



Electrocoagulation process performance in removal of TOC, TDS, and turbidity from surface water

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ABSTRACT

Removal of natural organic matter from surface water collected from the intake of the new Quhafah drinking water treatment plant, Fayoum, Egypt, was investigated in this research. An electrocoagulation (EC) cell using aluminum and iron electrodes was operated under various conditions of current density, initial pH, and retention time, connected in monopolar mode with a 1cm gap between the electrodes to assess the efficiency of EC in the removal of total organic carbon (TOC), total dissolved solids (TDS), and turbidity. Electric energy consumption and theoretical dose were also calculated. Aluminum exhibited better performance in the removal of TOC and TDS than iron, while both materials were almost equally effective in removal of turbidity. In the case of aluminum electrodes, the maximum removal efficiency for TOC was 74%; for turbidity and TDS, removal efficiency reached 99.10% and 84%, respectively, at optimal operating conditions of each parameter. In the case of iron electrodes, the maximum removal efficiencies for TOC, turbidity, and TDS were 64.8%, 98.3%, and 78%, respectively. Anodes were scanned using scanning electron microscopy to evaluate corrosion of the electrodes. Equilibrium studies were performed using Langmuir and Freundlich models. The adsorption kinetics fit a second-order kinetic model. Overall, the EC technique was capable of achieving satisfactory reductions of TOC, TDS, and turbidity at an economical cost using simple technology.

Keywords: Electrocoagulation; Aluminum electrodes; Iron electrodes; TOC; Surface water; SEM

1. Introduction

Natural organic matter (NOM) is a heterogeneous mixture of naturally occurring compounds found abundantly in surface waters. It is one of the most serious pollutants in drinking water treatment because it reacts with the chlorine compounds used as disinfectants, forming disinfection by-products suspected to act as carcinogenic substances. These by-products include trihalomethanes and haloacetic acids (HAAs). NOM is also a cause of membrane fouling and increases the absorption of UV radiation, decreasing the effectiveness of UV disinfection. In addition, NOM impacts aesthetic drinking water quality. Total organic carbon (TOC)

is one of the most commonly used measures for quantifying the amount of NOM in water. NOM-impacted waters exhibit high variation in TOC concentration due to seasonal changes, and thus treatment systems are needed that can respond quickly and automatically to demand [1]. TOC concentrations in surface water are generally less than 10 mg/L [2]. The average concentrations of TOC in three rivers in Tehran, Iran, in spring, summer, and fall, were 4, 2.41, and 4.03 mg/L, respectively [3]. TOC ranged from 8 to 10 mg/L in a drinking water source in Spain [4]. In Egypt, as in many other countries, there is no specified limit for TOC concentration in surface water, though it should be reduced to the minimum possible

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level to reduce the effects mentioned above. Accordingly, US Environmental Protection Agency guidelines require a 50% removal of TOC [5].

1.1. Electrocoagulation

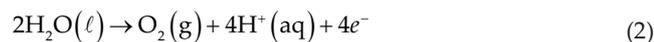
Using electricity to treat water dates back to the 19th century in the UK. However, due to the ready availability of mass-produced chemical coagulants, electrochemical treatment of water did not find widespread applications worldwide [6,7]. Today electrochemical technologies are considered a reliable and effective technology with many benefits compared to chemical coagulation (CC): the equipment required for the electrocoagulation (EC) process is simple, easy to operate, and has no moving parts. In EC, less sludge is produced compared with CC. EC also has the advantage of removing small colloidal particles, as the applied electric field makes them move faster, thus facilitating their agglomeration. Floccs formed by EC tend to be much larger, contain less bound water, and are more stable and, therefore, can be easily separated by sedimentation or filtration. The hydrogen bubbles produced during EC help carry the floccs to the top of the reactor so that they can be collected and removed easily. One of the drawbacks of CC is the anions produced from the addition of metal salts such as chlorides and sulfates. These anions increase the total dissolved solids (TDS) in the treated water and decrease the removal efficiency. In contrast, EC is considered a source of pure metal for hydroxide production because the dissolution of the electrodes is the source of metal ions (i.e., in situ generation of coagulants) [6,8,9].

Regarding the disadvantages of the EC process, the use of electricity is usually costly, the occurrence of an oxide film on the surface of the cathode causes a loss in the efficiency of the process, and the electrodes are dissolved into the solution as a result of oxidation, thus requiring them to be regularly replaced [10].

1.2. Principles of EC

EC consists of two sets of electrodes submerged in the EC cell: sacrificial anodes that undergo oxidation and cathodes where reduction takes place when a current is applied across the electrodes according to the following equations [11].

- Anode:



- Cathode:



where M is the metal used in the anode.

The electrochemical reactions that occur in the EC process depend on the electrodes' material. Aluminum (Al) and iron (Fe) are usually used as the electrode material in EC systems for different pollutants and types of water or

wastewater to be treated [12–14]. Al dissolves as Al^{3+} , and Fe dissolves as Fe^{2+} and Fe^{3+} [11,15]. Sasson et al. [11] studied Fe dissolution from anodes and found that at pH values of 5–9, more than 82% of the iron dissolved from the anode was in the form of Fe^{2+} . They suggested that the number of electrons in Faraday's Law (n) should be 2.2, assuming that 80% of the iron is Fe^{2+} and 20% is Fe^{3+} [11]. In general, Al appears to be a better material compared with Fe in most cases when only the efficiency of the treatment is considered, although Fe is lower in cost. Other metals have also been used as electrode materials. Table 1 summarizes the different materials used for different types of pollutants along with other operating conditions and the corresponding removal efficiencies achieved.

The current density governs the rate of the electrochemical reactions that produce the coagulant dose and the size and number of hydrogen bubbles [10]. In addition, current density affects the electrode potential, which defines the reactions occurring on the electrode surface. It is one of the most important operating conditions to be considered, as it also affects the electric energy consumed and subsequently the operating cost.

Reaction times ranging from 5 to 240 min have been studied; high removal efficiencies were obtained at low reaction times when coupled with higher current densities. The inverse was also observed.

The electrodes can be connected in monopolar or bipolar modes. The electrode connection mode affects the pollutant removal efficiencies and operating costs; the two modes have been compared in various studies: better removal efficiency was achieved when the electrodes were in the bipolar connection, although the monopolar connection had lower treatment costs [16,17].

The initial pH is an important parameter that has an influence on the electrochemical processes [11,18–20], as it affects the degree of hydrolysis of the metal ions and defines the type of the produced Al and Fe species [11]. In EC, the solution pH increases during the process due to hydrogen evolution at the cathode [19].

Other factors also influence the process, such as electrode gap, which influences the current between electrodes and solution conductivity.

Decreasing TOC concentrations to acceptable levels remains a challenge, both technically and economically. This study's goal was to assess the efficiency of the EC process using Al and Fe electrodes for TOC removal from surface water collected at the intake of a drinking water treatment plant, and to determine the optimum operating conditions leading to minimum operating cost. TDS and turbidity were also studied to assess the resulting water quality. Equilibrium adsorption behavior was performed using the models of Langmuir and Freundlich. Second-order kinetic models were used for the adsorption kinetics of electrocoagulants.

2. Materials and methods

2.1. Feedwater

Experiments were carried out using natural surface water collected from the intake of the new Quhafah drinking water treatment plant, Fayoum, Egypt, located on Bahr Yussef canal, which is connected to the Nile River by the Al-Ibrahimeya canal. The average composition of feedwater is shown in Table 2.

Table 1
Applications of EC in the treatment of surface water

Water type	Anode/ cathode material	pH	Electrode gap (mm)	Current density (mA/cm ²)	Treatment time (min)	EEC (KWh/m ³)	Pollutant	% removal	Reference
Surface water (Spain)	Al/SS	8	6	5	N.D.	N.D.	TOC	85%	[4]
Aq. sol. of Sr and Cs	Mg/galvanized iron	7	3	0.8	40	–	Turbidity Strontium Cesium	100% 97% 96.8%	[8]
Aqueous solution of (2,4-DP) herbicide	Al/SS	7	3	1	240	–	(2,4-DP)	93%	[9]
Aqueous solution of Cr ³⁺	Fe	3.4	22	10.84 in monopolar 32.52 in bipolar	60 50	–	Cr ³⁺	99.9% bipolar	[16]
Aqueous solution of F ⁻	Al	6.4	5	2.5–6.25	0–45	–	F	<1 mg/L	[17]
Surface water (Finland)	Al/inert electrode	4	10	0.48	4–12	–	TOC	78%	[18]
Industrial wastewater	Combination of Al and Fe	8	20	4.545	60	–	COD BOD Color Turbidity T.Coliform	69% 71% 83% 80% 99%	[21]
Paper mill wastewater	Al-Al Fe-Fe Fe-Al Al-Fe	5–7	10	70	60	–	COD	88.4%	[22]
Groundwater	Al	6.5	–	2.5	30	–	TOC TN	70% 40%	[23]
Humic substances of different sources	Hybrid (Al + Fe)	7.3	10	3	25	–	DOC	92.4%	[24]
Surface water	Al	7.6	10	5	20	–	TOC Oil NH ₃ -N	69.9 85.7 75	[25]
Municipal solid waste leachate	Fe	6.3	25	40	100	–	TOC COD	88.3% 91.1%	[26]
Textile wastewaters	Al Fe	5 7	20	3	15	–	COD	63% Al 65% Fe	[27]
Synthetic humic acid solution	Al	7	40	10 A (current)	30	0.5	Humic acid	96%	[28]
Aqueous solu- tions of Th, U, and Ce	Zn/SS	7	5	2	45	0.838 in bipolar connection	Th U Ce	98.4% 98.6% 97.7%	[29]

(continued)

Table 1 (continued)

Water type	Anode/ cathode material	pH	Electrode gap (mm)	Current density (mA/cm ²)	Treatment time (min)	EEC (KWh/m ³)	Pollutant	% removal	Reference
Aqueous solution of Pb	Mg/galvanized iron	7	5	8	25	0.72 in monopolar connection	Pb	99.3%	[30]
Aqueous solution of NaNO ₃	Zn/SS	7	3	1	35	–	Nitrate	69%	[31]
CBA (antibiotics)	Mg/SS	7	3	1	60	–	CBA	65%–85%	[32]
Aqueous solutions of Co, Cu, and Cr	Mg/galvanized iron	7	5	0.25	30	–	Co Cu Cr	90%–100%	[33]
Aqueous solution of B	Al/SS	7	5	2	90	1.007	Boron	93.2	[34]
Aqueous solution of Cu	Al	7	5	0.25	5	–	Cu	98.5	[35]
Ww high fluoride and turbidity levels	Ti/RuO ₂ anode/SS	5–6	1	150 mA (intensity)	20	0.4	F Turbidity	73% 97%	[36]
Surface water (Algeria)	Fe/Fe	–	15	(2–3) A (current)	30	–	Bacteria color	99% 93.24%	[37]
Surface water (Algeria)	Al	7.5	15	3 A (current)	60	–	COD Turbidity F.Coliform	80% 95% 99%	[38]
Landfill leachate	Al Fe	8.2	65	34.8	30	12.5	COD	45%Al 32% Fe	[39]

SS, Stainless steel; DOC, dissolved organic carbon; TN, total nitrogen; 2,4-DP, 2,4-dichlorophenoxy; N.D., not determined. T.Coliform, total coliforms; F.Coliform, fecal coliforms; Ww high fluoride, semiconductor industry wastewater.

Table 2
Surface water initial composition

Parameter	Result	Unit
pH	7.69 ± 0.1	
Turbidity	10.43 ± 1.57	NTU
TDS	275 ± 15	mg/L
TOC	3.89 ± 0.18	mg/L
Conductivity	598.5 ± 34.5	µS/cm

2.2. Experimental setup

EC experiments were conducted in a Plexiglas tank with a volume of 1.9 L. The EC cell consisted of 10 electrodes, made of Al in the first set of experiments and Fe in the second set: 5 electrodes as anodes and 5 electrodes as cathodes. These were connected to the power source using a monopolar arrangement, as shown in Figs. 1 and 2. The electrode dimensions were 11 cm × 8.5 cm. The gap between anodes and cathodes was 1 cm. A laboratory DC power source (EA-3048, Germany) was used in direct current mode in all experiments. Surface water was treated at room temperature of 20.75°C ± 1.75°C.

The experimental conditions were as follows: current densities of 3, 4, and 5 mA/cm²; detention times of 10, 20, 30, 40, 50, and 60 min; and initial pH values of 4, 5.5, and natural water pH. Experiments were conducted using the Al electrodes, and then repeated using the Fe electrodes. Hydrochloric acid (PioChem, Egypt) was used to adjust the pH, and electrode plates were washed strictly with 4% HCl and tap water after each experiment [11,39]. Chemicals used were of analytical grade.

2.3. Analytical methods

Samples were collected from the bottom of the EC cell at specified time intervals. All samples were left to settle for 10 min, filtered with double rings filter paper to simulate particle separation by sedimentation and filtration, and then analyzed for the removal of TOC, TDS, and turbidity. Water temperature and pH were measured at the start and end of each experiment.

The TOC was measured using a Phoenix 8000 UV-Persulfate TOC Analyzer (Teledyne Tekmar, Ohio, USA), turbidity was measured using a HACH, Colorado, USA 2100N Turbidimeter, TDS was measured using a WTW

inoLab Cond 720, pH and temperature were measured using the WTW inoLab pH 720 with a range of 0–14 and an accuracy of ±0.02 (WTW, Weilheim, Germany). All samples were analyzed in triplicate.

The percentage of removal is calculated as follows:

$$\% \text{ Removal} = \frac{(C_0 - C_t)}{C_0} \quad (4)$$

where C_0 and C_t are the initial concentration and concentration at time t of the studied parameters, respectively.

3. Results and discussion

3.1. Effect of pH

Fig. 3 shows the obtained results for TOC removal for both types of electrodes under different operating conditions. For

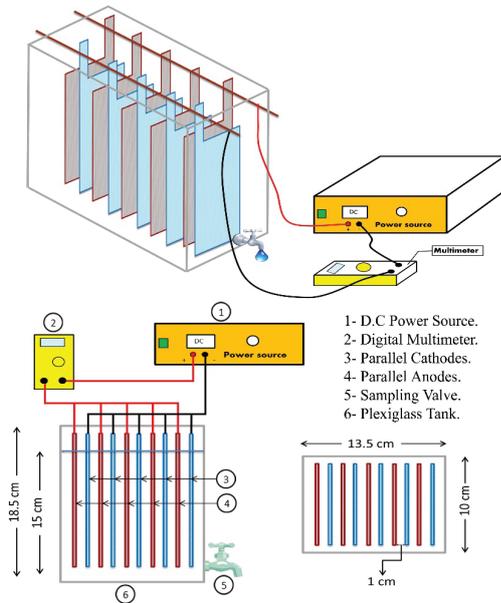


Fig. 1. Schematic diagram for the experimental setup.

Al electrodes, it was observed that the best TOC removal was at initial pH = 4, for which removal efficiency reached 74% after 60 min at a current density of 5 mA/cm². Removal values at pH = 5.5 and at natural pH were lower. At same time and current density but initial pH values of 5.5 and natural pH, removal reached 66.85% and 61.73%, respectively.

At the same initial pH = 4 and retention time 60 min, but at lower current densities (3 and 4 mA/cm²), removal efficiencies were 69.81% and 72.5%, respectively, which are higher values than those obtained at the other initial pH values studied at different current densities. It is observed that the removal efficiencies obtained at pH = 4 are usually 10% higher than those obtained for other pH values under the same operating conditions. This is why pH = 4 is considered the optimum pH value for Al electrodes in TOC removal.

Removal of NOM using Al electrodes is accomplished by charge neutralization and adsorption: at pH = 4, Al(OH)₂⁺, AlO⁺, and Al(OH)₃(aq) are the predominant Al species, charge neutralization is accomplished by Al(OH)₂⁺, AlO⁺, and Al(OH)₃(aq) while adsorption is increased with Al(OH)₃(s). The positively charged species attract the NOM molecules and promote floc aggregation, thus increasing the removal rates [28].

In contrast, for Fe electrodes, the best TOC removal was obtained at the highest pH studied, which is natural pH. It reached 64.78% after 60 min at a current density of 5 mA/cm², whereas at initial pH = 5.5 and 4, removal values obtained at the same time and current density were very similar and reached 58.87% and 57.64%, respectively. This can be explained by the fact that iron hydroxides are usually in suspension at alkaline



Fig. 2. Photo of the experimental setup.

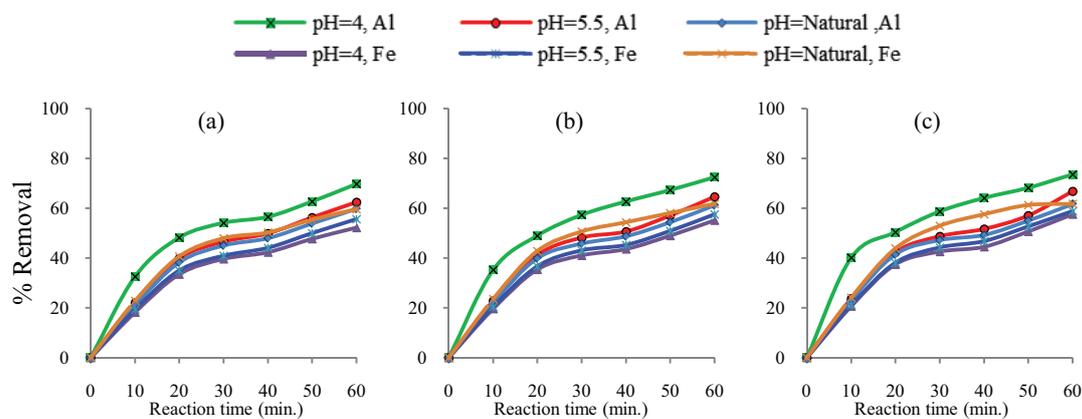


Fig. 3. TOC removal efficiency at current densities: (a) 3 mA/cm², (b) 4 mA/cm², and (c) 5 mA/cm².

pH values, enhancing the removal mechanism through coagulation, adsorption, and settling [40].

The removal of TOC achieved in the case of Fe electrodes is lower than the removal achieved by Al electrodes.

Fig. 4 shows the results obtained for TDS removal for both types of electrodes. For Al electrodes, it was observed that the best TDS removal was at initial pH = natural pH (in contrast to the TOC removal), removal efficiency reached 84% after 60 min at a current density of 5 mA/cm². Removal values at pH = 5.5 and 4 under the same conditions were lower and reached 75.77% and 71.15%, respectively.

For Fe electrodes, the best TDS removal was obtained at the natural water pH, as obtained for Al electrodes, but with lower removal values, with removal rates of 78%, 70%, and 67% after 60 min at a current density of 5 mA/cm² at pH = natural, 5.5, and 4, respectively. Again, for TDS removal, Al appears to be more efficient than Fe.

Fig. 5 shows the results obtained for turbidity removal for both types of electrodes at different current densities and pH values with reaction time. The results obtained for both types of electrodes are very close. Fe electrodes have better removal for the first 40 min, and then in the interval from 40 to 60 min, Al achieves a slightly higher removal than Fe. For Al electrodes, it was observed that the best turbidity removal was at initial pH = natural pH (contrary to the TOC removal

and similar to TDS). Removal efficiency reached 99% after 60 min at current density = 5 mA/cm². Removal values at pH = 5.5 and 4 were lower and reached 97.8% and 96.6%, respectively, after 60 min.

For Fe electrodes, the best turbidity removal was obtained at the natural water pH—similar to Al electrodes—but with lower removal values that reached 98%, 96.5%, and 95.9% after 60 min at current density = 5 mA/cm² and pH = natural pH, 5.5, and 4, respectively.

It is obvious that the EC process can achieve very high removal of turbidity for both types of electrodes.

As seen in Fig. 6, the initial pH values increased with time. The increase was much higher for the Fe electrodes than the Al electrodes, and this increase was also influenced by the current density. The pH increase during the EC process is a well-known phenomenon because of the hydroxyl ions produced at the cathodes, which are not totally consumed by the formation of aluminum, ferrous, or ferric hydroxides.

3.2. Effect of reaction time

From the previously shown figures, TOC, TDS, and turbidity removal efficiencies increased with reaction time for both types of electrodes but with different patterns for the different parameters. For TOC, the removal rate was high

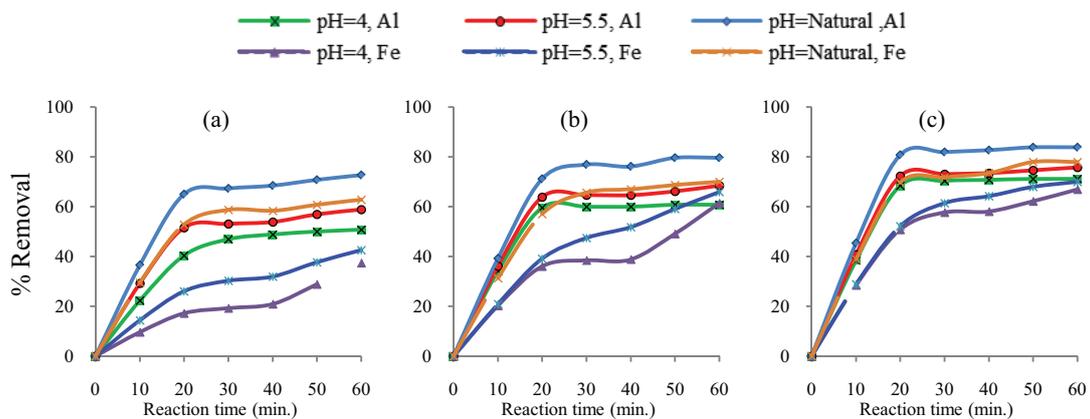


Fig. 4. TDS removal efficiency at current densities: (a) 3 mA/cm², (b) 4 mA/cm², and (c) 5 mA/cm².

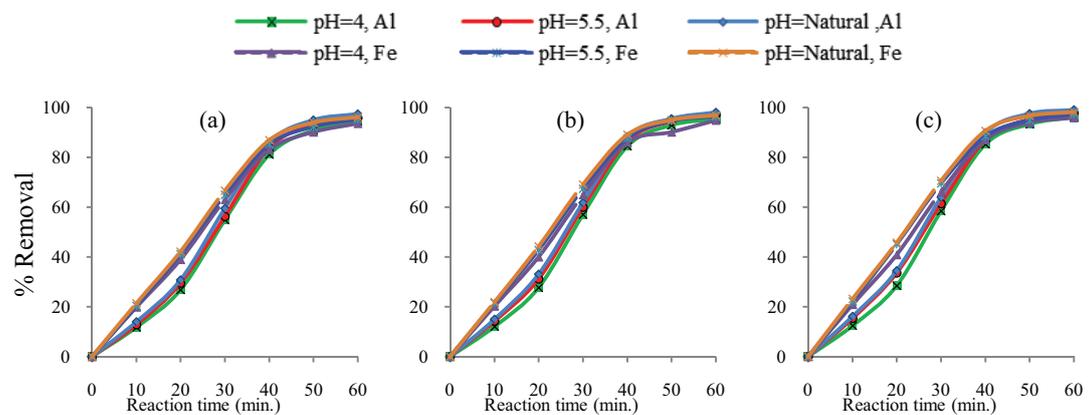


Fig. 5. Turbidity removal efficiency at current densities: (a) 3 mA/cm², (b) 4 mA/cm², and (c) 5 mA/cm².

in the first 20 min, and it continued to increase but at a slower rate until 60 min: 40%–50% of the removal rate was achieved in the first 20 min for Al electrodes, and 30%–40% for Fe. Then, 40%–50% of the removal occurred from 20 to 40 min for both electrodes, and the remainder was achieved between 40 and 60 min. TDS exhibited a similar pattern but with different percentages reached in each reaction time interval.

Turbidity presented a different pattern: approximately 30%–40% of the removal occurred in the first 20 min, and this rate doubled in the following 20 min, reaching 80%–85% at a reaction time of 40 min for both types of electrodes.

3.3. Effect of current densities

TOC and turbidity removal increased with the increase in current density, but the effect of the increase in current density was less than the effect of the increase in reaction time. For example, for Al electrodes, for optimum pH = 4 and reaction time 60 min, the TOC removal rates obtained at 3, 4, and 5 mA/cm² were 69.8%, 72.5%, and 73.6%, respectively. This means that the increase in current density does not have a very significant effect on removal, although it has a very significant effect on the energy consumed, as will be shown in Section 3.4. The same was concluded for turbidity.

On the other hand, the increase in current density had a much higher influence on TDS removal than on other parameters. For example, for Al electrodes, at the optimum pH for TDS removal and time of 60 min, removal rates were 72.7%, 79.6%, and 83.8%, respectively, for current densities of 3, 4, and 5 mA/cm². These values illustrate that the effect of current density on TDS is higher than on the other parameters.

Table 3 summarizes the obtained removal efficiency at time = 60 min.

3.4. Electrical energy consumption

The electrical energy consumption (EEC, kWh/m³) can be calculated using the following equation:

$$EEC = \frac{U \times I \times t}{60V} \tag{5}$$

U is the applied voltage (V); *I* is the applied current (A); *t* is the reaction time (min); and *V* is the volume of the treated water (dm³) [11].

Fig. 7 shows the EEC values at different reaction times for both Al and Fe electrodes at different initial pH values and different current densities. With the exception of Al

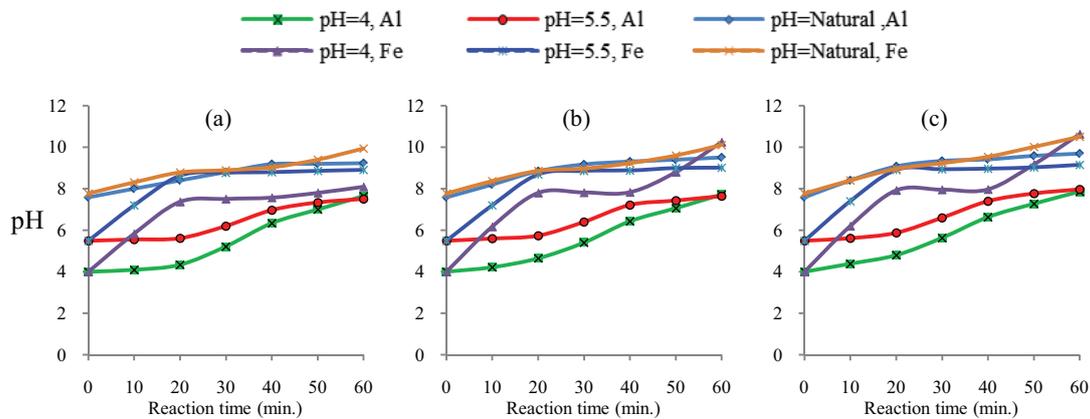


Fig. 6. Final pH values at current densities: (a) 3 mA/cm², (b) 4 mA/cm², and (c) 5 mA/cm².

Table 3
Removal of TOC, turbidity, TDS, and EEC value under different operating conditions, time 60 min

	Current density (mA/cm ²)	Al electrode			Fe electrode		
		TOC	Turbidity	TDS	TOC	Turbidity	TDS
pH = 4	3	69.81	94.7	50.77	52.22	93.58	37.46
	4	72.51	95.49	60.77	55.17	94.92	61.51
	5	74	96.16	71.15	57.64	95.92	67.01
pH = 5.5	3	62.53	95.94	58.85	55.67	95.25	42.61
	4	64.69	97.4	68.46	57.64	96.5	65.98
	5	66.85	97.86	75.77	58.87	97.33	70.1
pH = natural	3	59.84	97.52	62.69	59.61	96.25	62.89
	4	61.19	98.08	79.62	61.82	97	70.1
	5	61.73	99.1	83.85	64.78	98.25	78.01

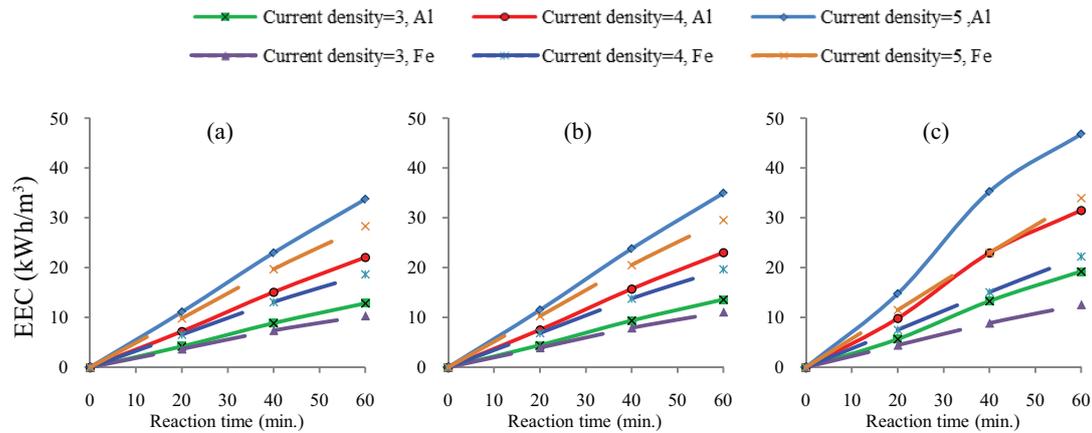


Fig. 7. EEC at initial pH values: (a) 4, (b) 5.5, and (c) natural pH.

electrodes at natural water pH, the EEC values were very similar for both Al and Fe electrodes at different pH values and had the same pattern: an almost linear rate of increase with reaction time. The effect of increase in current density on EEC was more influential than the increase in reaction time. In addition, the change in pH had a recognizable effect on the EEC, as the increase in pH increased the EEC. EEC values were lower for Fe than Al. The lowest EEC values were obtained for both materials at current density = 3 mA/cm² and time = 10 min. At initial pH = 4, 5.5, and natural pH, these values were as low as 1.85, 1.97, and 2.22 kWh/m³ for Fe electrodes and 2.1, 2.19, and 2.83 kWh/m³ for Al electrodes, respectively. The highest values were obtained at current density = 5 mA/cm² and time = 60 min for both materials. These maximum values reached 28.33, 29.56, and 33.99 kWh/m³ for Fe electrodes and 33.75, 34.98, and 46.80 kWh/m³ for Al electrodes at initial pH = 4, 5.5, and natural pH, respectively. These values are in the range reported in the literature that EEC was 12.5–39.7 kWh/m³ when the current density was 34.8–63.1 mA/cm² [39].

3.5. Electrode consumption (dose) calculation

The theoretical metal dose can be calculated based on Faraday's law [23]:

$$m_{\text{theoretical}} = \frac{A \times Q}{n \times F} \quad (6)$$

where A is the molar mass of the metal electrode (g/mol), Q is the amount of current passing through the solution (A·s), $Q = I \times t$; n is the number of electrons, and F is the Faraday constant = 96,485 C/mol.

m can be rewritten in the form

$$m = k \cdot i \cdot t,$$

where $k = (26.982 / (96,485 \times 3))$ for Al [41] and $k = (55.845 / (96,485 \times 2.2))$ for Fe [10], as most of the Fe dissolves as Fe²⁺, so 2.2 is taken as an average value of the number of electrons.

Theoretical electrode consumption was calculated for the different operating conditions studied: for Al electrodes,

it was in the range of 0.17–0.83 kg/m³. For Fe electrodes, it ranged between 0.47 and 2.33 kg/m³. Fe electrode consumption is higher due to its higher atomic weight relative to Al. If this consumption is calculated based on weight, similar electrode consumption values are obtained.

3.6. Isotherms and kinetics

Adsorption isotherm and kinetics were studied for different kinds of pollutants: strontium and cesium [8], lead [30], copper [33,35], CBA (cephalosporin-based antibiotics) [32], Co and Cr [33], boron using zinc electrodes [34], and triaryl methane dyes [42].

The adsorption capacity q_e (mg/g) was calculated as follows [8]:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (7)$$

where C_0 and C_e are the initial and equilibrium concentrations of the parameter measured (mg/L), respectively; V is the volume of the adsorbate solution (L); and m is the mass of the adsorbent (g).

Freundlich and Langmuir models were used to study TOC adsorption. The Freundlich model is expressed by Eq. (8) [42]:

$$\log q_e = \log k_f + 1/n \log C_e \quad (8)$$

where n and k_f are the Freundlich constants, and C_e (mg/L) is the equilibrium concentration (mg/L).

The Langmuir model is in the following form [42]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \quad (9)$$

where q_e is the adsorption capacity at equilibrium (mg/g); K_L and q_m are the Langmuir constants, and C_e is the equilibrium concentration (mg/L). The results showed that the adsorption followed the Freundlich isotherm but did not follow Langmuir's.

Table 4 gives the values of the different parameters for the Freundlich and Langmuir isotherms.

Kinetic studies were performed for TOC at optimum pH values for the two types of electrodes at different current densities. The experimental data were analyzed using first-order and second-order Lagergren model. The first-order Lagergren model is expressed as follows [35]:

$$\log(q_e - q_t) = \log(q_e) - k_1 t / 2.303 \tag{10}$$

The second-order Lagergren kinetic model is expressed as follows:

$$t / q_t = 1 / k_2 q_e^2 + t / q_e \tag{11}$$

where q_e (mg/g) and q_t (mg/g) are the adsorption capacities at equilibrium and at time t (min), respectively, k_1 (min⁻¹) is a rate constant of first-order adsorption, and k_2 (g/mg min) is the rate constant for the second-order kinetic model. For the first-order model, the calculated q_e (cal) value does not agree with the experimental q_e (exp) values and has a poor correlation coefficient (data not shown), whereas it was better fitted to the second-order Lagergren model. Calculated q_e values and R^2 values were as indicated in Table 5, and a plot of the second-order model is indicated in Fig. 8.

Table 4

Constant parameters and correlation coefficients calculated for Langmuir and Freundlich adsorption isotherm models for TOC

Isotherm	Parameter	Al (pH = 4)	Fe (pH = natural)
Freundlich	k_f (mg/g (mg/L) ^{-1/n})	1.2618	0.26399
	n	0.3033	0.327
	R^2	0.9696	0.9598
Langmuir	q_m (mg/g)	-0.6237	-0.48668
	K_L (L/mg)	-1.4972	-2.30632
	R^2	0.95	0.9744

3.7. Scanning of electrodes using SEM

Anodes were scanned using scanning electron microscopy (SEM) before and after use in the EC setup. Figs. 9 and 10 show the change in the surface of the Al electrodes: before treatment, the surface is smooth, whereas after treatment apparent corrosion can be observed, especially at higher magnification, at which fissures and grooves can be observed.

The corrosion in the Fe anodes was very distinct by visual inspection; anodes were scanned before and after treatment as shown in Figs. 11 and 12.

Table 5

The experimental and calculated q_e values at different current densities in second-order adsorption kinetics of TOC

Electrode	Parameter	Current density (mA/cm ²)	q_e (exp) (mg/g)	Second order		
				q_e (cal) (mg/g)	k_2	R^2
Al	TOC	3	1.8089	1.8839	0.6409	0.984
		4	1.409	1.4958	0.8104	0.9792
		5	1.144	1.21315	1.0045	0.9796
Fe	TOC	3	1.2333	1.304	0.9206	0.9779
		4	0.959389	1.0284	1.1743	0.9714
		5	0.804205	0.8654	1.3917	0.97

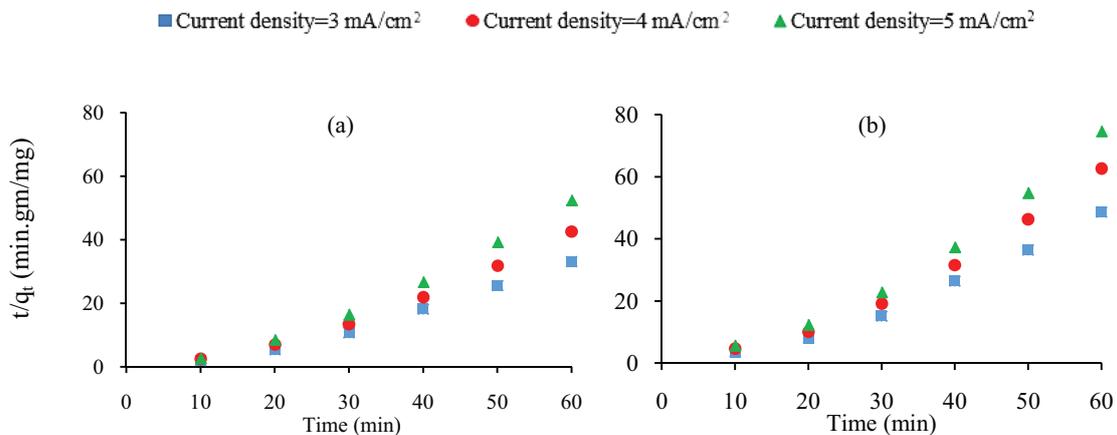


Fig. 8. Second-order kinetic model plots for adsorption of TOC at different current densities: (a) Al electrodes at pH = 4 and (b) Fe electrodes at pH = natural.

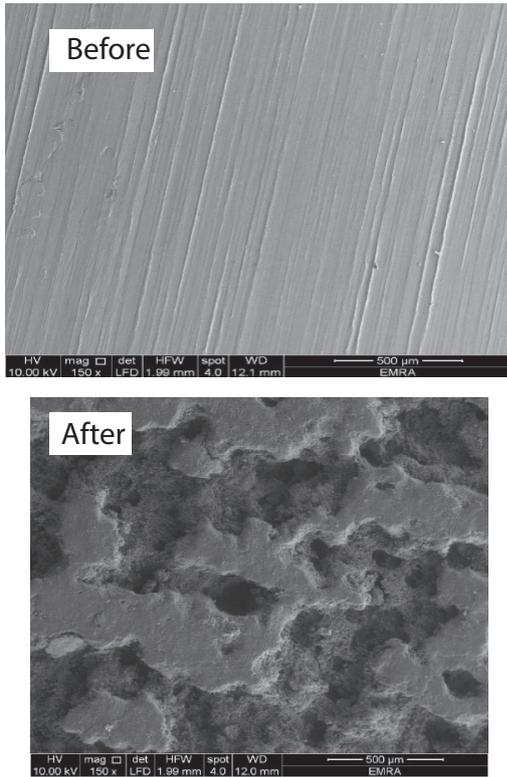


Fig. 9. Scanning electron microscopy (SEM) micrograph of Al electrodes before and after use in the EC setup, magnification 150×.

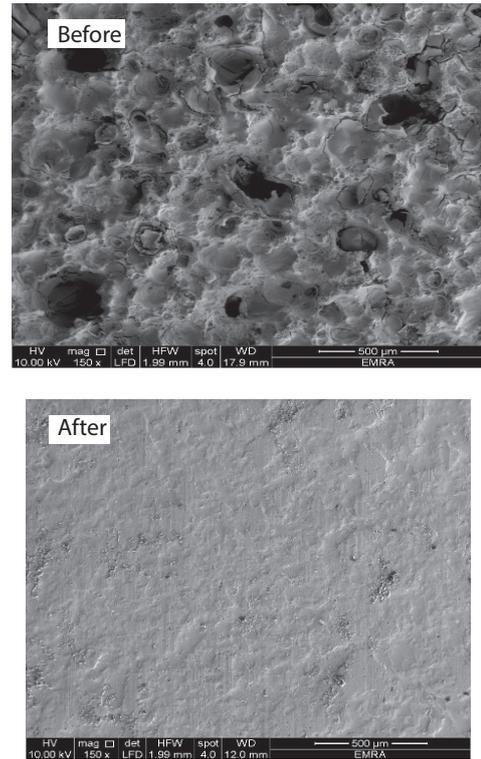


Fig. 11. Scanning electron microscopy (SEM) micrograph of Fe electrodes before and after use in the EC cell, magnification 150×.

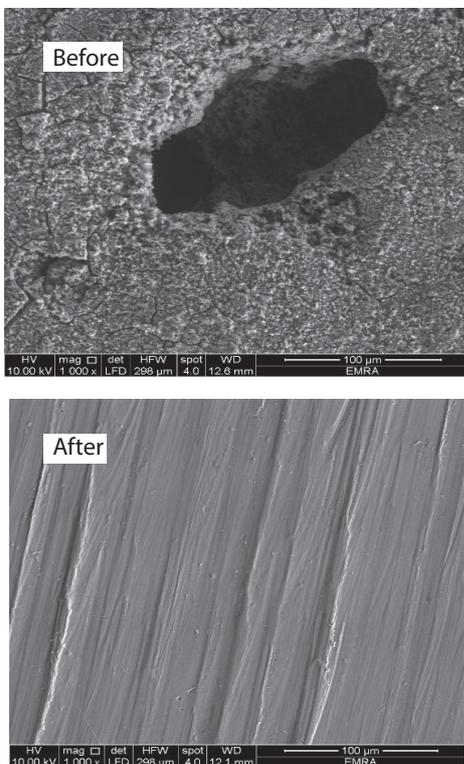


Fig. 10. Scanning electron microscopy (SEM) micrograph of Al electrodes before and after use in the EC setup, magnification 1,000×.

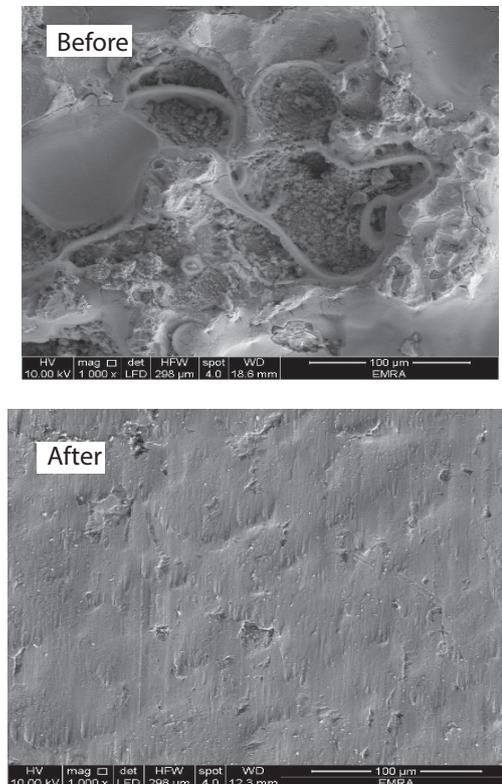


Fig. 12. Scanning electron microscopy (SEM) micrograph of Fe electrodes before and after use in the EC cell, magnification 1,000×.

4. Conclusions

EC is an efficient method for TOC, TDS, and turbidity reduction from surface water. The removal levels were high enough to reach satisfactory levels. Al electrodes achieved a slightly better removal efficiency than iron electrodes, especially in the TOC removal. The removal increased with the increase of reaction time and current density, but reaction time had a greater influence on removal than current density. Al electrodes' performance was best observed at a low pH value of 4 for TOC removal; for turbidity and TDS, it was best observed at the natural pH. Iron electrodes achieved their best performance at the natural pH for all parameters. The EC system was very efficient in turbidity removal, and removal reached 99% using Al electrodes and 98% using Fe electrodes. The EEC was in the ranges reported in the literature. Equilibrium studies were performed using Langmuir and Freundlich models. The adsorption kinetics fit the second-order kinetic model. SEM revealed obvious corrosion on the surfaces of the electrodes following EC.

References

- [1] D. Reckhow, P. Rees, K. Nusslein, G. Makdissy, G. Devine, T. Conneely, A. Boutin, D. Bryan, Long-Term Variability of BDOM and NOM as Precursors in Watershed Sources, Water Research Foundation Report Series, IWA Publishing, 2008.
- [2] Water Quality Assessments – A Guide to Use of Biota, Sediments and Water in Environmental Monitoring, 2nd ed., UNESCO/WHO/UNEP, 1996.
- [3] M. Ghoochani, N. Rastkari, R.N. Nodehi, A.H. Mahvi, S. Nasserli, S. Nazmara, Study on the TOC concentration in raw water and HAAs in Tehran's water treatment plant outlet, J. Environ. Health Sci. Eng., 11 (2013) 28.
- [4] J. Llanos, S. Cotillas, P. Cañizares, M.A. Rodrigo, Electrocoagulation as a key technique in the integrated urban water cycle – a case study in the centre of Spain, Urban Water J., 14 (2017) 650–654.
- [5] USEPA, National Primary Drinking Water Regulations: Disinfectants and Disinfection By-products, Final Rule, Federal Register, 63 (1998) 69390–69476. Available at: <https://www.gpo.gov/fdsys/pkg/FR-1998-12-16/pdf/98-32887.pdf>.
- [6] P.K. Holt, G.W. Barton, M. Wark, C.A. Mitchell, A quantitative comparison between chemical dosing and electrocoagulation, Colloids Surf., A, 211 (2002) 233–248.
- [7] M. Kobya, O.T. Can, M. Bayramoglu, Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes, J. Hazard. Mater., 100 (2003) 163–178.
- [8] R. Kamaraj, S. Vasudevan, Evaluation of electrocoagulation process for the removal of strontium and cesium from aqueous solution, Chem. Eng. Res. Des., 93 (2015) 522–530.
- [9] R. Kamaraj, D.J. Davidson, G. Sozhan, S. Vasudevan, Adsorption of herbicide 2-(2,4-dichlorophenoxy) propanoic acid by electrochemically generated aluminum hydroxides: an alternative to chemical dosing, RSC Adv., 5 (2015) 39799–39809.
- [10] M.Y.A. Mollah, P. Morkovsky, J.A. Gomes, M. Kesmez, J. Parga, D.L. Cocke, Fundamentals, present and future perspectives of electrocoagulation, J. Hazard. Mater., 114 (2004) 199–210.
- [11] M.B. Sasson, W. Calmano, A. Adin, Iron-oxidation processes in an electroflocculation (electrocoagulation) cell, J. Hazard. Mater., 171 (2009) 704–709.
- [12] E.A. Vik, D.A. Carlson, A.S. Eikum, E.T. Gjessing, Electrocoagulation of potable water, Water Res., 18 (1984) 1355–1360.
- [13] N. Mameri, A.R. Yeddou, H. Lounici, D. Belhocine, H. Grib, B. Bariou, Defluoridation of septentrional Sahara water of north Africa by electrocoagulation process using bipolar aluminium electrodes, Water Res., 32 (1998) 1604–1612.
- [14] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC)—science and applications, J. Hazard. Mater., 84 (2001) 29–41.
- [15] H.A. Moreno C., D.L. Cocke, J.A.G. Gomes, P. Morkovsky, J.R. Parga, E. Peterson, C. Garcia, Electrochemical reactions for electrocoagulation using iron electrodes, Ind. Eng. Chem. Res., 48 (2009) 2275–2282.
- [16] A. Golder, A. Samanta, S. Ray, Removal of Cr³⁺ by electrocoagulation with multiple electrodes: bipolar and monopolar configurations, J. Hazard. Mater., 141 (2007) 653–661.
- [17] D. Ghosh, C. Medhi, M. Purkait, Treatment of fluoride containing drinking water by electrocoagulation using monopolar and bipolar electrode connections, Chemosphere, 73 (2008) 1393–1400.
- [18] M. Vepsäläinen, M. Pulliainen, M. Sillanpää, Effect of electrochemical cell structure on natural organic matter (NOM) removal from surface water through electrocoagulation (EC), Sep. Purif. Technol., 99 (2012) 20–27.
- [19] P. Cañizares, C. Jiménez, F. Martínez, M.A. Rodrigo, C. Sáez, The pH as a key parameter in the choice between coagulation and electrocoagulation for the treatment of wastewaters, J. Hazard. Mater., 163 (2009) 158–164.
- [20] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol., 38 (2004) 11–41.
- [21] I. Linares-Hernández, C. Barrera-Díaz, G. Roa-Morales, B. Bilyeu, F. Ureña-Núñez, Influence of the anodic material on electrocoagulation performance, Chem. Eng. J., 148 (2009) 97–105.
- [22] R. Katal, H. Pahlavanzadeh, Influence of different combinations of aluminum and iron electrode on electrocoagulation efficiency: application to the treatment of paper mill wastewater, Desalination, 265 (2011) 199–205.
- [23] A. Baciú, A. Pop, K. Bodor, I. Vlaicu, F. Manea, Assessment of electrocoagulation process for drinking water treatment, Environ. Eng. Manage. J., 14 (2015) 1347–1354.
- [24] F. Ulu, S. Baris, M. Kobya, M. Sillanpää, An evaluation on different origins of natural organic matters using various anodes by electrocoagulation, Chemosphere, 125 (2014) 108–114.
- [25] X. Li, Q. Feng, Q. Meng, Y. Ceng, Electrocoagulation for the Drinking Water Treatment of Polluted Surface Water Supplies, Proc. 2nd International Conference on Bioinformatics and Biomedical Engineering, IEEE, Shanghai, China, 2008.
- [26] D. Sivakumar, D. Shankar, M. Mohana, Removal of TOC and COD from municipal solid waste leachate using aluminium electrode in electrocoagulation, Int. Res. J. Multidiscip. Sci. Technol., 2 (2017) 11–17.
- [27] M. Bayramoglu, M. Eyvaz, M. Kobya, Treatment of the textile wastewater by electrocoagulation: economical evaluation, Chem. Eng. J., 128 (2007) 155–161.
- [28] D. Ghernaout, B. Ghernaout, A. Saibaa, A. Boucherit, A. Kellil, Removal of humic acids by continuous electromagnetic treatment followed by electrocoagulation in batch using aluminium electrodes, Desalination, 239 (2009) 295–308.
- [29] R. Kamaraj, S. Vasudevan, Facile one-pot synthesis of nano-zinc hydroxide by electro-dissolution of zinc as a sacrificial anode and the application for adsorption of Th⁴⁺, U⁴⁺, and Ce⁴⁺ from aqueous solution, Res. Chem. Intermed., 42 (2016) 4077–4095.
- [30] R. Kamaraj, P. Ganesan, S. Vasudevan, Removal of lead from aqueous solutions by electrocoagulation: isotherm, kinetics and thermodynamic studies, Int. J. Environ. Sci. Technol., 12 (2015) 683–692.
- [31] R. Kamaraj, A. Pandiarajan, S. Jayakiruba, M. Naushad, S. Vasudevan, Kinetics, thermodynamics and isotherm modeling for removal of nitrate from liquids by facile one-pot electrosynthesized nano zinc hydroxide, J. Mol. Liq., 215 (2016) 204–211.
- [32] A. Pandiarajan, R. Kamaraj, S. Vasudevan, Enhanced removal of cephalosporin based antibiotics (CBA) from water by one-pot electrosynthesized Mg(OH)₂: a combined theoretical and experimental study to pilot scale, New J. Chem., 41 (2017) 4518–4530.
- [33] S. Vasudevan, J. Lakshmi, G. Sozhan, Simultaneous removal of Co, Cu, and Cr from water by electrocoagulation, Toxicol. Environ. Chem., 94 (2012) 1930–1940.

- [34] S. Vasudevan, J. Lakshmi, G. Sozhan, Electrochemically assisted coagulation for the removal of boron from water using zinc anode, *Desalination*, 310 (2013) 122–129.
- [35] S. Vasudevan, J. Lakshmi, Process conditions and kinetics for the removal of Copper from water by electrocoagulation, *Environ. Eng. Sci.*, 29 (2012) 563–572.
- [36] S. Aoudj, A. Khelifa, N. Drouiche, M. Hecini, Removal of fluoride and turbidity from semiconductor industry wastewater by combined coagulation and electroflotation, *Desal. Wat. Treat.*, 57/39 (2016) 18398–18405.
- [37] N. Boudjema, N. Abdi, H. Grib, N. Drouiched, H. Lounici, N. Mameri, Simultaneous removal of natural organic matter and turbidity from Oued El Harrach River by electrocoagulation using an experimental design approach, *Desal. Wat. Treat.*, 57/31 (2016) 14386–14395.
- [38] N. Boudjema, N. Drouiche, N. Abdi, H. Grib, H. Lounici, A. Pauss, N. Mameri, Treatment of Oued El Harrach river water by electrocoagulation noting the effect of the electric field on microorganisms, *J. Taiwan Inst. Chem. Eng.*, 45 (2014) 1564–1570.
- [39] F. Ilhan, U. Kurt, O. Apaydin, M.T. Gonullu, Treatment of leachate by electrocoagulation using aluminium and iron electrodes, *J. Hazard. Mater.*, 154 (2008) 381–389.
- [40] N. Huda, A.A.A. Raman, M.M. Bello, S. Ramesh, Electrocoagulation treatment of raw landfill leachate using iron-based electrodes: effects of process parameters and optimization, *J. Environ. Manage.*, 204 (2017) 75–81.
- [41] L. Smoczyńska, S. Kalinowska, H. Ratnaweerab, M. Kosobuckaa, M. Trifescua, K. Pieczulis-Smoczyńska, Electrocoagulation of municipal wastewater – a pilot-scale test, *Desal. Wat. Treat.*, 72 (2017) 162–168.
- [42] S.M. Wabaidur, M. Ali Khan, M.R. Siddiqui, Z.A. Allothman, S. Vasudevan, M.S. Al-Gamdi, I.H. Al-Sohami, Dodecyl sulfate chain anchored bio-char to sequester triaryl methane dyes: equilibrium, kinetics, and adsorption mechanism, *Desal. Wat. Treat.*, 67 (2017) 357–370.