CHEMICAL ENGINEERING TRANSACTIONS

VOL. 94, 2022

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Petar S. Varbanov, Yee Van Fan, Jiří J. Klemeš, Sandro Nižetić

ISBN 978-88-95608-93-8; **ISSN** 2283-9216

DOI: 10.3303/CET2294130

Electrocoagulation Treatment of Wastewater: A Pareto Frontier Identification Based on the Total Dissolved Solids and Cost

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In this research, a case study is presented for the electrocoagulation treatment of wastewater produced in a drilling oil site. The process variables of the electrolysis time and current density were investigated with the response parameters of total dissolved solids (TDS) and energy consumption. A process integration to identify the Pareto front is designed with respect to the removal of TDS and its respective electricity cost using the global solver of the LINGO 18.0 software. An essential equation generated by the response surface methodology is used in conjunction with the cost equation based on the consumption of energy in the aspect of electrocoagulation. Results in the identification of the Pareto front show a maximum TDS removal of 71.4 % with a corresponding electricity cost of 8.41 USD/m^3 under the conditions of 2 min (electrolysis time) and 140.4 mA/cm^2 (current density). On the other hand, the minimum cost resulted in 0.53 USD/m^3 which corresponds to a TDS removal of 29.2 % under the conditions of 0.5 min (electrolysis time) and 35.1 mA/cm^2 (current density). This study has established an appropriate trade-off between the TDS removal and electricity cost by producing the Pareto optimal curve. Hence, this can enable an appropriate decision-making strategy for the stakeholders for future applications in the electrocoagulation method.

1. Introduction

Water pollution is a serious threat to the environment causing tremendous stress to aquatic organisms. The wide variety of industries and the presence of various constituents in the wastewater is a challenge that requires expert application of technologies to reduce or eliminate the constituents that could pose serious and lasting damage to the ecosystem. AlJaberi et al. (2020) studied oily wastewater which is a result of oil drilling, petroleum refining, or petrochemical processing. This specific type of wastewater contains various pollutants such as organic hydrocarbons and inorganic compounds (chlorides, cyanide, ammonia, heavy metals, TDS, TSS, TOC). The concentration of these components of oily wastewater depends on the location of the well, the depth of the source, or the processing technique applied.

In the case of industrial effluents containing high total dissolved solids (TDS) various treatment techniques are available such as dewatering and gravity sedimentation. The biological treatment step is however inefficient because of high saline concentration of wastewater (> 1%) which results in a reduction of cell viability. An alternative technique is to apply electrochemical techniques such as electrocoagulation, electro-Fenton, and electro-oxidation.

Electrocoagulation has several advantages such as less reaction time, simple apparatus, low consumption of energy and electrodes, and active components come from the electrodes, therefore, does not require the addition of chemicals during treatment. This technique could also be combined with other wastewater treatments as a pre-treatment to adsorption or ion-exchange. The flexibility of this technique is very attractive owing to its simplicity and cost-effectiveness.

In electrocoagulation, the electric current applied to the electrode causes redox processes that provide the active components required in the removal of oil and other wastewater pollutants. The advantage of electrocoagulation is that the electrodes are the source of the metal cations such as Al^{3+} and Fe^{2+} that are necessary in the coagulation process. In the anode, Al^{3+} and Fe^{2+} are released from the metal matrix during oxidation. In the

Paper Received: 12 April 2022; Revised: 07 May 2022; Accepted: 14 May 2022
Please cite this article as: Ortenero J.R., Choi A.E.S., 2022, Electrocoagulation Treatment of Wastewater: A Pareto Frontier Identification Based on the Total Dissolved Solids and Cost, Chemical Engineering Transactions, 94, 781-786 DOI:10.3303/CET2294130

cathode, the reduction of water molecules to hydrogen gas and hydroxyl ions provides the necessary chemical species for the formation of electrocoagulants such as $Al(OH)_3$.

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^- \quad (1)$$

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

$$Al^{3+} + 3OH^- \leftrightarrow Al(OH)_3 \quad (3)$$

The hydrogen gas evolved from the cathode during the reduction process causes bubbles that carry dissolved and suspended particulate matters in the wastewater. The electrocoagulants $Al(OH)_3$ and $Fe(OH)_3$ produced from the metal ions and hydroxide ions cause the agglomerization of the particles in the wastewater and the hydrogen bubbles generated during the redox process carry it to the surface where it can be subsequently removed. The electrocoagulants are more effective than the chemical coagulants due to larger size, hence, different physico-chemical activity toward pollutants.

There are various configurations and designs for an electrocoagulation set-up, which depends on the mode of operation (batch or continuous), the applied current (AC/DC), the type of electrodes used, and other components of the electrocoagulation chamber. AlJaberi et al. (2020) employed the design consisting of three aluminum tubes arranged concentrically (monopolar and parallel). The inner and outer tubes served as the anode and the middle tube as the cathode.

AlJaberi et al. (2020) treated oily wastewater from crude oil drilled from a certain well in Basra, Iraq. This research has analyzed the effect of applied current and reaction time on the % removal of high saline oily wastewater with the following initial concentration: 113,400 ppm TDS; 65,623 ppm TSS; 477 ppm HCO_3^-; 102,000 ppm Cl^-; 5,600 ppm Ca^{2+}. The typical design of the experiment is conducting a parametric screening analysis followed by the response surface methodology (RSM) (Choi et al., 2021b). The aforementioned study employed only the RSM for the optimization of a response variable concerning the TDS removal. The weakness of RSM is the presence of multiple local optimums, hence, further analysis of data is necessary (See et al., 2022). In addition, operational cost (energy consumption) was not discussed, which could affect the cost-competitiveness of the technology. This is essential in analyzing multiple criteria that affect environmental and economic factors (Ortenero and Tan, 2021).

This paper expounds on the result of AlJaberi et al. (2020) by utilizing the concept of the Pareto front to properly identify a set of compromise solutions based on the TDS removal and the cost of operation. The energy consumption of the electrochemical oxidation process was determined as the basis for the operation cost. Specifically, the RSM model equation was utilized as a part of the objective function.

2. Methodology

2.1 Summarized experimental method

AlJaberi et al. (2020) performed the experiment for the batch electrocoagulation of saline oily wastewater sourced from a certain drilling site in Iraq. The methodology is summarized as follows. Before the electrocoagulation process, the samples were preserved in polypropylene containers where the temperature was maintained at 4 ºC. The electrocoagulation reactor was made of three concentric aluminum tubes (monopolar and parallel), the inner and outer tube served as the anode and outer tube as cathode, with an effective area of 285 cm^2. The tubes were immersed at a depth of 4 cm. The reactor was connected to a power supply operated at potentiostatic mode whereby voltage was fixed and the current was varied at predetermined values. The DC power supply had a capacity of 0 V to 30 V and 0 A to 5 A manufactured by SHADGONG company, China (model 305D). The electromagnetic stirrer (ALFA: HS-860, 0 rpm to 1,000 rpm) was used to homogenize the solution during the electrocoagulation treatment at an agitation speed of 200 rpm.

During the electrocoagulation treatment, sample of the saline oily wastewater was poured on the reactor. The depth of immersed electrode was maintained at 4 cm. An electromagnetic stirrer was used to maintain uniformity of the solution. The initial composition of the solution was measured in terms of HCO_3^-, Cl^-, and Ca^{2+} content, and the TDS concentration. The applied current from a DC supply was applied to the solution for a certain period and the corresponding composition of the solution in terms of HCO_3^-, Cl^-, and Ca^{2+} content, and the TDS concentration was again measured to quantify the effectiveness of the treatment in terms of the % reduction of these constituents in the solution. The applied current was varied from 0.5 A to 2.0 A and the electrocoagulation time from 10 min to 40 min to determine the optimum condition. The generated TDS equation from the central composite design (CCD) under the RSM was used for the case study of this research.

2.2 Pareto front identification method

This case study uses concept of the Pareto analysis to identify probable compromise parametric conditions of the TDS removal and electricity cost. Table 1 lists the process variables (time and applied current) and the cost of the energy consumed in the electrocoagulation treatment. Lingo 18.0 (Lindo Systems, Chicago, IL, USA) was utilized to determine the Pareto front. The software selected the global optimizer subjected to non-linear programming.

Table 1: Factors for consideration

Factors	Units	Value
Time	min	0.5 to 2.0
Applied current	A	10 to 40
Energy consumption cost	USD/kWh	0.21

The Pareto frontier analysis is applied in the decision-making strategies to identify appropriate courses that incur a significant overall impact upon cases of numerous opposing feasible solutions (Pirouzan et al., 2014). The method of a Pareto front identification was used due to the ability in determining the initial optimum solutions with various weights on its objective function (Aviso et al., 2010). The methodology was utilized to identify a specific range for the TDS removal (Y: %) and electricity cost (C: USD/m^3) by its incurring energy consumption. Eq(4) pertains to the initial objective function based on the variables of time (X_1: min) and applied current (X_2: A). The parameter Y is first maximized to simultaneously identify the upper limit of the TDS removal as well as its corresponding cost. Conversely, the subsequent parameter in Eq(5) is minimized to appropriately identify the lower limit of both cost and TDS removal.

$$Y = 24.18 - 7.574X_1 + 0.648X_2 + 3.596X_1^2 + 0.0138X_2^2 - 0.0004X_1X_2 \quad (4)$$

$$C = e \cdot E_C \quad (5)$$

Eq(6) to Eq(8) are the corresponding constraints subjected towards the objective functions to identify the boundary limits for the Pareto front. Eq(6) is the constraint of the energy consumption (E_C: kWh/m^3) that correlates the total electricity cost of the electrocoagulation process with respect to time (t: h), applied current (I: A), voltage (V: V), and volume (v: m^3). Finally, Eq(7) and Eq(8) show the constraint for the feasible regions of time and applied current, towards the response parameter of TDS removal.

$$E_C = (V \cdot I \cdot t)/(60 \cdot v) \quad (6)$$

$$0.5 \leq X_1 \leq 2.0 \quad (7)$$

$$10 \leq X_2 \leq 40 \quad (8)$$

3. Results and discussion

3.1 Analysis of TDS removal and electricity cost at the time of electrolysis

The removal of TDS from the oily wastewater is affected by the formation of bubble generated at the cathode (Muhammad Niza et al., 2021). It can be observed from Figure 1a that there is a drop in the % removal of TDS during the initial stage of electrocoagulation. It can be explained by the reduction in the electrodeposition of dissolved salts on the surface of the cathode as the bubbles generated on the cathode surface form a film that blocks this surface from deposition of ions (Iwata et al., 2021). However, as the electrodeposition time increases and as the current density is increased smaller bubbles are formed rapidly which aid in better TDS removal. The TDS removal increased from 46.1 % at 0.5 min to just 48.2 % at 2 min of electrocoagulation. This is a negligible increase in the TDS removal compared with the TSS removal. The energy consumption on the other hand linearly increases from 6.3 kWh/m^3 to 25 kWh/m^3 which is a 297 % increase in energy consumption and turn translates to the similar percentage increase in electricity cost. The negligible change in TDS removal within this period is not enough to substantiate the corresponding increased cost. It is therefore cost-effective to carry out the electrocoagulation time near the lower end of the range to avoid excessive electricity consumption.

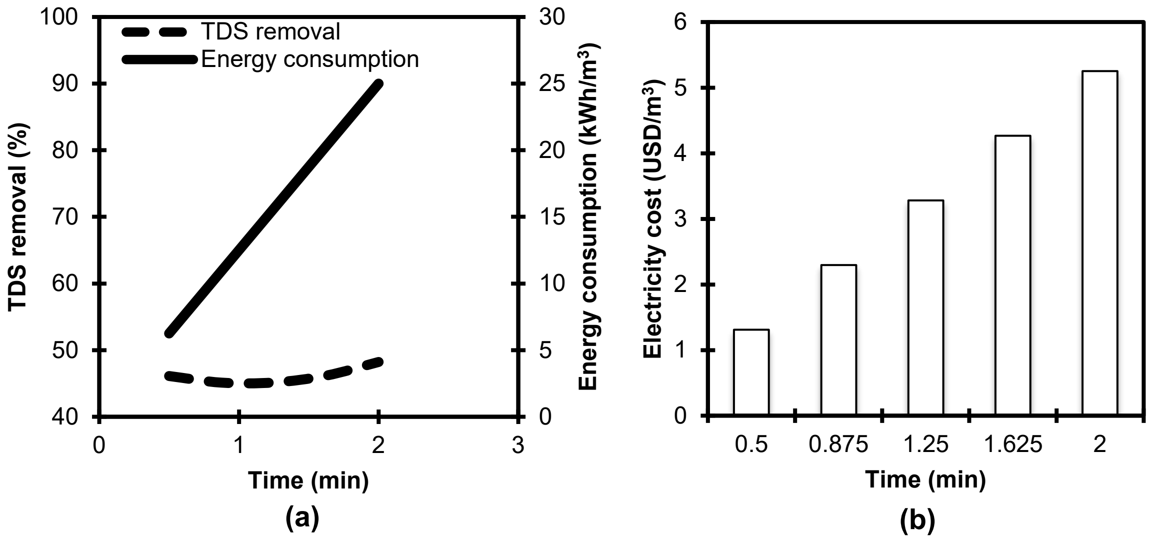

Figure 1: Process variable analyses of reaction time towards (a) TDS removal, energy consumption, and (b) total operating cost in an electrochemical system

3.2 Analysis of TDS removal and electricity cost on the current

The applied current density is important in generating the required aluminium ion and iron ion on the anode for the generation of electro-coagulants $Al(OH)_3$ and $Fe(OH)_3$. The reduction of water to form hydrogen gas at the cathode is equally important as it carries the flocs generated from the coagulants and pollutants to the surface of the solution. As current density is increased, more electrons and ions are driven at the surface of the electrodes which increases the rate of formation of the Al^{3+}, Fe^{3+} and H_2 gas.

This can be observed in Figure 2a where an increase in current density allows faster deposition of dissolved salts on the surface of electrodes and the generation of the coagulant precursors which translate to an increase in % TDS removal.

The % TDS removal increased from 28.2 % at 35.1 mA/cm^2 to 68.3 % at 140.4 mA/cm^2 which is a 142 % increase in removal efficiency. There is a non-linear relationship between the % TDS removal and applied current density as shown by the dashed line. This non-linearity is due to bubble film forming on the surface of the cathode as it slightly affected the deposition of dissolved salts and the liberation of the precursor metal ions for coagulation (Iwata et al., 2021). However, the electric current density is a more dominant variable in TDS removal as shown by the steepness of the curve compared with the electrolysis time within the intervals considered.

The increase in applied current density caused a linear increase in energy consumption per cubic meter of the solution as shown by the solid curve in Figure 3a. There is a corresponding 297 % increase in energy consumption from 6.3 kWh/m^3 to 25 kWh/m^3 within the interval of 35.1 mA/cm^2 to 140.4 mA/cm^2. This energy consumption is substantiated by the corresponding improvement in TDS removal from 28.2 % to 68.3 %. The total operating cost similarly increased linearly from 1.31 USD/m^3 to 5.25 USD/m^3 which is a 300 % increase in electricity consumption cost.

Further increase in applied current density will yield a further increase in TDS removal following the trend in the curve, however, it should be considered if a linear increase in electricity cost yields a diminishing effect on the TDS removal or other parameters because it will have a commanding effect on the overall cost-effectiveness of the technology.

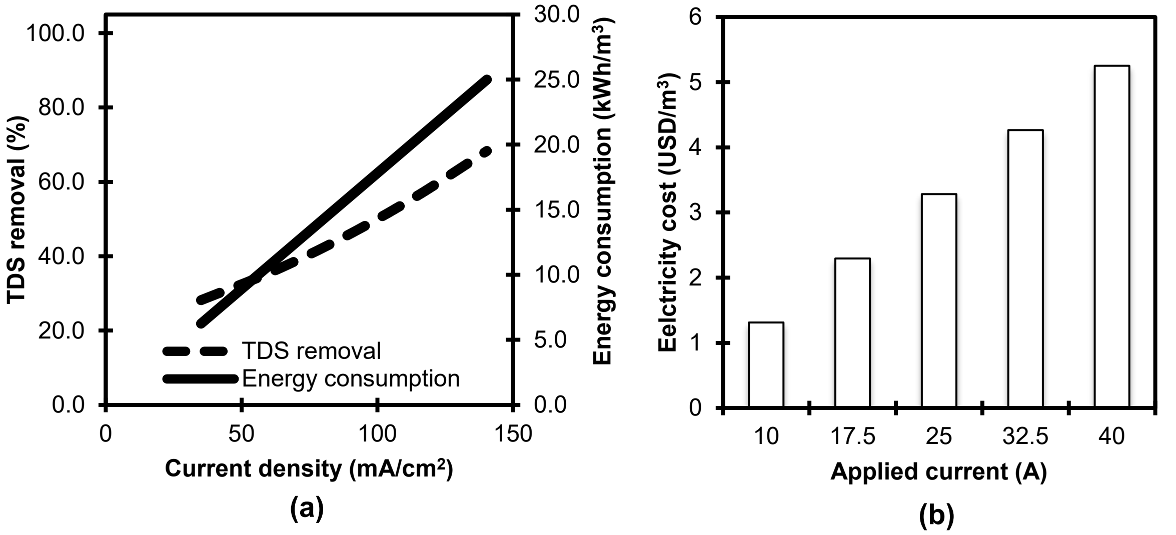

Figure 2: Process variable analyses of amplitude towards: (a) TDS removal, energy consumption, and (b) total operating cost in an electrochemical system

3.3 Pareto frontier based on TDS removal and operating cost

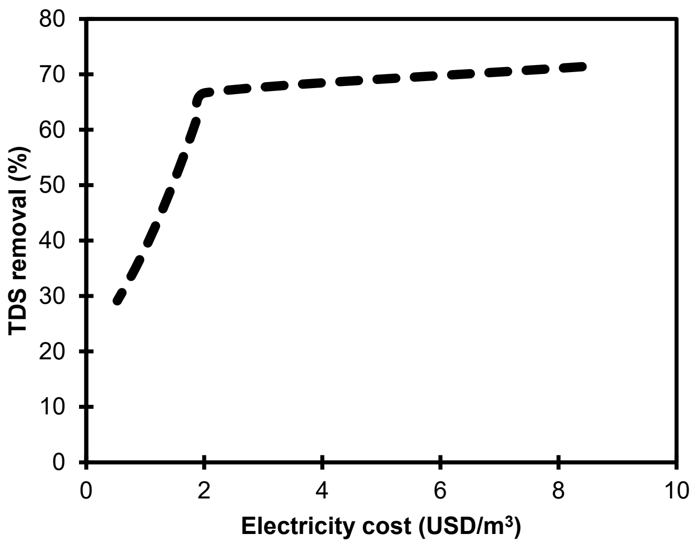

Figure 3: Identified Pareto front of TDS removal and electricity cost

The determination of limits is vital to identify the suitable boundary limits of the Pareto front in the removal of the TDS and the total electricity cost in the system of the electrocoagulation treatment. For the processing system, the ensuing results are based on the concurrent application of the cost equation and the generated CCD equation. In the case study of this research, non-linear model equations were employed that can produce multiple local optimum solutions. Therefore, a global optimum solver was applied utilizing the Lingo software to research a global optimum result to generate the Pareto front curve (Choi et al., 2021a).

The upper boundary limits based on the global optimum solver for the electrocoagulation system resulted in the subsequent maximization of the TDS removal as the objective function. This led to the following operating condition of 2 min (electrolysis time) and 140.4 mA/cm^2 (current density). On the other hand, the lower boundary conditions have led to 0.5 min (electrolysis time) and 35.1 mA/cm^2 (current density). The identified Pareto front for the TDS removal is from 29.2 % to 71.4 %, while the electricity cost is from 0.53 USD/m^3 to 8.41 USD/m^3.

From a graphical point of view, the curve for the Pareto front can be concisely depicted by its appropriate boundary limits in Figure 3. The trend for the TDS removal is observed to increase with its corresponding electricity cost. The implication of the figure suggests that intensive conditions in the process variables are needed to sufficiently remove the TDS in the electrocoagulation system. This is consistently observed in the study of Hansen et al. (2019) which shows a higher energy requirement as a higher contaminant dosage is removed in the electrochemical oxidation treatment process. Moreover, incurring more associated costing interprets towards the need of a higher operating conditions. This can then directly contribute to added expenses with regard to the energy requirement that fundamentally enhances the elimination of TDS.

4. Conclusions

The research done in this case study integrates the cost criteria in conjunction with the generated CCD model equation in the aspect of TDS removal for the electrocoagulation treatment process. Upon the analysis of the TDS removal, it was observed that the highest removal based on the process variable of electrolysis time are in its upper and lower bound. For the process variable of applied current, it was observed that the upper limit reached the highest TDS removal. On the other hand, the cost criteria were seen to be at its most expensive at the upper levels of the process variables. The identification of the Pareto front can aid in the decision-making process based on a systematic method that simultaneously consider the TDS removal and its corresponding electricity cost by utilizing the variables of electrolysis time and applied current. Based on the identification of the Pareto front, the ranges for the TDS removal and electricity cost are from 29.2 % to 71.4 % and from 0.53 USD/m^3 to 8.41 USD/m^3. The results of this study have generated a feasible range useful for an adequate criterion to indicate a proper decision-making analysis. This is beneficial as to permit a more quantifiable basis to select a proper preference criterion in the electrocoagulation process. This case study has effectively shown favorable results that can be further supplemented for its environmental applications in future works based on its process system. To be specific, a fuzzy optimization analysis is the suggested approach for the decision analysis in arriving with a plausible compromise solution essential for stakeholders.

Nomenclature

Y – TDS, %
X_1 – time, min
X_2 – applied current, A
C – cost, USD/m^3
e – electricity price, USD/kWh
E_C – energy consumption, kWh/m^3
V – average voltage, V
I – applied current, A
t – duration of the treatment process, h
v – total volume, L

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