

## A Combined Electrocoagulation-Electrooxidation Process for Carwash Wastewater Reclamation

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Received: 18 December 2014 / Accepted: 19 February 2015 / Published: 24 June 2015

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Wastewater from a carwash was treated by a combined electrocoagulation and electrooxidation process. Electrocoagulation is effective at reducing organics, but even more so when coupled with electrooxidation. Electrocoagulation with iron and aluminum produced similar results, but iron imparted color to the solution, so aluminum was used. Aluminum electrocoagulation at pH 7 with a current density of 150 A/m<sup>2</sup> for 60 min reduced turbidity by 98%, color by 96%, oils by 92%, chemical oxygen demand by 76%, biochemical oxygen demand by 74%, and methylene blue active substances by 56%. The electrooxidation process with BDD electrodes at 210 A/m<sup>2</sup> for 120 min was effective in reducing chemical oxygen demand 82%, color 81%, methylene blue active substances 81%, biochemical oxygen demand 73%, and chlorides 72%. The combined process was very effective in reducing oils 100%, color 99.3%, turbidity 98.4%, chemical oxygen demand 96%, biochemical oxygen demand 93% and methylene blue active substances 92%. Finally, the organic characteristics of the wastewater are well below the limits set by the governments of Mexico and the US. However, it could also be reused as wash water in the carwash.

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**Keywords:** Boron doped diamond electrodes, carwash wastewater, electrocoagulation, electrooxidation, metal electrodes.

### 1. INTRODUCTION

Continuous population growth in urban areas increases demand for public services including transportation, which includes private and public cars, trucks and buses. The number of motor

vehicles, in the city of Toluca, Mexico, has increased significantly which led to more car wash facilities. In Mexico, car washes are either automated conveyor type or manual hand-held spray wand. Customers can choose either exterior only wash of just the body or full service including the engine and chassis. The wastewater is complex and varies substantially. In addition to detergent and dirt, there are varying amounts of grease, oil, emulsified oil, heavy metals, and organic pollutants, which can foul or pass through traditional municipal wastewater treatment processes causing environmental issues [1–6].

The free oils can be readily separated from the aqueous phase by physical processes. The simplest method uses the conventional oil-water separator endorsed by API (American Petroleum Institute). In this system, oily wastewater is dumped into a holding tank for gravity separation of the oil, which is subsequently skimmed from the water surface. In addition to the API separator, there are two other common gravity separators - the corrugated plate interceptor (CPI) and the parallel plate inceptor (PPI) [1, 7]. With any oil-water separator the emulsified oil is not removed, so it remains in the separator's aqueous phase which goes into the public sewer system [1, 4].

Oil in emulsion may be broken commonly by chemical or physical methods. Chemical methods are the most widely used in the treatment of emulsions in oily wastewater. Chemical treatment of an emulsion may be accomplished in two different ways, through direct destabilization of the dispersed oil droplets or the destruction of emulsifying agents at the interface. In both cases the oil droplets coalesce forming an oil layer that can be mechanically removed [8]. The most frequently used agents for de-emulsification are various salts of calcium, aluminum and iron. The process usually consists of a rapid mixing stage to optimize homogenization of the coagulant in the wastewater, then slow mixing to promote drop growth [9].

Chemical coagulation is commonly used to treat oily wastewater. In research studies of breaking oil-water emulsions by inorganic salts, the removal efficiencies were around 90% when wastewater from steel and metal-finishing industries [10], car washes [4] and grease filter wash water [11] was treated. Likewise, chemical coagulation of synthetic wastewater prior to dissolved air flotation reduced more than 90% of the initial oil content [12, 13].

On the other hand the electrochemical process of electrocoagulation has proven to be effective for wastewater treatment and water purification [14]. This technique has several advantages as compared to traditional chemical methods in terms of use of simple equipment, ease of operation and reduction of added chemicals. Furthermore, flocs formed by electrocoagulation tend to readily settle and are produced in smaller quantities compared with traditional chemical treatment [15, 16]. It has been used to successfully treat numerous wastewaters including leachate from solid wastes, municipal wastewater, industrial wastewater and wastewater contaminants such as phenol, oil, boron, petroleum hydrocarbons, fluoride, black liquor and reactive dyes [17, 18].

Additionally, electrooxidation using boron-doped diamond electrodes (BDD) has been recently used for industrial wastewater treatment and the destruction of organic pollutants in aqueous effluents [19–25]. BDD electrodes exhibit very high over-potentials -1.5 to +2.3 V, inert surfaces with low adsorption properties, and remarkable corrosion stability, even in strongly acidic media.

Despite the efficiency shown by electrocoagulation and electrooxidation treatment of wastewater with several pollutants, its application as a possible technique for the treatment of car wash wastewater is rather scarce in the literature. Therefore, this research was focused on evaluation of these electrochemical processes as a way to break the emulsified oil and oxidize soluble organic compounds of the effluent from carwashes, exploring the effect of current density, pH and reaction time.

## 2. MATERIALS AND EXPERIMENTAL METHODS

### 2.1. Wastewater samples

The wastewater samples were obtained at the outflow streams from a car wash in Toluca, Mexico. Samples of wastewater were collected in glass containers and cooled to 4 °C, then transported to the laboratory for analysis and electrochemical treatment. Wastewater initial pH was adjusted before the electrochemical processes by adding the required amount of 1 M H<sub>2</sub>SO<sub>4</sub> or 1 M NaOH. The parameters analyzed are shown in Table 1.

### 2.2. Preliminary sedimentation of wastewater

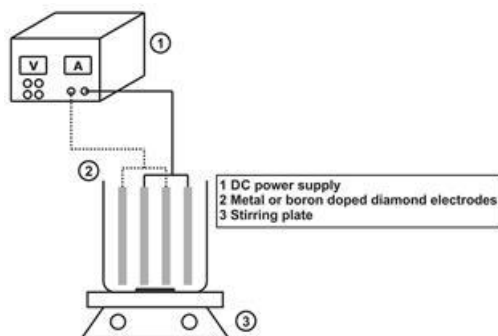
The wastewater used in this research was subjected to sedimentation before carrying out electrochemical treatments. The assay was performed with a separation funnel with six-liter capacity which is filled to approximately 90% of its volume. The sample was allowed to settle in the funnel for 30 minutes. At the end of that time, the oil fraction was skimmed off and the sediment in the bottom was removed. The remaining liquid contains emulsified oil and unsettled suspended solids and is referred to as “settled” water, which was subsequently used as the influent of the electrochemical processes.

### 2.3. Electrocoagulation treatments

The electrochemical cell used in electrocoagulation step was an acrylic container with internal dimensions of 0.1 x 0.1 x 0.15 m, as shown in Fig. 1. Four aluminum or iron plates, with dimension of 0.128 × 0.019 × 0.0012 m were used in the reactor as electrodes (partially immersed). The corresponding area for each electrode was 0.00486 m<sup>2</sup>. The spacing between electrodes was 0.01 m with a gap of 0.008 m between the bottom of the electrodes and the base of the cell for the movement of the magnetic stirrer. All the runs were performed with 1 liter of wastewater in the electrochemical cell. The current density was controlled by a BK Precision 1621A digital DC power supply. Samples of the liquid were taken periodically and analyzed for COD and turbidity. Settled wastewater pH was adjusted to the desired value by addition of H<sub>2</sub>SO<sub>4</sub> or NaOH solutions.

#### 2.4. Electrooxidation treatments

Electrochemical oxidation was performed using the same acrylic container. Five 0.205 x 0.025 x 0.003 m Boron Doped Diamond (BDD) electrodes on silicon substrates (Condias brand) were used. Two of the electrodes served as cathodes and three as anodes, yielding a surface area of 0.0165 m<sup>2</sup> for oxidation (partially immersed). The electrode spacing was 0.003 m with an 0.008 m gap at the bottom. The treated liquid volume, stirring, power supply, and pH adjustment were the same as in the previous electrocoagulation process.



**Figure 1.** Schematic diagram of electrochemical device.

#### 2.5. Methods of analysis

The effect of the electrochemical treatment was determined by analysis of the total chemical oxygen demand (COD<sub>T</sub>), turbidity and color at different time intervals. COD was determined through oxidation by the mixture of chromic-sulfuric acid in closed reflux and spectrophotometric reading while turbidity and color through spectrophotometry. However, once the optimal conditions were found, the raw and treated wastewater samples were also analyzed for soluble chemical oxygen (COD<sub>S</sub>), demand biochemical oxygen demand (BOD<sub>5</sub>), methylene blue active substances (MBAS), nitrates, ammoniacal nitrogen, sulfates, chlorides, chlorine residual, alkalinity, aluminum (by atomic absorption spectroscopy), oil & grease (O&G) and total dissolved solids (TDS) (gravimetrically), as indicated in standard methods for examination of water and wastewater [26]. Conductivity and pH with an electrochemical meter.

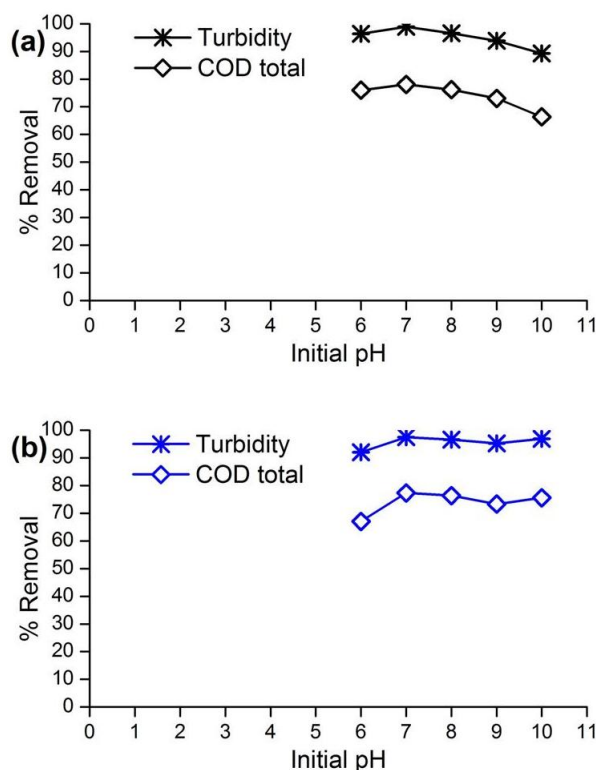
#### 2.6. Sludge characterization

The sludge produced by the electrocoagulation process was analyzed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) on a Phillips XL-30 microscope to determine the composition and structure of the dried solids. SEM provides images of surface feature while EDS offers *in situ* chemical analysis.

### 3. RESULTS AND DISCUSSION

#### 3.1. Influence of initial pH on electrocoagulation process

The pH influences the electrocoagulation process performance because the initial pH affects the stability of the generated hydroxide species [27]. The influence of initial pH on the removal of COD<sub>T</sub> and turbidity was studied in the range 6 to 10. Figure 2 clearly shows the effect of pH on these parameters. In the pH range investigated turbidity removal was higher than that for COD<sub>T</sub> when either iron or aluminum electrodes were used. The best removal percentages achieved with aluminum electrodes were 99 and 78% in terms of turbidity and COD<sub>T</sub>, respectively. Both occurred at an initial pH value of 7. This behavior is attributed to the aluminum hydroxide product being soluble in acidic or basic solution due to its amphoteric nature. Similar results have been obtained by other authors [28]. With iron electrodes there was a similar decrease in turbidity and COD<sub>T</sub> at pH 7 compared to pH 10, consistent with other research [29]. The turbidity and COD<sub>T</sub> removals for iron were around 97 and 76%, respectively.

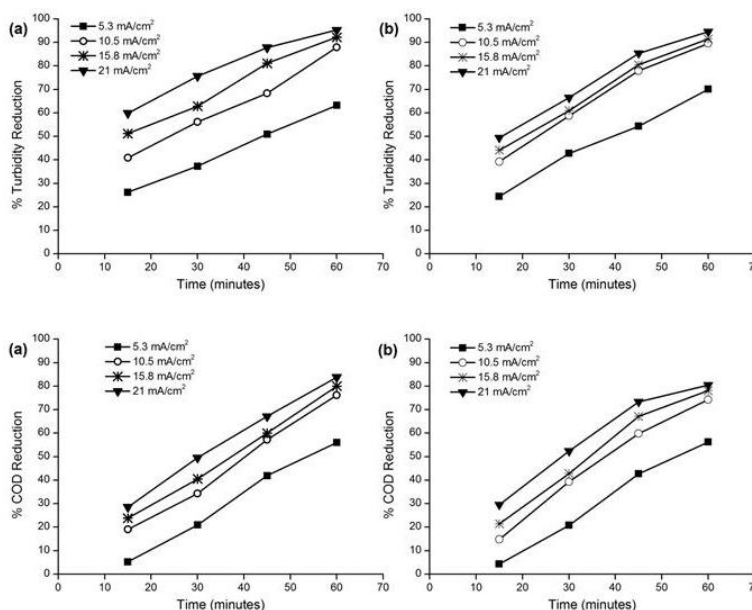


**Figure 2.** The effect of pH on the COD<sub>T</sub> and turbidity removal of (a) aluminum and (b) iron electrocoagulation process. The current density was 105 A/m<sup>2</sup> during the reaction time of 60 min.

One drawback was the notorious yellowish green color remaining in the water after treatment with iron electrodes; therefore electrooxidation assays were conducted only with aluminum electrodes.

3.2. The effect of applied current density on electrocoagulation process

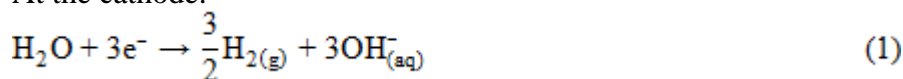
The current density is a parameter that has a major effect on the electrocoagulation efficiency. Therefore, experiments were carried out by varying the current density between 53 and 210 A/m<sup>2</sup> in order to investigate its effect on COD<sub>T</sub> and turbidity removal for iron and aluminum electrodes. As shown in Fig. 3, aluminum electrodes achieved a maximum turbidity reduction of 95% and COD<sub>T</sub> reduction of 84%, at a current density of 210 A/m<sup>2</sup> and pH 7 in 60 minutes. The iron electrodes (Fig. 3b) yielded 94 and 80%, respectively, under the same conditions. This result agrees with previous investigations in which an increase in the current density produces higher removal efficiencies [30, 31]. Conversely, if the current density decreases, the time required to achieve similar efficiencies increases. It is important to note that the current density has an impact on operating costs, so it is necessary to select a value of current density for efficient treatment and minimum cost. The current density of 105 A/m<sup>2</sup> is a reasonable compromise in this application because higher values show only small improvements.



**Figure 3.** The effect of current density on COD<sub>T</sub> reduction for electrocoagulation with (a) aluminum and (b) iron electrodes at an initial pH of 7.

In electrocoagulation, an electrode is oxidized continuously while the electric current is applied. The process of oxidation leads to the release of metal ions. These ions disrupt the stability of suspensions and emulsions and facilitate particle agglomeration and separation. If an aluminum electrode is used, the reactions are as follows [32, 33]:

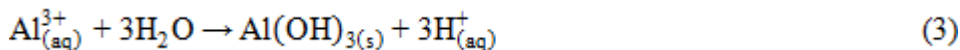
At the cathode:



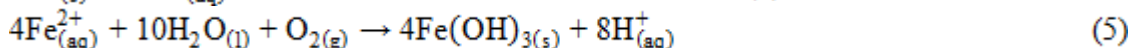
At the anode:



In the solution:

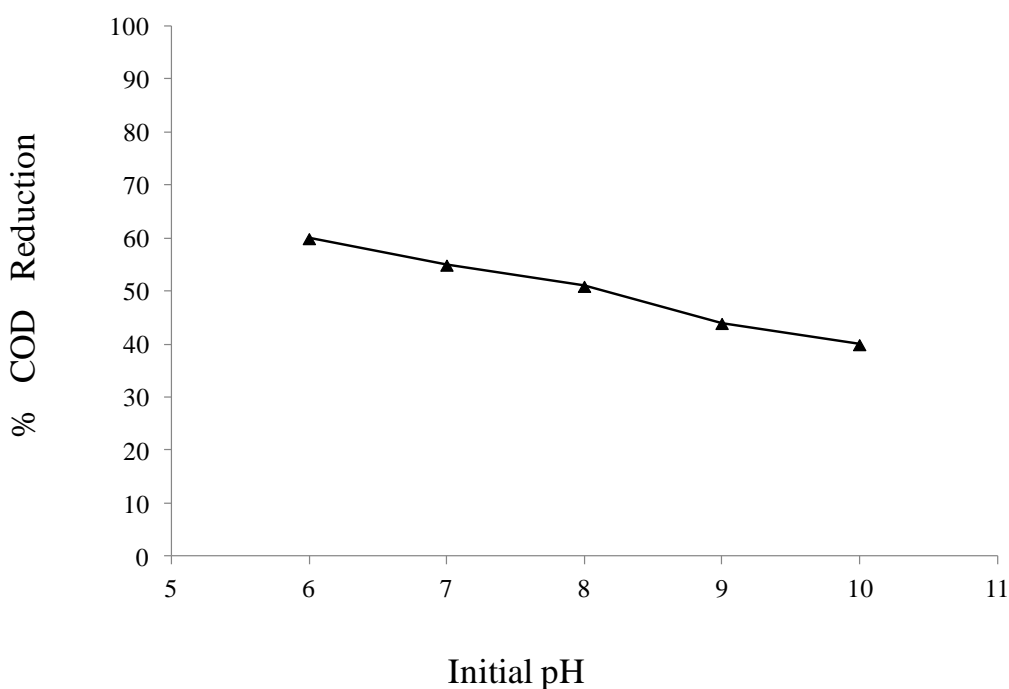


For iron oxidation, the cathode reaction is similar, producing iron(II) ions, but the iron(II) hydroxide is produced at the anode rather than in solution. The anode reaction has been proposed by the mechanism [34]:



### 3.3. Influence of initial pH on electrooxidation process

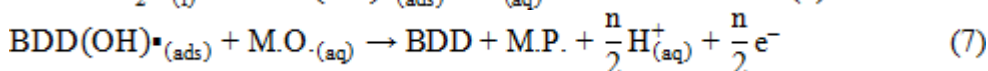
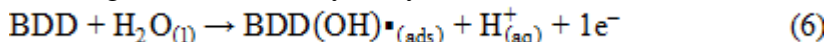
The effect of initial pH on  $\text{COD}_T$  reduction by electrooxidation was evaluated for pH values between 6 and 10. As shown in Fig. 4, the  $\text{COD}_T$  reduction is similar for pH 6, 7, and 8, and decreases significantly above 8. This observation is consistent with other work [35] and is attributed to oxygen evolution during the process. Since the electrocoagulation process is most effective at an initial pH of 7 and the pH rises to 8 during the process, an initial pH of 8 for the subsequent electrooxidation would be convenient, since no pH adjustments would be necessary. The electrooxidation process seems to be effective at pH 6, 7, and 8. Therefore, pH was used as the initial pH for electrooxidation.



**Figure 4.** The effect of pH on the  $\text{COD}_T$  removal with Al electrodes. The current density was  $105 \text{ A/m}^2$  and the reaction time of 60 min.

3.4. The effect of applied current density on electrooxidation process

The effect of current density on the COD<sub>T</sub> and color removal from the electrocoagulation effluent is shown in Fig. 5. COD<sub>T</sub> and color reduction increases somewhat linearly in time for all three current densities, with higher current density showing proportionally higher reductions. With a current density of 150 A/m<sup>2</sup> and 120 min of treatment, electrooxidation reduced the COD<sub>T</sub> and color of the electrocoagulation effluent by 76 and 88%, respectively. The proposed mechanism for organic compounds oxidation with the concomitant oxygen evolution takes place on the surface of the BDD electrode through formation of hydroxyl radicals. The reactions are as follows:



where M.P. are the products of mineralization. Organic contaminants (M.O.) are mainly degraded by the hydroxyl radical (OH•) having a high oxidizing power (E° = 2.80 V). It has been proposed that the electrochemical oxidation of organic compounds involves the formation of carboxylic acids before carbon dioxide [36].

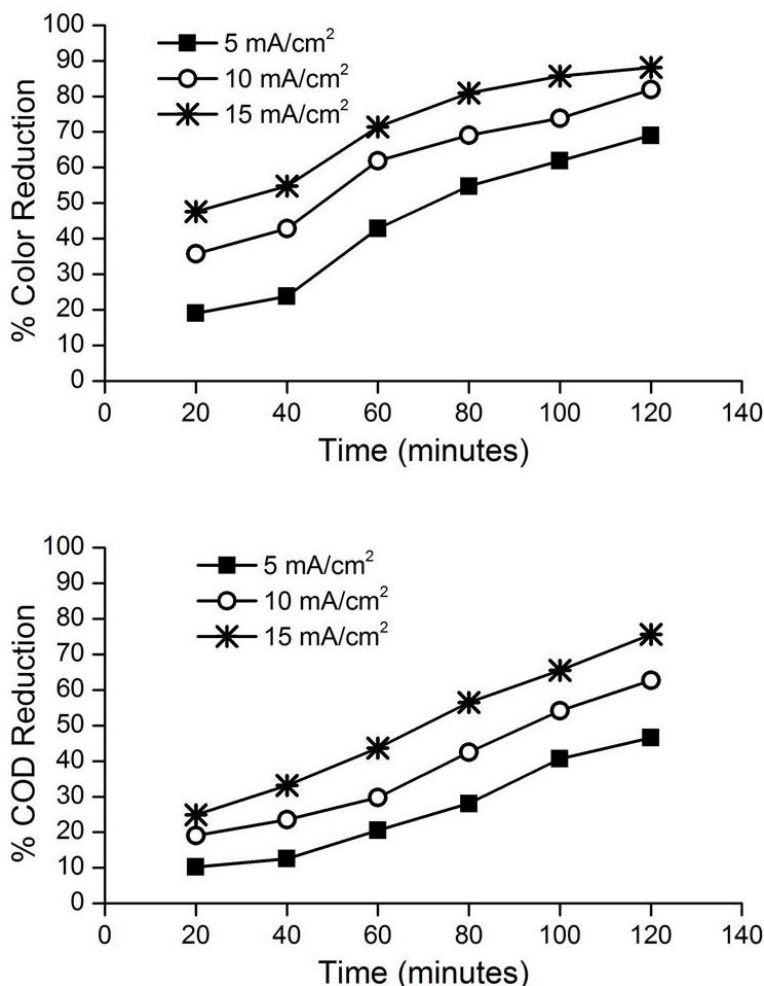


Figure 5. The effect of current density on the color and COD<sub>T</sub> removal by electrooxidation with Al electrodes.

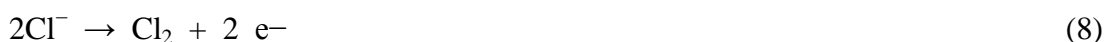


### 3.5. Residual contaminants level before and after the electrochemical treatments

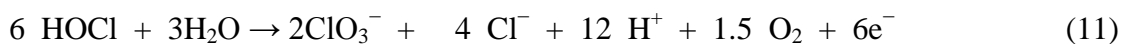
The values of the parameters of the car wash wastewater before and after the electrocoagulation and electrooxidation processes and the upper limit allowed by the Mexican official standard [37] are presented in Tab. 1. The values after electrocoagulation and electrooxidation are based on the best conditions for each treatment. For electrocoagulation, the current density, reaction time and initial pH were 105 A/m<sup>2</sup>, 60 minutes and 7, respectively, while for electrooxidation they were 150 A/m<sup>2</sup>, 120 minutes and 8, respectively. The consecutive decrease of concentration/quantity of these parameters is clear. After electrocoagulation, the organic parameters COD<sub>T</sub>, COD<sub>S</sub> and BOD<sub>5</sub>, decreased by about 75%, while the O&G and MBAS were reduced by 92 and 56%, respectively. The turbidity and color removal were around 96%, while alkalinity and sulfates decreased 50% and the chlorides reduction was 30%. Subsequent electrooxidation reduced the electrocoagulation effluent COD<sub>T</sub>, color, and MBAS by over 80%, the BOD<sub>5</sub> and chlorides by over 70%, the COD<sub>S</sub> and aluminum by over 60%, and eliminated the little O&G left. However, it had little effect on the conductivity, alkalinity, ammoniacal nitrogen, and total solids.

The combined electrocoagulation-electrooxidation system completely eliminated O&G and reduced color by over 99%, turbidity by over 98%, COD<sub>T</sub> by 96%, BOD<sub>5</sub> by 93%, MBAS by 92%, Al by 90%, COD<sub>S</sub> by 89%, and chlorides by 80%. However, it only reduced sulfates by 68%, alkalinity by 51%, ammoniacal nitrogen by 50%, total solids by 46%, and conductivity by 11%, and it actually produced residual chlorine. The reduction in chlorides and increase in residual chlorine is due to the formation of hypochlorite through indirect oxidation of chloride ions [38]. Chlorine is easily produced in wastewater containing chloride and plays a very important role in the electrolysis of many actual wastes.

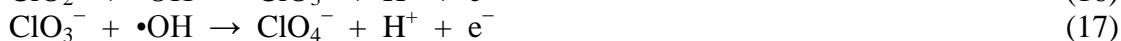
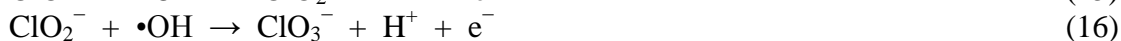
Chlorine is produced on the anode surface (8) and it suffers disproportionation (9) to hypochlorous acid, and hydrolysis to hypochlorite (10) [39].



Production of chlorates may occur either electrochemically (11) or chemically (12-13) [39].



In BDDelectodes perchlorate is formed during the electrolysis, because of the action of hydroxyl radicals [39].



The combined system seems most effective on organic pollutants. In particular, the final concentration of BOD<sub>5</sub> was below the EPA allowed value, corresponding to guidelines under the condition for restricted urban reuse [40].

**Table 1.** Physical and chemical parameters measured in settled wastewater and after each treatment step

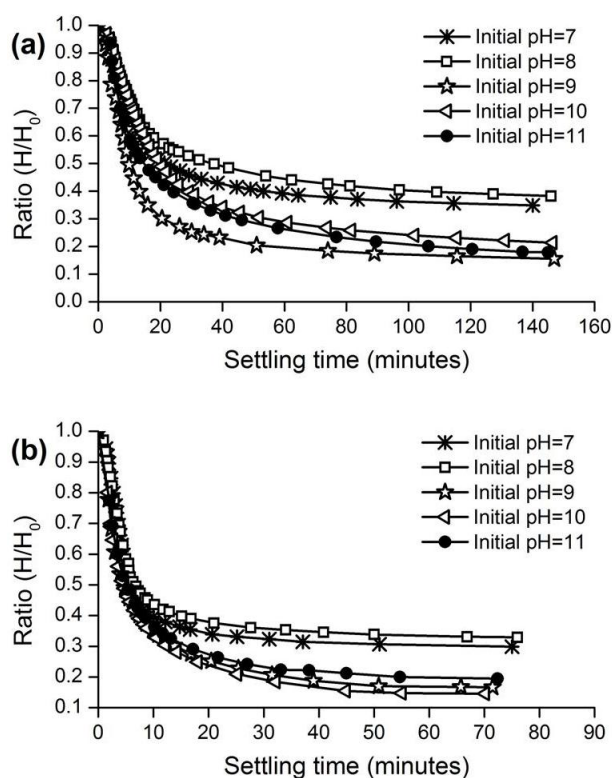
Parameter	Settled wastewater	Electrocoagulation	Electrooxidation	Maximum contaminant level (DOF)	Maximum contaminant level (EPA)
pH	7.30	8.00	8.33	–	–
Conductivity (ms/cm)	796.00	715.00	712.00	–	–
COD <sub>T</sub> (mg O <sub>2</sub> /L)	1295.00	306.00	56.00	–	–
COD <sub>S</sub> (mg O <sub>2</sub> /L)	488.00	147.00	55.00	–	–
Color (Pt Co units)	4200.00	160.00	30.00	–	–
Turbidity (NTU)	898.00	17.00	14.00	–	–
Alkalinity (mg/L CaCO <sub>3</sub> )	259.70	134.26	126.42	–	–
Aluminium (mg/L)	38.25	9.10	3.68	–	–
Chlorides (mg/L)	26.32	18.92	5.35	–	–
Chlorine residual (mg/L)	Not detected	1.00	42.50	–	–
BOD <sub>5</sub> (mg O <sub>2</sub> /L)	150.96	39.36	10.56	20 mg/L	5–30 mg/L
O&G	368.82	29.00	Not detected	15 mg/L	–
Nitrates (mg/L NO <sub>3</sub> -N)	< 5.00	< 5.00	< 5.00	–	–
Ammoniacal nitrogen (mg/L NH <sub>3</sub> -N)	1.14	0.52	0.54	–	–
MBAS (mg/L)	68.33	30.00	5.60	–	–
Total solids (mg/L)	1299.00	719.00	705.00	–	–
Sulfates (mg/L)	585.45	248.86	188.26	–	–

### 3.6. Sedimentation tests after electrocoagulation

The wastewater treated by electrocoagulation for 60 minutes was poured into a glass graduated cylinder to observe sedimentation characteristics. During the sedimentation test the interface between the liquid and solids was clearly distinguished, which is typical in a zonal or delayed settling mechanism. The assay was performed taking into account different initial pH values with aluminum and iron electrodes separately.

The dimensionless ratio estimated with  $H/H_0$ , the height of the interface at time  $t$  divided by the initial height of the graduated cylinder, vs. settling time is shown in Fig. 6. The range of initial pH values was from 7 to 11. At the beginning, the flocs formed have a marked spacing among them to fall

freely through the graduated cylinder. A clearly distinguishable solid-liquid interface was observed in all experiments as well as a decrease in the settling rate as a function of time. As expected, sedimentation at the end took place by compression mechanism. A slightly faster sedimentation was achieved at pH 9, 10 and 11 compared with the other pH values. Moreover, the electrode type was influential in settling time (Fig. 6a vs Fig. 6b). When aluminum electrodes are used, sedimentation is slower compared to iron electrodes, regardless of the solution pH. An explanation of this is due to the density difference of the two metals used, iron is almost three times denser than aluminum, in turn producing denser flocs which settle in less time. Finally, one can notice high sedimentation levels, 85% in 45 minutes with iron electrodes to a pH value of 10, or 68% under the same conditions but with aluminum electrodes [41].



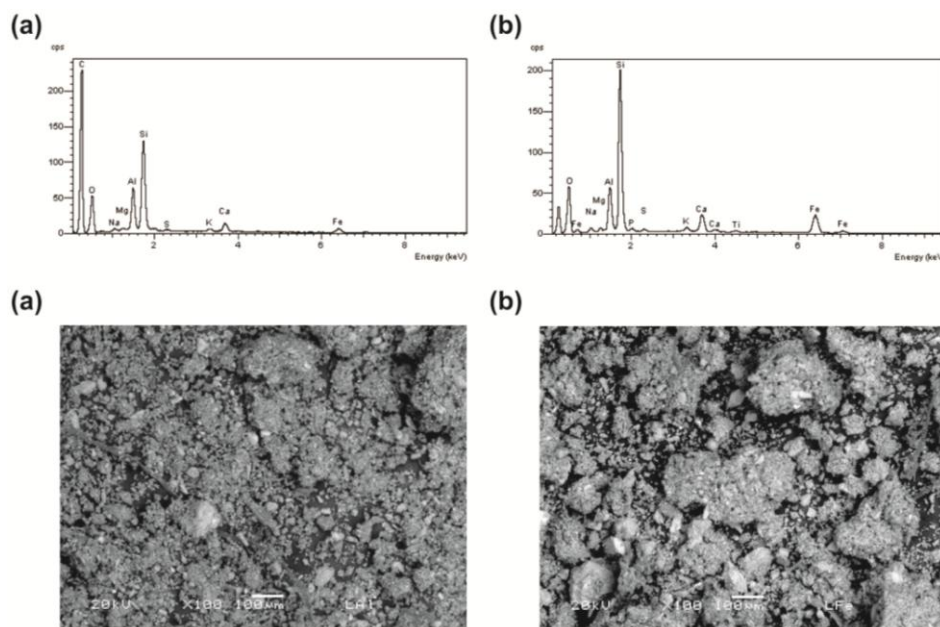
**Figure 6.** Sedimentation of sludge obtained in (a) aluminum and (b) iron electrocoagulation process at 105 A/m<sup>2</sup> of current density.

### 3.7. Sludge characterization

The sludge generated by electrocoagulation was analyzed for particle shape and elemental composition. After settling and compacting, the liquid was decanted and the solid sludge was sun-dried in a glass jar. The SEM/EDS spectra for the aluminum and iron electrocoagulation are shown in Fig. 7. Elements such as C, O, Na, Mg, Al, Si, S, K, Ca, Ti, Fe were identified. The figures reveal that the weight percentage of aluminum in the sludge is higher if aluminum electrodes are used, just as there is more iron in the iron electrocoagulation sludge. This presumably represents evidence of hydroxide

species formation such as  $\text{Fe}(\text{OH})_{3(s)}$  and  $\text{Al}(\text{OH})_{3(s)}$  to destabilize and precipitate suspended matter [42].

Sludge produced images with aluminum and iron electrodes taken by a scanning electron microscope are shown in Fig. 7. The morphology indicates that aluminum electrodes produced dustier and smaller aggregates than those generated by the iron electrodes.



**Figure 7.** Elemental analysis and micrographs of the sludge generated by (a) aluminum and (b) iron electrocoagulation process. The current density was  $105 \text{ A/m}^2$ , the initial pH of 7 and the reaction time of 60 min.

#### 4. CONCLUSIONS

A sequential combined electrocoagulation–electrooxidation process was used for the treatment of car wash wastewater. The electrocoagulation step was very effective in reducing color, turbidity, and O&G with either iron or aluminum electrodes. Aluminum was pH dependent with maximum effectiveness at pH 7, but iron was rather pH independent. With a current density of  $210 \text{ A/m}^2$  applied for 60 minutes at an initial pH of 7, turbidity decreased 94.5 and 95.3% and COD dropped 81 and 84% with iron and aluminum electrodes, respectively. The sludge from the iron settled faster, but the aluminum didn't generate any appreciable color to the solution. Therefore, aluminum was used for the electrooxidation experiments. Since electrocoagulation was most effective at an initial pH of 7 (the initial pH of the wastewater as received) and the electrooxidation was fairly pH independent, the process was done without adjusting the pH.

The combined process was very effective in reducing O&G (100%), color (99.3%), turbidity (98.4%),  $\text{COD}_T$  (96%),  $\text{BOD}_5$  (93%), MBAS (92%), Al (90%), and  $\text{COD}_S$  (89%). It was less effective at reducing chlorides (80%), sulfates (68%), alkalinity (51%), total solids (46%), and conductivity

(11%). The combined system is very effective on organics (detergents, soaps, oils, greases, etc.), but less effective on inorganics. The organic characteristics of the wastewater (COD, BOD<sub>5</sub>, O&G) are well below the limits set by the governments of Mexico and the US. Thus, this treated wastewater could be safely discharged. However, it could also be reused as wash water in the car wash. With the detergents and organics removed it could easily be reused in the wash cycle, but the presence of inorganics restricts its use in the rinse cycle.

#### ACKNOWLEDGEMENTS

The authors wish to gratefully acknowledge the National Science and Technology Council of Mexico (CONACyT) who funded this research (153828) as well as to the carwash shop owners for their help and cooperation during collection of wash wastewater.

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