

Post-treatment of secondary treated effluent by Electrocoagulation: nutrients removal and process optimization

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Abstract. The level of nutrients in the treated effluent should be maintained at a low level to mitigate the rapid algal bloom and the associated risks in the receiving water bodies. Electrocoagulation (EC) was proven to be an effective method to remove a broad range of impurities in different water matrices. This study evaluated the EC technique as a polishing step for the treated effluent targeting phosphate, nitrate, and dissolved organic matter (DOM). A factorial design was implemented to evaluate the effects of two factors (voltage, and treatment time) at three levels (high, centre, and low) on the EC process. Two electrode types (Fe and Al) performances were compared. The results revealed that both electrodes were capable of high removal of phosphate (100%) from the treated effluent within 10 minutes for both tested voltages 3 and 5 volts. However, the nitrate showed a high persistence for both electrode types and the removal never exceeded 10%. Interestingly, aluminum electrodes achieved higher removal (54.5%) of DOC compared to 25.7% by iron electrodes. The main drawback of using the iron electrode was its contribution to the original turbidity which makes it less favourable compared to the Al electrode. The results of this study revealed that the aluminum-based EC process could achieve the target level of nutrient removal without compromising the water quality.

1 Introduction

The presence of nutrients (nitrate, phosphate) in water bodies leads to environmental risks and disturbing the aquatic life. The nutrients might be generated from different sources including domestic wastewater, industrial effluent, and agriculture run-off (pesticides, fertilizers) [1, 2]. High levels of nutrients result in eutrophication conditions which affect the flora and fauna of aquatic ecosystems. Consequently, the algal blooms (massive population of microalgae species (toxic and non-toxic) will thrive rapidly leading to disturbing of the ecosystem. The algal bloom is known as a harmful algal bloom (HAB) based on the effects caused due to natural toxicity and oxygen depletion or any other negative impacts [3]. Therefore, nitrate and phosphate should be monitored regularly and their levels must comply with the standard limit to mitigate the potential risks. The World Health Organization (WHO) and the Environmental Protection Agency (EPA) put a limit on nitrate levels to be 50 mg/L and 10 mg/l respectively [1]. For the phosphate as per the European standard, it must be less than or 0.1 mg/l for discharge into moving water (River) and 0.05 mg/l for stagnated water e.g. lake.

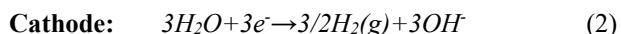
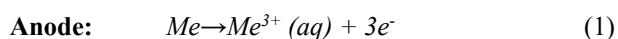
There are different techniques which were proven to be effective to reduce the level of nutrients in the water bodies including conventional chemical coagulation, reverse osmosis, precipitation, ion exchange, adsorption, electrooxidation, and electrocoagulation (EC) [2]. The electrocoagulation technique attracted the attention of many researchers due to its efficacy, simplicity, the possibility of automation, and lower production of sludge (lower by 60%) compared to the conventional chemical coagulation process. EC is capable of producing in-situ coagulant species to remove targeted impurities in a short time and lower cost [2].

The EC was well documented to successfully improve the water quality from different sources. Studies showed that EC removed 99% of phosphate from river water [2], wastewater [4-7], and simulated effluent [8]. Moreover, EC showed high removal of nitrate from groundwater [9], and also the organic matter [10].

The electrolysis cell in the EC process is composed of two electrodes (anode and cathode), an external power supply and an electrolyte. The electrodes can be from the same material or different materials. The anode and cathode can be produced from different materials such as aluminum, iron, graphite, stainless steel and titanium

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[11]. Aluminum and iron electrodes are widely used for treating different water matrices (domestic wastewater, industrial wastewater, surface water and groundwater) and were evidenced to achieve high removal of different pollutants. Stepwise reactions take place at both electrode sides (equations 1 and 2). The anode is oxidized and releases positively charged metal ions. The water is reduced at the cathode, producing oxygen and hydroxide ions. Eventually, the metallic hydroxide is produced which works effectively as a coagulant[14].



There are several factors that influence the EC process include: pH, electrode type, current intensity, exposure time, inter-electrode distance, and supporting electrolyte. The pH value controls the dominant metal species (free ions, metallic hydroxides) present in the solution based on their solubility range. For example, for aluminum electrodes, the best working pH is 4 to 7 while for iron-based electrodes the typical pH is 5 to 9 [4]. The behaviour and the removal capacity of the electrode types vary significantly depending on the targeted pollutants. For explanation, studies showed that aluminum surpassed iron electrodes in the removal of COD while both electrodes showed comparable performance in the removal of phosphate and nitrate [15]. The exposure time and the current intensity affect positively the efficiency of the EC process yet the optimization of the operating parameters is always required.

The aim of this study is to evaluate the efficiency of the EC process in the removal of the nitrate and phosphate presented in authentic treated effluent from municipal wastewater treatment plants. The optimization process is done based on 2 levels (high and low) factorial design considering the main factors: current intensity, exposure time, and electrode type in a batch reactor mode.

2 Methodologies

2.1 Sample collection and testing parameters

The authentic treated effluent samples were collected from a local municipal secondary wastewater treatment plant located in Muscat Sultanate of Oman, after chlorination before sending treated effluent (TE) to the customers. All analyses were conducted at the University of Technology and Applied Sciences Muscat. The sample was analyzed for basic parameters such as pH, EC, and TDS using a portable multi-meter electrode (RIVOSUN). The turbidity was measured using a turbidity meter (Hach, 2100 Q is). The samples were filtered and acidified prior to the analyses (phosphate, nitrate, UV254, metals) using a cellulose membrane

filter with a pore size of 0.45 μm , and a diameter 47 mm. The samples were also acidified using concentrated sulfuric acid to suppress the change in the levels of the targeted parameters and minimize error levels. The dissolved organic contents were checked by measuring UV₂₅₄ level using a Uv vis spectrophotometer (UV-1900, Shimadzu, Japan, wavelength 190-1100 nm). The phosphate and nitrate were tested using UV visible spectrophotometer under different wavelengths of 220 and 830 nm respectively. The elemental analysis was performed using atomic absorption spectrophotometer (ICE 3000 Series, Thermo Scientific, Germany).

2.2 Electrolysis cell arrangement

The electrocoagulation (EC) treatment was conducted using a batch reactor (1000 mL, glass beaker) provided with a magnetic stirrer to assure the homogeneity of the sample and maintain a continuous mixing (800 rpm) regime during the electrocoagulation process (Figure 1). Monopolar electrodes were connected vertically in either iron or aluminum for each run. The size of each electrode was 100 mm x 25 mm x 2 mm. The XRD analysis (data not presented) showed the composition of each electrode was greater than 95% of the concerned metal. The electrodes were connected in series to a power supply unit (BK Precision, 42 V, 20 A) to provide direct current and a multi-meter (AstroAI DT132A) to measure the voltage and the current. There was no supporting electrolyte used for all runs and the pH was not adjusted. After each run, the sample was allowed to settle for 10 minutes and the sample was collected from a lower outlet in the reactor (2 cm from the bottom) for further analysis. Prior to each run, the electrodes were cleaned using sandpaper and distilled water to assure the removal of the passive layer. The experiment conditions are shown in the table below (Table 1). In order to evaluate the individual and interaction influences of the tested factors A three-level factorial design with two independent factors (voltage and time) was implemented (3^2) (Table 1). For each factor three levels were tested: high, centre and low and encoded as +1, 0- and -1 respectively. The distance between the electrodes was fixed to be 1 cm. The selected voltages: 1, 3 and 5 volts, whereas the selected times: 5, 15 and 30 minutes.

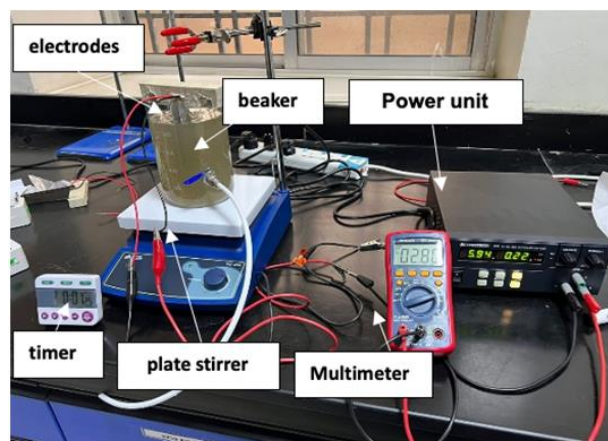


Fig. 1. Electrocoagulation setup (batch reactor, power supply, electrical connection, multimeter, magnetic stirrer plate)

Table 1. Experimental Conditions factorial design 3²(three levels (high +1, centre 0, low -1) and two factors (voltage and time).

Experiment	level	
	Voltage, V	Time, min
1	+1	+1
2	+1	0
3	+1	-1
4	0	+1
5	0	0
6	0	-1
7	-1	+1
8	-1	0
9	-1	-1

2.3 Characteristics of the treated effluent

The characteristics of the treated effluent are shown in Table 2.

Table 2: Characteristics of treated effluent from domestic wastewater treatment Plant

Parameter	Units	value
pH	pH_unit	7.7
Biochemical Oxygen Demand (BOD ₅)	mg/L	2.4
Chemical oxygen demand (COD)	mg/L	16.3
Total Suspended Solids (TSS)	mg/L	1.6
Phosphorus Total as P	mg/L	3.3
TKN	mg/L	1.1
Nitrate as NO ₃	mg/L	27.9

Electrical Conductivity (EC)	mS/cm	4.264
Aluminium as Al	ug/L	30.0
Calcium as Ca	mg/L	95.6
Magnesium as Mg	mg/L	63.1
Sodium as Na	mg/L	603.0
Orthophosphate, PO ₄ ³⁻	mg/L	3.2
Organic Nitrogen	mg/L	1.9
Total Nitrogen	mg/L	9.7
UV ₂₅₄	cm-1	0.1
Total dissolved solids (TDS)	g/L	2.125
Turbidity	NTU	<1

3 Results and Discussions

3.1 Basic parameters removals:

Different parameters were checked to evaluate the efficiency of each electrode at different experimental conditions. In particular, the pH of the raw sample was 7.7 and showed slight changes during the course of the experiments for both electrode types (Figure 2). The evolution of the pH was expected due to the production of the hydroxyl ions (eq 2 above) during water reduction at the cathode which was reported in a previous study [16]. The discrepancy might occur due to the differences in the type of used water in this study an authentic raw sample was used compared to a synthetic one in the previous study. Most of the screened studies focused on the effect of pH values rather than the evolution of pH [2,3,11,14].

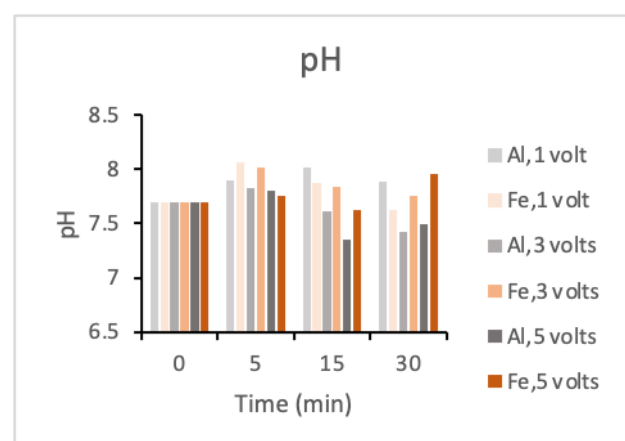


Fig. 2. pH values for aluminum and iron electrodes, different volts treatment 1,3, and 5 volts, at different times: 5, 15 and 30 min.

Turbidity was tested and found to increase drastically (183 NTU, 5 volts, 15 minutes) when the iron electrode was used while the increment was insignificant with the aluminum electrode (Figure 3). As per Omani standards for the reuse/discharge of TE, the maximum allowable turbidity value is 5 NTU [17]. That might be explained

by the presence of the iron nanoparticles in suspension which can't be removed by natural settling (preliminary runs revealed that a settling time of 60 minutes had no significant effect). It was reported in a previous study that iron electrodes generated higher amount of loosely small particles (0.2 to 0.6 μm) compared to 1.7 to 2 μm of aluminum electrodes [7]. The main concern here is that the discharged water with high turbidity will lead to hindering light penetration through the water surface affecting the photosynthetic process. That eventually will deteriorate the ecosystem. It is also aesthetically not acceptable and restricts human activities. Unfortunately, most of the previous studies overlooked this fact and focused only on the removal of the targeted compounds [12,13]. Therefore, more in-depth investigation is required to rule out the effects of iron nanoparticles and it is suggested that a hybrid process be implemented when EC with the iron electrode is used. The enhancement might include using an adsorbent or combined coagulation process (chemical and EC).

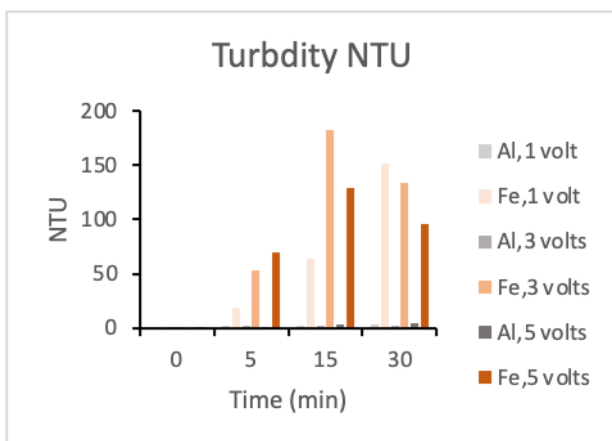


Fig. 3. Turbidity values for aluminum and iron electrodes, different volts treatment 1,3, and 5 volts, at different times:5,15 and 30 min.

TDS and EC levels of the tested samples showed a consistent trend for both aluminum and iron electrodes at different time intervals (Figures 4& 5). At low voltage (1 volt) and low and center time (5 and 15 min), the TDS and EC values increased. On the other side, at higher time (30 min) and higher voltage (5 volts), reductions in TDS and EC levels were observed. That might be attributed to the presence of more soluble metal species within the solubility limits at low voltage. However, at high voltage the generation of metal species will be very high and exceed the solubility limits of the concerned metals therefore it will be precipitated eventually [7]. As per Omani standards for TE reuse/discharge the acceptable limit for TDS and EC are 1.5 to 2 g/L and 2 to 2.7 mS/cm[17].

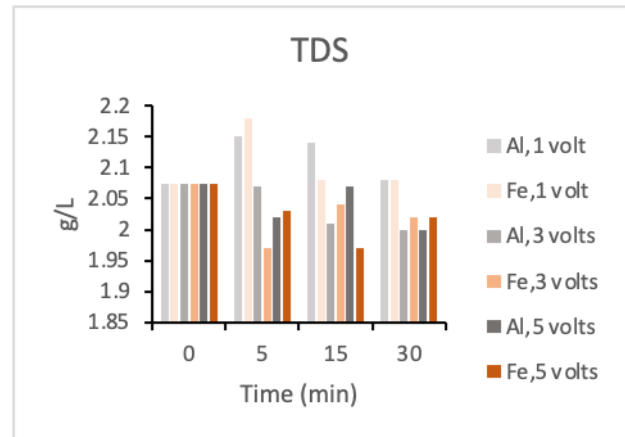


Fig. 4. TDS values (g/L) for aluminum and iron electrodes, different volts treatment 1,3, and 5 volts, at different times:5,15 and 30 min.

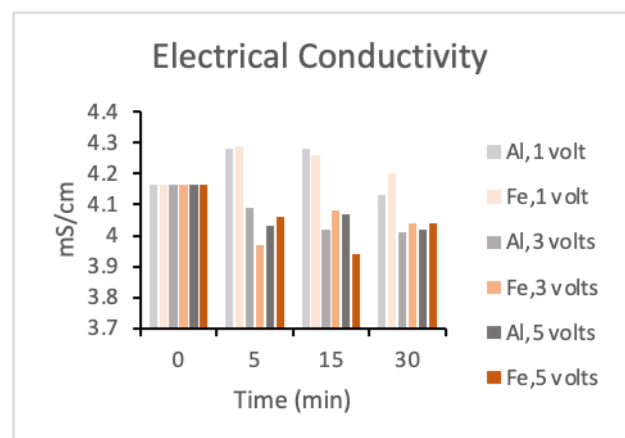


Fig. 5. Electrical conductivity values (mS/cm) for aluminum and iron electrodes, different volts treatment 1,3, and 5 volts, at different times:5,15 and 30 min

3.2 Nutrients Removal

Nutrient removal was explored in this research targeting phosphorus and nitrate. Unfortunately, both electrodes showed insignificant removal of nitrate achieving 4.7% and 7% using iron and aluminum electrodes respectively (5 volts, 30 minutes) (Figure 6). Studies showed that nitrate is removed more efficiently at lower pH values (4) as it is involved in nitrate reduction into ammonium[1, 16]. In a previous study [15], using synthetic water with an initial nitrate concentration of 100 mg/L, results revealed that aluminum electrodes showed better performance (50% of removal) than iron electrodes (25% of removal). In this study, at low voltage (1 and 3 V) and shorter time negative values of removal were observed (most likely due to hydrolysis of organic nitrogen). These findings came in line with an earlier study conducted by [6,7].

The acceptable levels of nitrate in the discharged water set by the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA) are 50 mg/L and 10 mg/L respectively [5].

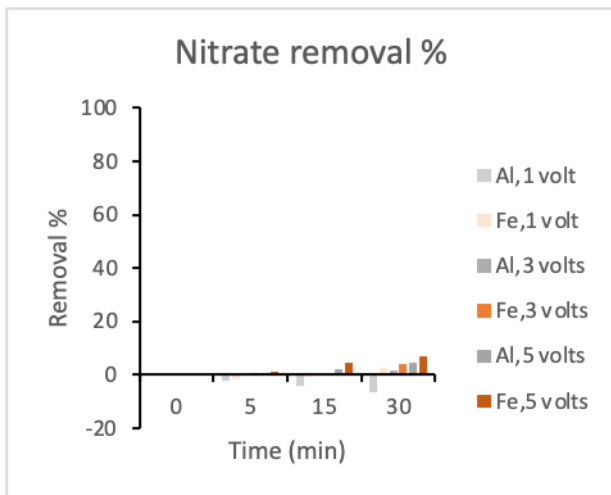


Fig. 6. Nitrate removal percentages for aluminum and iron electrodes, different volts treatment 1,3, and 5 volts, at different times: 5,15 and 30 min

In contrast, both electrodes showed high removal of phosphate achieving nearly 100% at a high voltage of 5 Volts within 5 minutes (Figure 7). In a previous study, phosphate removal from lake water was 99% using aluminum electrodes within 60 minutes and the current density was 6 mA/cm² [2]. The removal of phosphate was suggested to be achieved by metal complexation or adsorption into the formed metal hydroxide species. Indeed, the formed flocs of iron hydroxide and aluminum hydroxide during the EC process are classified as strong adsorbents for phosphate ions[19]. The EPA set the discharge limit for phosphate to be 0.05 and 0.1 mg/L for lakes (stagnated water) and rivers (running water) respectively [5].

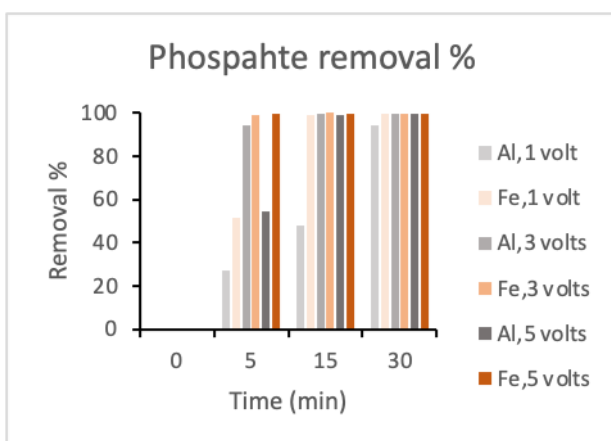


Figure 7: Phosphorus removal percentages for aluminum and iron electrodes, different volts treatment 1,3, and 5 volts, at different times: 5,15 and 30 min

UV₂₅₄ is used as an indicator for the presence or absence of dissolved organic matter in the water. The results from this project revealed that the aluminum electrode surpassed iron electrodes in the removal of UV₂₅₄. At 30

minutes with a voltage of 5, the Al electrode removed 54 % of UV₂₅₄ compared to 24% by the iron electrode under the same conditions. These findings disagreed with other findings and showed that iron electrodes surpassed aluminum electrodes in the removal of COD with obtained removal of 90 % of COD respectively [18,19]. The removal of dissolved organic matter is of importance as it might lead to the formation of by-products such as Trihalomethane when chlorine is used as a disinfectant.

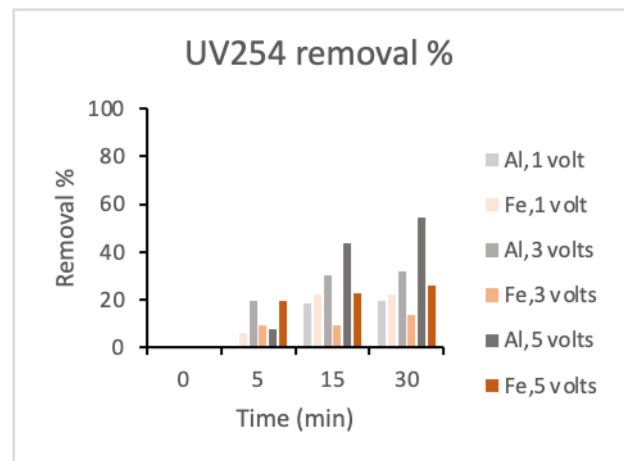


Figure 8:UV₂₅₄ removal percentages for aluminum and iron electrodes, different volts treatment 1,3, and 5 volts, at different times: 5,15 and 30 min

4 Conclusions and Recommendations

This work evaluated the EC process for the removal of nutrients and dissolved organic matter from treated effluent using aluminum and iron electrodes. The effects of time and voltage were evaluated under three different levels. The results revealed that both electrodes could achieve high removal of phosphate reaching 100% while the removal of nitrate was less than 10%. For the dissolved organic matter, aluminum electrodes showed an outstanding performance of 54% removal compared to 25% using iron electrodes. The level of turbidity was observed and showed increment after EC using iron electrodes due to the presence of iron nanoparticles in the treated water. Always it is recommended to tackle turbidity levels whenever iron EC is involved and enhancing steps must be considered. This study concluded that using aluminum electrodes in the EC process could achieve the target levels of nutrient removals without compromising the treating water quality. This study is believed to pave the way for more in-depth analyses toward full-scale application. Investigating the removal mechanisms, effects of pH and inter-electrodes distance, using supporting electrolytes might need to be studied in the future.

5 References

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