenech, Hydrochemical Equilibrium Constants Database (MEDUSA), Royal Institute of Technology, Stockolm, 1997.

[32] G. Mouedhen, M. Feki, M. De Petris Wery, H.F. Ayedi, Behavior of Aluminium electrodes in electrocoagulation process, J. Hazard. Mater. 150 (2008) 124–135.

[33] M. Kobya, H. Hiz, E. Senturk, C. Aydiner, E. Demirbas, Treatment of potato chips manufacturing wastewater by electrocogulation, Desalination 190 (2006) 201–211.

[34] T. Picard, G. Cathalifaud-Feuillade, M. Mazet, C. Vandensteendam, Cathodic dissolution in the electrocoagulation process using aluminium electrodes, J. Environ. Monit. 2 (2000) 77–80.

[35] D. Ryan, A. Gadd, J. Kavanagh, M. Zhou, G. Barton, A comparison of coagulant dosing options for the remediation of molasses process water, Separ. Purif. Technol. 58 (2008) 347–352.

[36] M.Y.A. Mollah, P. Morkovsky, J.A.G. Gomes, M. Kesmez, J. Parga, D.L. Cocke, Fundamentals, present and future perspectives of electrocoagulation, J. Hazard. Mater. B 114 (2004) 199–210.

[37] N. Daneshvar, A.R. Khataee, A.R. Amani Ghadim, M.H. Rasoulifard, Decolorization of C.I. Acid Yellow 23 solution by electrocoagulation process: investigation of operational parameters and evaluation of specific electrical energy consumption (SEEC), J. Hazard. Mater. 148 (2007) 566–572.

[38] M. Bayramoglu, M. Kobya, O.T. Can, M. Sozbir, Operating cost analysis of electrocoagulation of textile dye waste water, Separ. Purif. Technol. 37 (2004) 117–125.

[39] B. Boye, M. Dieng, E. Brillas, Degradation of herbicide 4-chlorophenoxyacetic acid by advanced electrochemical oxidation methods, Environ. Sci. Technol. 36 (2002) 3030–3035.