Vol. 23, No. 1(2024) IA24164
Revista Mexicana de Ingeniería Química
Ingeniería Ambiental

Water treatment applying electrocoagulation and filtration processes with a functionalized membrane of a contaminated water body from San Cayetano de Morelos, Toluca

Tratamiento de agua aplicando procesos de electrocoagulación y filtración con membrana funcionalizada de un cuerpo de agua contaminado en San Cayetano de Morelos, Toluca

J. Bastida-Vázquez, G. Roa-Morales*, R. M. Gómez-Espinosa*, P. Balderas-Hernández, R. Natividad-Rangel
Centro Conjunto de Investigación en Química Sustentable. Carretera Toluca- Atlacomulco Km 14.5, Unidad San Cayetano, 50200 Toluca de Lerdo, México.

Received: September 20, 2023; Accepted: January 16, 2024

Abstract

Water for human consumption is found on the continents as fresh water in rivers, lakes, reservoirs, and underground aquifers; this water is in decrease due to anthropogenic activity and eutrophication of water bodies. This research evaluates the treatment of contaminated water in a water body in the town of San Cayetano de Morelos, Toluca, combining electrocoagulation and the use of modified membranes. Aluminum electrodes for electrocoagulation were used as the first treatment, followed by a membrane filtration process as the second treatment. The water shows the presence of phosphates and nitrates, with initial values of BOD_5, TOC, and COD of 31.7 mg/L, 78.8 mg/L, and 152.3 mg/L, respectively. After 25 minutes of electrocoagulation treatment, a 39.1% reduction in BOD_5, 73.7% in TOC, and 86% in COD was achieved. A quantification of aluminum in the water resulting from electrocoagulation was carried out, and a concentration of 0.561 mg/L was found; after filtration, it was reduced to 0.245 mg/L.

Keywords: Electrocoagulation, Total Organic Carbon (TOC), functionalized membranes.

Resumen

El agua para consumo humano se halla en los continentes en forma de agua dulce en ríos, lagos, embalses y en acuíferos subterráneos, dicha agua se encuentra en decremento debido a la actividad antropogénica y a la eutrofización de cuerpos de agua. El presente trabajo de investigación evalúa el tratamiento de agua contaminada en un cuerpo de agua de la población de San Cayetano de Morelos, Toluca, combinando la electrocoagulación y el uso de membranas modificadas. Se utilizaron electrodos de aluminio para la electrocoagulación como primer tratamiento, seguido de un proceso de filtración con membranas como segundo tratamiento. El agua proveniente del cuerpo de agua muestra la presencia de fosfatos y nitratos, teniendo los valores iniciales de DBO_5, COT y DQO de 31.7 mg/L, 78.8 mg/L, y 152.3 mg/L respectivamente. Después de 25 minutos de tratamiento de electrocoagulación, se logró la reducción del 39.1% en DBO_5, 73.7% en COT y 86% en DQO. Se realizó una valoración de aluminio en el agua resultante de la electrocoagulación y se encontró una concentración de: 0.561 mg/L, después de la filtración, se redujo a 0.245 mg/L.

Palabras clave: Electrocoagulación, Carbono Orgánico Total (COT), membranas funcionalizadas.

---

*Corresponding author. E-mail: groam@uamex.mx, rmgomeze@uaemex.mx;
https://doi.org/10.24275/rmiq/IA24164
ISSN:1665-2738, *issn-e*: 2395-8472

1 Introduction

Water is a natural resource that is running out (Tahreen *et al*., 2020), it currently represents less than 1% of the total water on the planet (Al-Qodah and Al-Shannag, 2017), so we must be aware of its use. Water pollution has increased due to population growth, the increase in industrial activities (Crini and Lichtfouse, 2019), as the low amount of reused water (Syam, *et al*., 2020).

In studies on water bodies, eutrophication characteristics are reported considering phosphate values of 5 ppm and 30 ppm of Nitrogen (Han *et al*., 2021); other studies consider above 100 mg/L of Nitrogen compounds. The eutrophication of water bodies has increased as a result of the anthropogenic activity (Akansha *et al*., 2020), and agricultural activities. It generally begins with the increase in the concentration of nutrients such as phosphates and nitrates (Gao *et al*., 2010), which give rise to the proliferation of *cyanobacteria*. These promote the conditions for the development of microalgae (Amarine *et al*., 2020), causing major changes in the habitat.

For decades, research has been performed on the different water treatment techniques to measure their efficiency (Asfaha *et al*., 2021); at that time, it has been identified that these techniques do not have sufficient robustness to eliminate the total of components found in the wastewater matrix (Bazrafshan *et al*., 2016), also considering petroleum derivatives (Almeida *et al*., 2019) and oil motor additives (Houbron *et al*., 2021) as pollutants hard to remove.

Individual techniques are not as efficient as they are in combination with other techniques and have been analyzed complementing them, to remove a broader range of contaminants (Rubí *et al*., 2015). An example of a combination of techniques is the case of coagulation and ozonation, where the results show an improvement in the chemical oxygen demand (COD) once they are combined. Initially, in the chemical coagulation process with ferric chloride ($FeCl_3 \cdot 7H_2O$), the COD showed a reduction of 37% and after the ozonation process the COD was reduced by 70.75% (Massoudinejad *et al*., 2015). In another study, the effectiveness of the combination coagulation-flocculation and Fenton oxidation was evaluated in treating wastewater containing natural rubber latex, aluminum was used as a coagulant. The results showed a COD reduction of 56%. The Fenton oxidation process was applied to wastewater after coagulation and a maximum COD reduction of 90% was obtained (Pendashteh *et al*., 2017). Electrochemical systems combined with filtration have been reported in the literature, where such combination is more efficient than the individual technique by itself (Tatoulis *et al*., 2017), a bioelectrochemical system combined with membranes has shown improvements in the reduction of ammonia of 95 % in 13 days (Song *et al*., 2020). According to the purpose, a combination of techniques can be used to avoid membrane fouling during wastewater treatment (Espinoza *et al*., 2020), extending operations until 71.4% (Song *et al*., 2020).

In the case of electrocoagulation, metal ions are released during the formation of the coagulant (Zhang *et al*., 2013), which must be removed using another methodology to ensure water quality, as modified starches from taro (López *et al*., 2014); another alternative is functionalized membrane filtration to remove said ions; therefore, it is necessary to develop a treatment train that allows primary treatment and filtration with a modified membrane to achieve the required quality (Hernández *et al*., 2016).

Electrocoagulation is a technique that has been studied for several years and is currently the subject of research in some areas (Hakizimana *et al*., 2017). It consists of adding electrogenerated coagulants, which help us to remove suspended solids, colloids, metals, and dissolved material (Garcia *et al*., 2017), forming metallic flocs. The sacrificial electrodes commonly used are iron and aluminum metals (M); the general reactions at the anode and the cathode are shown below.

Anodic Reaction

$$M_{(s)} \rightleftharpoons M^{z+}_{(aq)} + Ze^- \tag{1}$$

$$2H_2O \rightleftharpoons O_{2(g)} + 2H_{2(g)} + 4e^- \tag{2}$$

Where Z represents the oxidation state (superscript) of the metal ion.

Cathodic reaction

$$2H_2O + 2e^- \rightleftharpoons H_{2(g)} + OH^-_{(aq)} \tag{3}$$

Reactions in solution

$$M^{z+}_{(aq)} + ZOH^-_{(aq)} \rightleftharpoons M(OH)_{z(s)} \tag{4}$$

The use of membrane technology is a relatively new discipline and is changing daily; it is considered that it still has an empirical component. The membranes commonly used for this purpose are polymeric due to their morphological structure, and compositional variety. Traditionally, they have been used as filter materials, removing contaminants by size; however, recently, in our research group it has been found that the modification of a polymeric matrix can increase its applications, where the functional groups grafted on the matrix act as active sites for the removal of specific metallic contaminants, for this reason, it is important to take advantage of this capacity for the elimination of released ions in the electrocoagulation treatment.

Membrane modification can occur in two general ways: one consists of the mixture of components and the other in the modification of the surface. In the modification on the surface of the membrane, functional groups are grafted to the surface, and the physicochemical properties such as polarity, reactivity, hydrophilicity, and selectivity to specific ions are changed. The novelty of the research was to use the functionalized membranes because the membrane has not been used for this purpose before in a combined process.

In this work, a combined treatment of EC and filtration with functionalized membrane was carried out to improve water quality, in the particular case of Toluca, State of Mexico, in the San Cayetano area, there are several water bodies that are used for agriculture and livestock, since local residents use the water from the water bodies to irrigate their agricultural lands and they take their livestock, mainly sheep and cattle, to feed and drink water, and there is no exact information on when said water body was eutrified. Additionally, they are recipients of fauna that migrates from Canada to the local area, such as a Canadian duck that is not seen in this particular water body for several years.

2 Materials and reagents

2.1 Reagents

The water was sampled at coordinates 19.385054, -99.701750, San Cayetano de Morelos, Toluca, State of Mexico, by the Mexican Standard for wastewater sampling NMX-AA-3-1980.

The determination of ions was carried out by chromatography, using sodium sulfate, Reasol brand, sodium carbonate, sodium chloride, potassium phosphate was Brand: J. T. Baker, sodium nitrate, Brand: Fermont, and deionized water (18 MΩ), High Purity brand.

The quantification of the Chemical Oxygen Demand (COD) used the reagents indicated in the Mexican Standard NMX-AA-028-SCFI-2001, potassium dichromate, Merck brand, mercury sulfate, brand: Merck, silver sulfate, J.T. Baker brand, potassium biphthalate, brand J.T. Baker and sulfuric acid brand Fermont, all reagents were used without pretreatment.

The determination of the Biochemical Oxygen Demand (BOD_5) used the reagents indicated in the official Mexican Standard NMX-AA-028-SCFI-2001: monobasic potassium phosphate, brand: J. T. Baker, dibasic potassium phosphate, brand: J. T. Baker, dibasic sodium phosphate heptahydrate, brand: J.T. Baker, ammonium chloride, brand: J.T. Baker, magnesium sulfate heptahydrate, calcium chloride anhydrous, brand: Merck, ferric chloride hexahydrate, brand: J.T. Baker, concentrated sulfuric acid, Fermont brand, sodium hydroxide, Brand: J.T. Baker, sodium sulfite, Brand: J.T. Baker, 2-Chloro-6 (trichloromethyl)pyridine, Brand: Sigma Aldrich, glucose primary standard grade, Brand: J.T. Baker, glutamic acid primary standard grade, Brand: J. T. Baker, hydrochloric acid, brand: J. T. Baker, nitric acid, brand: J. T. Baker, all analytical reagent grade without pretreatment.

2.2 Materials

Microporous polypropylene membrane from the company 3M, 0.45 μm pore size with a thickness of 114 μm and a porosity of 84.6%. Commercial acrylated epoxidized soybean oil (AESO) and Sigma-Aldrich dimethylformamide (DMF).

3 Methodology

3.1 Electrocoagulation

A batch reactor of cylindrical geometry with a capacity of one liter was used for electrocoagulation using a pair of rectangular aluminum electrodes 11.8 cm long, 8.7 cm wide, and 0.10 cm thick, with a separation between them of one centimeter, two current densities were applied: 4.87 mA/cm^2 and 9.74 mA/cm^2 at different times and with stirring at 380 rpm.

For the chemical and biological analyzes the initial and final samples were taken directly and however for the TOC analysis several samples were analyzed.

3.2 Membranes preparation

The membranes were functionalized with epoxidized acrylated soybean oil, cut into 4 cm diameter circles, and placed in filter holders; these were adapted to a peristaltic pump, MasterflexTM brand, variable speed, analog console: L/STM with a head pump easy-load II, MasterflexTM and high-performance casing, 500 mL of sample water to be treated were used, recirculating the water for 30 minutes, after this time the sample was collected and analyzed (Palacios *et al*., 2012).

4 Analytical techniques

4.1 Ions chromatography

Equipment: Thermo Scientific Dionex, Model Dionex Aquion, Dionex As-DV autosampler, equipped with an electrical conductivity detector (ECD). The software used for data analysis was Chromeleon 7. The assay conditions were: 30 mM NaOH mobile phase, 1.5 mL/min flow, an IonPac AS11-CH column, 4 mm diameter, nine μ particle size was used, 2000 A pore size, 250 mm length, part number 052960.

4.2 *Total Organic Carbon (TOC) and total nitrogen*

The quantification of total organic carbon allows us to determine the amount of organic carbon in the water bodies; since it increases, it has an impact on the ecosystem cycle; for example, when combined with oxygen, it reduces the amount of free oxygen, causing a substantial impact on the fish population among others.

Equipment: TOC-5050 Shimadzu, Shimadzu Corporation. Combustion occurs at 680 °C in a furnace containing an alumina-supported platinum catalyst.

Total Organic Carbon was quantified through a calibration curve using potassium biphthalate, considering 5ppm, 15ppm, 40ppm, 75ppm, and 100ppm. The reactor samples were analyzed taking 10 mL every 5 min.

4.3 *BOD_5*

The BOD_5 indicates the amount of oxygen used to metabolize biodegradable organic matter; the increase in the BOD_5 concentration affects the decrease in the dissolved oxygen content in water bodies with the consequent affectation on aquatic ecosystems, according to the Mexican Standard NMX-AA-028-SCFI-2001, "Determinación de la demanda bioquímica de oxígeno en aguas naturales, residuales (DBO_5) y residuales tratadas".

The vial of microorganisms used in this study corresponds to the Polyseed HACH Capsule. Equipment used: Luminescent Oxygen Sensor, Hach brand, model: HQ40d.

4.4 *COD*

COD indicates the amount of organic matter oxidized by chemical action to CO_2 and H_2O increase in COD values indicates the presence of substances from non-municipal discharges. Determination of COD was according to the Mexican Standard NMX-AA-030/2-SCI-2011, "Determinación de la demanda química de oxígeno en aguas naturales, residuales y residuales tratadas (método de tubo sellado y pequeña escala)". Equipment used in the determination of COD: UV/VIS spectrophotometer, Hach brand, model DR/4000U.

4.5 *Microbiological*

The contamination of water bodies related to eutrophication is given by an increase in its nutrients, such as phosphates and nitrates, coming from agricultural activities; the increase in these causes a growth in the population of *cyanobacteria* that modify ecosystems, giving rise to the proliferation of microalgae and consequently the eutrophication of water bodies.

The analysis of microalgae and *cyanobacteria* was carried out using a Quasar trinocular optical microscope, model QM30, with a 40X objective.

4.6 *FT-IR-ATR*

FT-IR-ATR spectroscopy provides information related to the functional groups present on the surface of the membrane; it measures the interaction of infrared radiation with matter by reflection. An FTIR spectrum coupled to a Perkin-Elmer brand ATR was used, acquired at 64 scans with a window of 500-4000 cm^{-1} and 2 cm^{-1} resolution. The functionalized membrane was monitored by FT-IR-ATR, showing the presence of the -C=O, -OH groups.

4.7 *Spectrophotometry UV/VIS*

UV/VIS spectrophotometry allowed us to identify and quantify organic and inorganic substances, as well as to identify specific functional groups of the molecules, and for this study, it shows us if there are additional contaminants in the water. Perkin Elmer UV/VIS, lambda 365. Range: 200nm - 700nm.

5 Discussion and results

5.1 *Sampling*

The sampling water was taken at 5 meters from the shore of the water body, by the Mexican Standard for wastewater sampling NMX-AA-3-1980. The water body presented significant changes in its coloration since March 2020, the color was light green (figure 1a), but in March 2022, the water had a more intense green color (figure 1b). The water had a more intense green color (Figure 1b). The change in the n of microalgae, Figure 1. The water sample showed that phosphates and nitrogen were out of range, as indicated by the Mexican Standard NOM-001-ECOL-1996; the total phosphate and nitrate values were 6.3 ppm and 16 ppm, respectively. These nutrients favor the growth of microalgae, reducing the passage of light and causing changes in the color and the ecosystem of the water body.

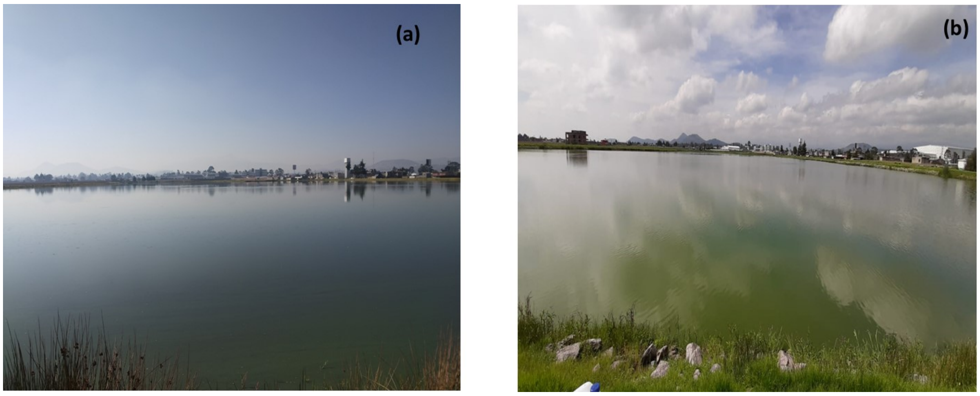

Figure 1. Water body is located in San Cayetano de Morelos. (a) Image obtained in March 2020, (b) in March 2022.

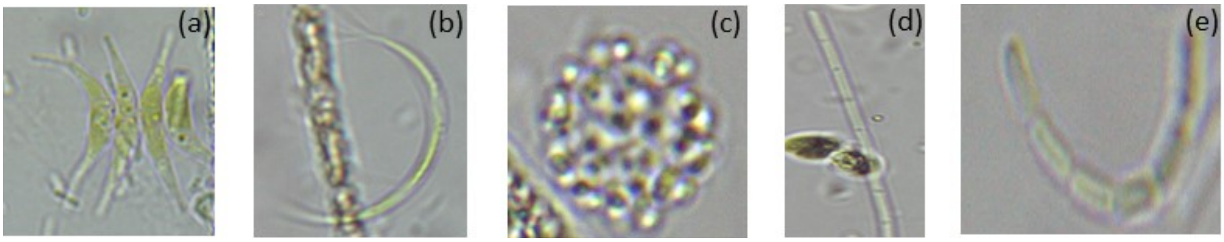

Figure 2. Bright-field microscope images, with a 40X objective, of microalgae and *cyanobacteria* present in a sample of a water body in San Cayetano. (a) *Scenedesmus acuminatus*, (b) *Monoraphidium* sp, (c) *Eudorina* sp, (d) Elongated *cyanobacteria*, (e) *cyanobacteria* sp.

The microbiological study of the water showed the presence of the following species, such as *Scenedesmus acuminatus*, *Monoraphidium* sp, *Eudorina* sp, as well as the presence of *cyanobacteria*, see figure 2.

5.2 *Physicochemical assay*

5.2.1 *Electrocoagulation*

Electrocoagulation was carried out in a batch reactor with a capacity of a liter, using aluminum electrodes. Experiments were performed using two current densities, 4.87 mA/cm^2 and 9.74 mA/cm^2, with and without supporting electrolyte (0.05M Na_2SO_4). The turbidity results of the four experiments showed the same removal efficiency of said parameter, without significant differences, so it was decided to work with the lowest current (4.87 mA/cm^2) without supporting electrolyte, favoring energy saving and avoiding the use of additional reagents, the treatment time was carried out for 25 minutes.

The UV-VIS spectra of raw water and electrochemically treated water are shown in figure 3. In the absorption spectrum for raw water, a high absorbance can be observed from the beginning of the scan, this can be related with high turbidity and color, in addition to presenting an absorption wave between 200 nm and 300 nm, this behavior is associated with organic and inorganic contaminants present in raw water. After electrocoagulation treatment, the spectra show a hypochromic effect due to the removal of contaminants, which indicates a 71% reduction in absorbance initial recorded at a wavelength of 200 nm.

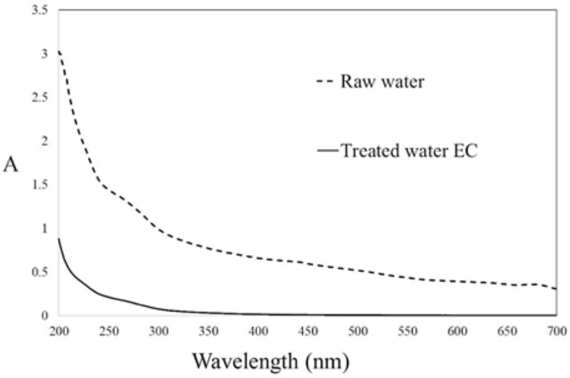

Figure 3. UV-VIS spectra of raw water and electrochemically treated water.

The kinetics of the electrocoagulation treatment (Figure 4) was performed by taking a sample every 5 minutes and evaluating the total organic carbon (TOC) as a function of time. Figure 4a shows a tendency to remove 80 % of TOC in 15 minutes. The results fit to a second-order kinetics (R^2= 0.99). The diffusion event is diminished due to the stirring process at 380 rpm, which increases the interaction between Al^{3+} and OH^-, resulting in a bigger mass

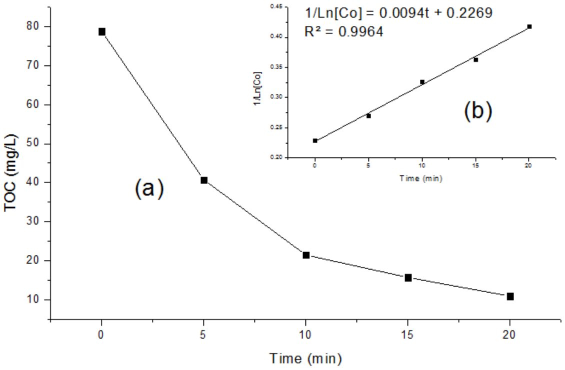

Figure 4. Kinetics of removal in (a) TOC values, (b) model to which the kinetics fit.

transfer (Comninellis and Chen 2010). It is suggested that a part of the organic matter is being adsorbed in the electrogenerated coagulant, with a removal rate constant of 0.0094 mg/min L (Figure 4b).

The kinetics results can be explained by analyzing the oxidation and reduction reactions that take place during the electrocoagulation reaction. The oxidation reaction of the aluminum electrode is carried out in the sacrificial anode generating Al^{3+}, see equation 5.

Anode:

$$Al_{(s)} \rightleftharpoons Al^{3+}_{(aq)} + 3e^{-} \tag{5}$$

In equation 2, the reduction reaction takes place at the cathode, where water is reduced, generating hydroxide and hydrogen.

Once the Al^{3+} is released from the electrode, it reacts with the hydroxide in the solution, generating aluminum hydroxide (equation 6), and the coagulant was formed.

Precipitation:

$$Al^{3+}_{(aq)} + 3OH^{-}_{(aq)} \rightleftharpoons Al(OH)_{3(s)} \tag{6}$$

With these results, it is observed that at 15 min the TOC decreases significantly since 80% of TOC is eliminated using 41.94 mg of electrogenerated Al^{3+}, subsequently in 20 and 25 min 86% TOC is eliminated using 55.92 mg of Al^{3+} and 69.9mg of Al^{3+} respectively. Therefore, it is considered that after 15 minutes of treatment it could be stopped.

Figure 5 (a) shows the water with a greenish coloration before treatment. Figure 5 (b) shows the change of the color in the water, after the electrocoagulation treatment, where the coagulant is electrogenerated and the process of adsorption of polluting organic matter take place (Ruiz, A. A., 2005). Flocs are formed with the hydrogen release, formation of bubbles (see equation 2), which causes electroflotation (Garcia *et al.*, 2017), sending the lightest flocs to the surface of the reactor and is visualized in the form of foam with the organic material (Figure 5 b). With this process it is possible to observe the separation of the microalgae on the surface of the reactor.

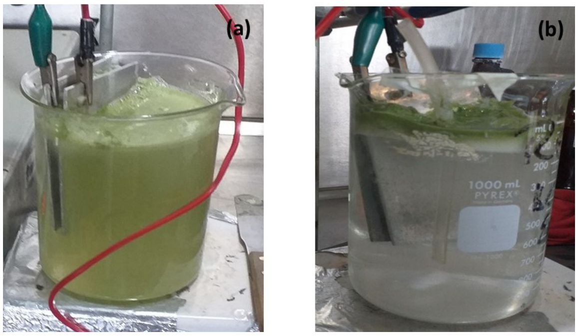

Figure 5. Sample of the water body in San Cayetano (a) before and (b) after electrocoagulation treatment.

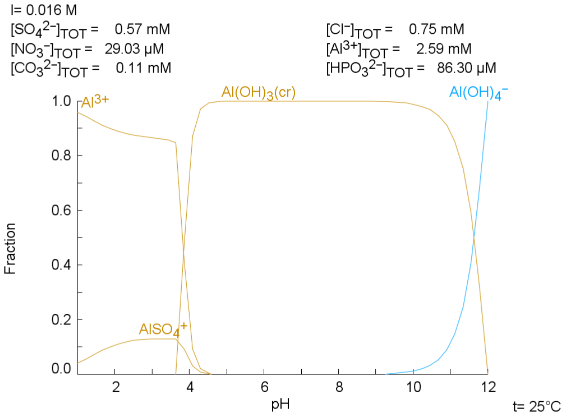

Figure 6. Species distribution diagram of [Al(III)] = 2.59 mM, with an ionic strength of 0.016 M a 25 min of treatment.

The formation of $Al(OH)_3$ is suggested, and it was verified by making the theoretical calculation of the aluminum that is released using the Faraday equation (Equation 7).

$$n_{e^-} = \frac{I * t}{Z * F} \tag{7}$$

Where n_{e^-}, is the number of moles of electrons, I, is the current in Amperes, t, is the electrolysis time in seconds, Z number of electrons transferred, and F is Faraday's constant (96500 C/mol).

The number of moles calculated with equation 7, at a current of 4.87 A/cm^2, 25 minutes, and a liter of sample of the water body, gives a concentration of 2.59 mM. A species distribution diagram was made (Figure 6), using the "Chemical Equilibrium Diagrams" software (Puigdomenec, 2015). Observing that aluminum hydroxide predominates at a pH range between 4.5 and 10.5, the water under study has a pH of 6.5 at the beginning and 7.1 at the end, corroborating that the species that predominates is $Al(OH)_3$ during the treatment.

Table 1 shows the physicochemical parameters that were measured in the water before and after treatment. The DBO_5 and COD that the water presented before the treatment showed a value of 31.7 mg/L and 152.3 mg/L respectively. The ratio of the biodegradability based on DBO_5 and COD (0.2) indicates that the water is contaminated according to the classification of industrial, non-biodegradable water (Guzmán *et al.*, 2020) (Barrera, 2014). The turbidity value was 266 FAU, it is out of the limit indicated by the Mexican Standard NOM-001-SEMARNAT-1996 and the project of modification of the Official Mexican Standard PROY-NOM-001-SEMARNAT-2017.

After the electrocoagulation process, the evaluated parameters of the quality of the water decreased significantly, obtaining removal efficiencies for BOD_5: 39.1%, COD: 73.7%, TOC: 86%, Turbidity: 100%, Phosphates: 100%, Total Nitrogen: 92.7%. As shown in Table 1. According to SEMARNAT and the Mexican Standard NOM-003-SEMARNAT-1997 and standard project PROY-NOM-014-CNA-2003 the values of BOD_5: 19.3 mg/L, COD: 30.0 mg /L and TOC: 10.9 mg/L indicate that the water is classified as "acceptable", which demonstrates the efficiency of the electrochemical treatment, changing from contaminated water to reuse water useful for irrigation.

Table 1 shows the values of nitrates and phosphates before and after water treatment, an important fact since the presence of nutrients such as nitrates and phosphates is an indicator of contamination in water, according to directives 75/440/EEC and 79/869/EEC of the European Community, indicate a permissible limit of 0.7 mg/L for phosphates and 15 mg/L for total nitrogen. Therefore, the water sampled from the water body at the beginning of the treatment is unsuitable for human consumption. Still, the water after treatment could be acceptable for secondary uses, such as car washing or irrigation.

5.3 Cost and energy consumption

The energy consumption, EC, was calculated as is described below:

The energy consumption, EC is defined by Eq. (8) (García *et al.*, 2016), where U is voltage (V), i, is current (A), t is time in h, v is the sample volume (L),

$$EC\left(\frac{kWh}{L}\right)=\frac{Uit}{v} \tag{8}$$

Energy consumption when treating one liter of water from the water body, it would consume EC: 0.003215 KWh/L.

The electricity cost in Mexico is US$ 0.056 per kWh, according to the Mexican supplier Comisión Federal de Electricidad (CFE).

The cost per liter of wastewater treated can be calculated with Eq. (9) (Garcia *et al.*, 2022), where the cost is expressed in US dollars per liter (US$/ L).

$$Cost(US\$/L)=EC(kWh/L)(0.056) \tag{9}$$

The cost obtained in eletrocoagulation per liter is about 0.000175 US$/L. The cost of the treatment is comparable with other electrocoagulation reactors reported in the literature, where the total operating cost reported is 4.15$/$m^3$ (Ebba *et al.*, 2020), and other studies report in Kg of COD removed as 0.9 $/ Kg COD (Elazzouzi, et. al 2016). The cost could be lower using solar-photovoltaic cells to supply electrical energy (Garcia *et al.*, 2022).

Table 1. Results before and after the electrocoagulation treatment.

Parameter	Electrocoagulation Before	 after	Limits	Removal %	Reference standard
pH	6.5	7.1	6.5-8.5	NA	NOM-127-SSA1-1994
DBO_5 (mg/L)	31.7	19.3	30	39.1 %	NOM-003-SEMARNAT-1997 (Services to the public with direct contact)
COD (mg/L)	152.3	30	40	73.7 %	NOM-003-SEMARNAT-1997
COT (mg/L)	78.8	10.9	16	86%	PROY-NOM-014-CNA-2003
Turbidity (FAU)	266	0	5 (NTU)	100%	NOM^{-1}27-SSA1-1994
Conductivity (mS/cm)	0.898	0.650	1000	27.6%	DIRECTIVES 75/440/CEE and 79/869/CEE (European Community)
Phosphates (mg/L)	6.2	ND	0.7	100%	DIRECTIVES 75/440/CEE and 79/869/CEE (European Community)
Total Nitrogen (mg/L)	16.30	1.195	15	92.7	NOM-001-ECOL-1996 (Protection of aquatic life)
Total Coliforms (MPN/100mL)	140	ND	Absent or ND	100%	NOM-112-SSA1-1994

NA=No Aplicable, ND = No Detectable.

Conventional coagulation has been proven to be efficient; however, electrocoagulation offers additional physicochemical processes, such as electroflotation, the electrogeneration of small quantities of coagulant, which makes the removal of organic matter efficient, because the flocs are more efficient. The lighter flocs are removed by electroflotation and the heavier flocs ones are removed by sedimentation. In addition, electrocoagulation generates OH$^-$ ions that increase the stability of the coagulant, improving the removal of contaminants. Chemical coagulation, it is estimated that for this water sample, the cost per L would be 0.007 US$/L, so it is less expensive to use electrocoagulation.

5.4 Filtration with functionalized membrane

The electrocoagulation process using aluminum electrodes turns out to be an attractive process for improving water quality, however, it releases aluminum into the water, becoming another pollutant, this fact limits its application in the water treatment process. During the treatment, the formation of flocs takes place, which are responsible for the elimination of contaminants, but aluminum is a metal that persists after the electrocoagulation treatment. It was important to look for alternatives to remove aluminum from the resulting solution, this is where the combined treatment becomes important, and the use of a modified membrane enhances its applications. The functional groups (-C=O, -OH), grafted onto the membrane, act as ligands that coordinate with aluminum, removing it from the solution, Figure 7.

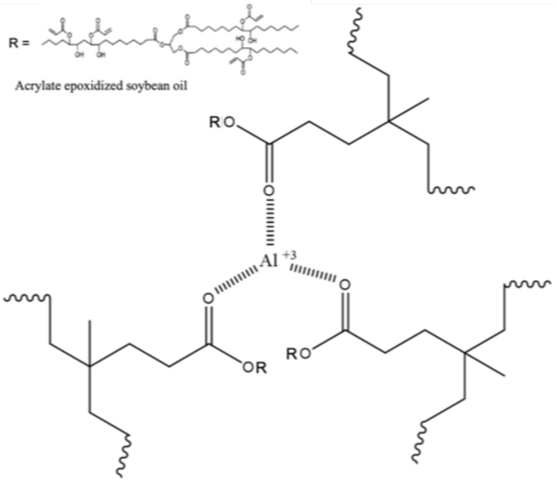

Figure 7. Coordination proposal between carbonyl groups (-C=O, OH) grafted on the functionalized membrane and aluminum.

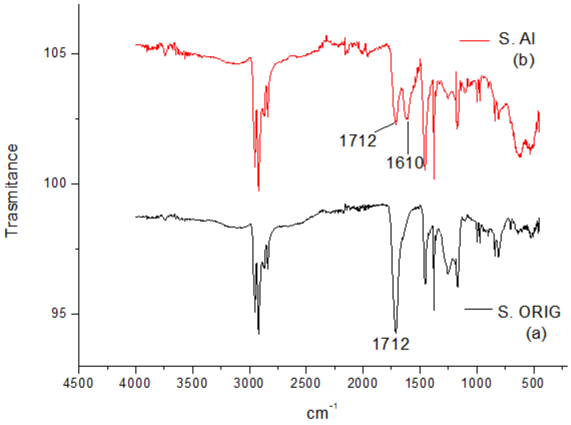

Figure 8. FTIR spectrum of the modified membrane a) before contact with the aluminum solution and b) after contact.

The coordination of aluminum with the functionalized membrane was evidenced by FT-IR-ATR spectroscopy. At 1710 cm^{-1} the vibration corresponding to the carbonyl group is observed, which corroborates the functionalization of the polypropylene with the acrylated epoxidized soybean oil (Figure 8 a). When the functionalized membrane is put in contact with the water, obtained after the electrocoagulation treatment, a splitting of the 1712 cm^{-1} band is observed, finding two vibrations, one at 1712 cm^{-1} and the other at 1610 cm^{-1}. These bands are attributed to the coordination of aluminum with the functional groups (Figure 8 b). This led us to propose the coordination of the functional groups present in the membrane, removing them from the solution and maintaining them on the surface of the functionalized membrane.

In addition to corroborating the removal of aluminum by FT-IR-ATR, a complementary analysis by atomic absorption was performed, using the low internal method reported in the Mexican Standard NOM^{-1}17-SSA1-1994. The electrocoagulated water showed a value of 0.561 mg/L of aluminum, and after contact with the functionalized membrane a value of 0.245 mg/L of aluminum was found, corresponding to 56.3% removal of Al present in the water, which shows the importance of the use of combined methods that help improve the water quality, increasing its applications and reuse of water, not to mention that aluminum has shown to be beneficial at low concentrations (71 and 185 μM) at pH greater than 6 for some plant species (Marschner, P., 2012), in this case the final concentration is 9.07 μM of Al with a final pH of 7.1, which could be considered adequate for irrigation. Aluminum is not among the essential nutrients of plants, and in the absorption processes it competes with necessary ions, affecting the metabolism and growth of plants (Blancaflor *et al.*, 1998), according to the concentration and pH at which it is found (Bojórquez *et al.*, 2017).

Conclusions

The water on the water body (raw water) is considered contaminated water because the BOD_5 and COD concentrations were out of range concerning the SEMARNAT water classification scales and the Mexican Standard NOM-003-SEMARNAT-1997.

The treatment with electrocoagulation improved the quality of the water, obtaining BOD_5 values of 19.3mg/L and COD of 30.0 mg/L, which were within the range according to the Mexican Standard NOM-003-SEMARNAT-1997, having a reduction of 39.1% in BOD_5 and 86% in COD, which corroborates the efficiency of both treatments.

The treatment with a functionalized membrane removed 56 % of the remaining aluminum after electrocoagulation; the value obtained is very close to the acceptance limit of aluminum for drinking water according to the Mexican standard NOM-127-SSA1-1994.

Treatment with a functionalized membrane complements the use of electrocoagulation since it directly favors one of the limitations of this technique, which is providing more substances to the solution.

The green color of the water was attributed to the presence of *cyanobacteria* and green algae such as *Scenedesmus acuminatus*, *Monoraphidium* sp, and *Eudorina*, eutrophication of the water body was observed since an excess of nutrients such as phosphates and nitrates was found, which favor the growth of these microorganisms.

Acknowledgment

The authors express their gratitude to the Centro Conjunto de Investigación en Química sustentable UAEM-UNAM for the use of the facilities and for financial support through projects CONACYT (309265) and UAEM (6484/2022CIB, 6983/2024CIB) for the development of this research and CONACYT for scholarship No. 752591.

References

Akansha, J., Nidheesh, P. V., Gopinath, A., Anupama, K. V., & Suresh Kumar, M. (2020). Treatment of dairy industry wastewater by combined aerated electrocoagulation and phytoremediation process. *Chemosphere 253*, 1-6. https://doi.org/10.1016/j.chemosphere.2020.126652

Al-Qodah, Z., & Al-Shannag, M. (2017). Heavy metal ions removal from wastewater using electrocoagulation processes: A comprehensive review. *Separation Science and Technology (Philadelphia) 52*(17), 2649-2676. https://doi.org/10.1080/01496395.2017.1373677

Almeida, F. B. P. S., Meili, L., Soletti, J. I., Esquerre, K. P. S. O. R., Ribeiro, L. M. O., & de Farias Silva, C. E. (2019). Oil produced water treatment using sugarcane solid residue as biosorbent. *Revista Mexicana de Ingeniería Química 18*(1), 27-38. DOI: 10.24275/uam/izt/dcbi/revmexingquim/2019v18n1/Almeida

Amarine, M., Lekhlif, B., Sinan, M., El Rharras, A., & Echaabi, J. (2020). Treatment of nitrate-rich groundwater using electrocoagulation with aluminum anodes. *Groundwater for Sustainable Development 11*, 1-9. https://doi.org/10.1016/j.gsd.2020.100371

Asfaha, Y. G., Tekile, A. K., & Zewge, F. (2021). Hybrid process of electrocoagulation and electrooxidation system for wastewater treatment: A review. *Cleaner Engineering and Technology 4*, 1-10. https://doi.org/10.1016/j.clet.2021.100261

Barrera, C. E., (2014). *Aplicaciones Electroquímicas al Tratamiento de Aguas Residuales*. Editorial Reverte. 1st edition. México.

Bazrafshan, E., Alipour, M. R., & Mahvi, A. H. (2016). Textile wastewater treatment by application of combined chemical coagulation, electrocoagulation, and adsorption processes. *Desalination and Water Treatment 57*(20), 9203-9215. https://doi.org/10.1080/19443994.2015.1027960

Blancaflor, E. B., Jones, D. L., & Gilroy, S. (1998). Alterations in the cytoskeleton accompany aluminum-induced growth inhibition and morphological changes in primary roots of maize. *Plant Physiology 118*(1), 159-172. https://doi.org/10.1104/pp.118.1.159

Bojórquez, E., Escalante, C., Echevarría, I., & Martínez-Estévez, M. (2017). Aluminum, a friend or foe of higher plants in acid soils. *Frontiers in Plant Science 8*, 1-18. https://doi.org/10.3389/fpls.2017.01767.

CFE (Comisión Federal de Electricidad) Consulta tu tarifa. 2023. Available at https://app.cfe.mx/aplicaciones/ccfe/tarifas/tarifas/Tarifas_casa.asp? Accessed December 19, 2023.

Comninellis, C., & Chen, G. (Eds.). (2010). *Electrochemistry for the Environment* (Vol. 2015, p. 251). New York: Springer.

Crini, G., & Lichtfouse, E. (2019). Advantages and disadvantages of techniques used for wastewater treatment. *Environmental Chemistry Letters 17*(1), 145-155.

Ebba, M., Asaithambi, P., & Alemayehu, E. (2021). Investigation on operating parameters and cost using an electrocoagulation process for wastewater treatment. *Applied Water Science 11*, 1-9. https://doi.org/10.1007/s13201-021-01517-y

Elazzouzi, M., Haboubi, K., & Elyoubi, M. S. (2017). Electrocoagulation flocculation as a low-cost process for pollutants removal from urban wastewater. *Chemical Engineering Research and Design 117*, 614-626. https://doi.org/10.1016/j.cherd.2016.11.011.

Espinoza, E., Soto, G. M., & Pérez, J. de J. (2020). Prospects for the use of electrooxidation and electrocoagulation techniques for membrane filtration of irrigation water. *Environmental Processes 7*(2), 391-420. https://doi.org/10.1007/s40710-020-00439-2

Gao, S., Yang, J., Tian, J., Ma, F., Tu, G., & Du, M. (2010). Electro-coagulation-flotation process for algae removal. *Journal of Hazardous Materials 177*(1-3), 336-343. https://doi.org/10.1016/j.jhazmat.2009.12.037

García, V. M., Barrera, C. E., Roa, G., & Linares, I. (2016). A comparative electrochemical-ozone treatment for removal of phenolphthalein. *Journal of Chemistry 2016*, 1-9. https://doi.org/10.1155/2016/8105128

García, V. M., Linares, I., Natividad, R., Balderas, P., Alanis, C., Barrera, C. E., & Roa, G. (2022). Solar-photovoltaic electrocoagulation of wastewater from a chocolate manufacturing industry: Anodic material effect (aluminium, copper and zinc) and life cycle assessment. *Journal of Environmental Chemical Engineering 10*, 1-13. https://doi.org/10.1016/j.jece.2022.107969

García, S., Eiband, M. M. S. G., de Melo, J. V., & Martínez, C. A. (2017). Electrocoagulation and advanced electrocoagulation processes: A general review about the fundamentals, emerging applications and its association with other technologies. *Journal of Electroanalytical Chemistry 801*, 267-299. https://doi.org/10.1016/j.jelechem.2017.07.047

Guzmán, T. M., Pérez, O., & Valdés, O. (2020). Biodegradación de residuos sólidos urbanos utilizando cultivos microbianos y biofiltro estático de *Eisenia foetida*. *Tecnología Química 40*(1), 81-92. ISSN 2224-6185

Hakizimana, J. N., Gourich, B., Chafi, M., Stiriba, Y., Vial, C., Drogui, P., & Naja, J. (2017). Electrocoagulation process in water treatment: A review of electrocoagulation modeling approaches. *Desalination 404*, 1-21. https://doi.org/10.1016/j.desal.2016.10.011

Han, X., Qu, Y., Dong, Y., Chen, D., Liang, D. D., Liu, J., . . . , Feng, Y. (2021). Simultaneous electricity generation and eutrophic water treatment utilizing iron coagulation cell with nitrification and denitrification biocathodes. *Science of the Total Environment 782*, 1-6. https://doi.org/10.1016/j.scitotenv.2021.146436

Hernández, O. A., Núñez, A., Tapia, M., & Espinosa, R. M. (2016). Surface modification of polypropylene membrane using biopolymers with potential applications for metal ion removal. *Journal of Chemistry 2016*, 1-10. https://doi.org/10.1155/2016/2742013

Houbron, E., Cruz, E., Ponciano, A., Rustrián, E., & Canul, M. (2021). Motor oil wastewater treatment in a packed bed bioreactor using immobilized native microbial consortium. *Revista Mexicana de Ingeniería Química 20*(2), 761-773. https://doi.org/10.24275/rmiq/IA2271

López, R., Laines, J. R., Hernández, J. R., & Aparicio, M. A. (2014). Evaluation of taro starches (*Colocasia esculenta*) as flocculant aids in turbidity removal for water treatment process turbidity removal for water treatment process. *Revista Mexicana de Ingeniería Química 13*(3), 855-863. ISSN 1665-2738.

Marschner, P. (2012). *Marschner's Mineral Nutrition of Higher Plants*. Elsevier Ltd, 3rd edition. Australia.

Massoudinejad, M., Mehdipour-Rabori, M., & Dehghani, M. H. (2015). Treatment of natural rubber industry wastewater through a combination of physicochemical and ozonation processes. *Journal of Advances in Environmental Health Research 3*(4), 242-249. https://doi.org/10.22102/jaehr.2015.40208

Palacios, M. L., Cortes, F., González, D. A., & Gómez, R. M. (2012). Surface modification of polypropylene membrane by acrylate epoxidized soybean oil to be used in water treatment. *Journal of Applied Polymer Science 124*(S1), E147-E153. https://doi.org/10.1002/app.35269

Pendashteh, A. R., Asghari Haji, F., Chaibakhsh, N., Yazdi, M., & Pendashteh, M. (2017). Optimized treatment of wastewater containing natural rubber latex by coagulation-flocculation process combined with Fenton oxidation. *Journal of Materials and Environmental Science 8*(11), 4015-4023. ISSN : 2028-2508

Puigdomenech, I. (2015), Chemical Equilibrium Diagrams (Java), KTH Royal Institute of Technology, V. 1. Available at: https://www.kth.se/che/medusa/downloads-1.386254. Accessed: December 19, 2023.

Rubí, H., Barrera, C. E., Linares, I., Fall, C., & Bilyeu, B. (2015). A combined electrocoagulation-electrooxidation process for carwash wastewater reclamation. *International Journal of Electrochemical Science 10*(8), 6754-6767

Ruiz, A. A. (2005). La electrocoagulación: una alternativa para el tratamiento de aguas residuales. *Revista Lasallista de Investigación 2*(1), 49-56. ISSN: 1794-4449.

Song, J., Yin, Y., Li, Y., Gao, Y., & Liu, Y. (2020). In-situ membrane fouling control by electrooxidation and microbial community in membrane electro-bioreactor treating aquaculture seawater. *Bioresource Technology 314*, 1-17. https://doi.org/10.1016/j.biortech.2020.123701

Syam, D., Anantha, T. S., Nidheesh, P. V., & Suresh, M. (2020). Industrial wastewater treatment by electrocoagulation process. *Separation Science and Technology (Philadelphia) 55*(17), 3195-3227. https://doi.org/10.1080/01496395.2019.1671866

Tahreen, A., Jami, M. S., & Ali, F. (2020). Role of electrocoagulation in wastewater treatment: A developmental review. *Journal of Water Process Engineering 37*, 1-9. https://doi.org/10.1016/j.jwpe.2020.101440

Tatoulis, T., Stefanakis, A., Frontistis, Z., Akratos, C. S., Tekerlekopoulou, A. G., Mantzavinos, D., & Vayenas, D. V. (2017). Treatment of table olive washing water using trickling filters, constructed wetlands and electrooxidation. *Environmental Science and Pollution Research 24*(2), 1085-1092. https://doi.org/10.1007/s11356-016-7058-6

Zhang, S., Zhang, J., Wang, W., Li, F., & Cheng, X. (2013). Removal of phosphate from landscape water using an electrocoagulation process powered directly by photovoltaic solar modules. *Solar Energy Materials and Solar Cells 117*, 73-80. https://doi.org/10.1016/j.solmat.2013.05.027.