



Treatment of whey wastewater by electrocoagulation and electro-Fenton methods in batch mode

Umran Tezcan Un^{a,*}, Ayse Kandemir^b

^aDepartment of Environmental Engineering, Anadolu University, Eskisehir 26555, Turkey, Tel. +90 222 321 35 50 Ext. 6418; Fax. +90 222 323 95 01, email: utezcan@anadolu.edu.tr

^bGraduate School of Science, Anadolu University, Eskisehir 26555, Turkey, email: ayse.kandemir@hotmail.com

Received 3 May 2017; Accepted 26 September 2017

ABSTRACT

In the present study, real cheese whey wastewater was treated using a uniquely designed batch-type electrocoagulation reactor with a horizontal rotating screw type iron anode. The treatment efficiency and energy consumption under different operational conditions including current density (30, 35 and 40 mA/cm²), initial pH (3, 5, 7 and 9), supporting electrolyte type and concentration (NaNO₃, KNO₃, KCl, NaCl, Na₂SO₄ and K₂SO₄ at 0.1, 0.15 and 0.20 M) were investigated. The effect of electro-Fenton by addition of hydrogen peroxide (0.05, 0.10 and 0.20 M) was also determined. The best performing operating condition was obtained at pH 3 and current density of 40 mA/cm² with the addition of 0.20 M Na₂SO₄ and 0.20 M H₂O₂. The initial chemical oxygen demand (COD) concentration of 15,500 mg/L was reduced to 1,408 mg/L with the removal efficiency of 90.92% after 90 min of the reaction demanding 10.60 kWh per kg of removed COD. In addition, the sludge obtained after electrocoagulation was analyzed to determine its characteristics using X-ray diffraction and X-ray fluorescence. It was revealed that hematite (Fe₂O₃) and magnetite (FeO.Fe₂O₃) phases were present in the dried sludge. It is concluded that the proposed configuration can be applied as an effective pretreatment step for the treatment of cheese whey wastewater and the obtained sludge can be used as an iron source in other applications.

Keywords: Whey wastewater; Electrocoagulation; Iron electrode; Batch-type reactor; Electro-Fenton

1. Introduction

The dairy industry is known to produce highly polluted wastewater with a high biological oxygen demand and chemical oxygen demand (COD). In Turkey, the permitted COD limit to the surface waters for the dairy industry is 170 mg/L. These effluent standards often require removal efficiencies of more than 95% of COD. Some researchers studied the possibility of recycling and reusing it [1]. Biological aerobic and anaerobic methods with differences in design regarding reactor type, number of stages or contact type has been studied and used for decades [2,3]. Membrane technology, which come in different pore size ranges and designs are very promising, since product recovery is feasible and produces

effluent with high quality specifications suitable for direct reuse [4]. Physical and chemical treatment processes, such as coagulation/flocculation and adsorption, are being applied for the removal of suspended, colloidal and dissolved constituents [5]. Coagulation causes the combining of insoluble particles and/or dissolved organic matter into large aggregates, thereby facilitating their removal in subsequent sedimentation, floatation and filtration stages [6,7].

Electrocoagulation (EC) technique has been used successfully to treat wastewater of various industries such as metal plating [8,9], baker's yeast [10], paper industry [11], olive mill [5] and dye industry [12]. Effective removal of specific elements like boron and fluoride [13,14] and municipal effluents treatment are also reported [15]. EC is the in situ generation of M³⁺ ions into wastewater using sacrificial anodes, with hydrogen gas and (OH)⁻ ions produced at the cathode. A further reaction between M³⁺_(aq)

* Corresponding author.

and OH⁻ ions produces amorphous M(OH)₃ flocs that are capable of adsorbing soluble organic compounds and trapping colloidal particles. The further polymerization of these flocs to M_n(OH)_{3n} allows for easy settling of the flocs from wastewater by sedimentation or/and flotation by hydrogen gas [16]. The main reactions during EC are as follows:

Anode reaction:



Basic condition:



Acidic condition:



Oxygen synthesise:



Cathode reaction:



Fenton-based processes are among advanced oxidation processes. In the electro-Fenton method, (·OH) radicals are produced in the bulk of the solution from the reaction H₂O₂ and Fe²⁺ (Eq. (6)) [17]. This reaction is propagated from ferrous ion regeneration, mainly by the reduction of the produced ferric species with hydrogen peroxide (Eq. (7)). As a result, an improvement in EC performance will occur due to a higher production rate of hydroxyl radicals, which are actually the main oxidizing agent facilitating oxidation of organic material.



Güven et al. [18] studied electrochemical treatment of deproteinated whey in batch mode and reported COD removal of 53.32% at 8 h. Valente et al. [19] used iron electrodes in EC treatment of dairy wastewater and obtained 58% COD abatement. Kushwaha et al. [20] used an aluminum electrode in a similar work. EC of yogurt industry wastewater and use of sludge in ceramic pigment production was also studied in our previous work [21]. Aitbara et al. [22] studied continuous mode treatment of dairy wastewater using EC and reported 90% COD removal. Literature do not conform on ranges of effective factors on EC especially for current density (CD) and supportive electrolytes probably because in many of the works synthetic wastewater with variable initial COD concentrations has been used. Although there are many publications on EC application for dairy wastewater treatment, they failed to examine a different electrode configuration. To the extent of our knowledge, no publication reported energy consumption of EC for real dairy wastewater.

We assessed the effect of different factors including CD, initial pH, supporting electrolyte type and concentration and electro-Fenton method on EC treatment of real cheese whey wastewater. A uniquely designed horizontal rotating screw type iron anode was used in batch mode. We preferred iron because of its better performance characteristics regarding removal efficiency [23] and also its lower price than aluminum and easier manufacturing. This paper reports significant outcomes of the configuration and evaluates the effect of operating factors on removal efficiency and energy consumption of the process.

2. Materials and methods

2.1. Wastewater

Cheese whey wastewater used in the experiments was obtained from a small production facility located in Eskisehir, Turkey. This small plant produces white cheese. A coarse screening process separates cheese whey from cheese curds. The separated cheese whey mixes up with processed water prior to the treatment plant. Our samples were collected from the mixing point. The wastewater properties are given in Table 1.

2.2. Experimental details

A uniquely designed batch-type EC reactor implemented. The design included a horizontal rotating screw type iron anode (Fig. 1(a)). Reactor vessel was the iron cathode with a U-shaped cross-section. Its dimension was 20 cm length and 50 cm² cross-sectional area, providing 1,000 cm³ volume. The screw type anode had a horizontal rotating shaft and impellers with a surface area of 350 cm². The horizontal screw type anode was placed 1 cm above the cathode bottom and submerged into the wastewater. The experimental setup is shown in Fig. 1(b). Reactor operated in batch mode. The pH and the conductivity were monitored during EC using a pH meter (Hanna Instruments 301, USA) and a conductivity meter (Radiometer Pioneer 30). The samples were taken periodically and centrifuged (EBA 20; Hettich, Germany). The supernatant was analyzed for the determination of COD.

The calculation of COD removal efficiency after EC was performed using following equation:

$$\text{RE}(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (8)$$

where C₀ and C_t are the concentrations of COD before and after EC in mg/L, respectively.

Table 1
Characteristics of wastewater

COD, mg/L	15,500
Conductivity, mS/cm	17.0
pH	5.2

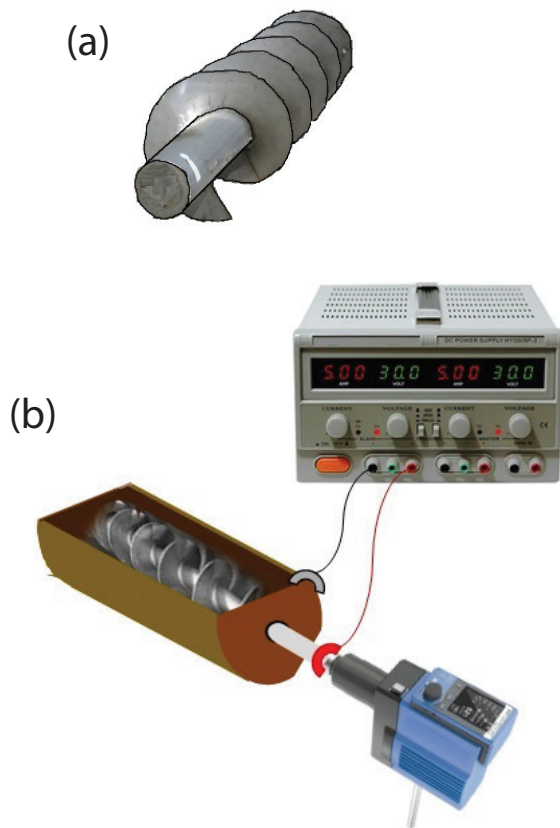


Fig. 1. (a) Rotating screw type iron anode and (b) experimental batch type EC reactor setup.

2.3. Analytical procedure

Samples were digested by means of a COD digestion reagent (Hach) then COD was determined titrimetrically. All the analyses were conducted twice. The electrodes were polished and then washed with dilute H_2SO_4 and rinsed with distilled water before each run following the same procedure in our previous work [21].

After EC, the bulk containing sludge and treated wastewater was poured into a glass column to settle the sludge, and left for 24 h. The sludge was separated from the treated wastewater by discarding the supernatant. Then the sludge was dried in a drying oven (Model FN 120; Nuve, Turkey) at $100^\circ C$ for 24 h to eliminate its moisture until no moisture remained. Careful sampling and homogenizing were employed to assure a reasonable consistency in the sludge. The chemical composition of the sludge was determined using an X-ray fluorescence spectrometer (XRF; Rigaku, Rix 2000, Japan). The phases present in the sludge were determined using an X-ray diffractometer (XRD; Rigaku, D/Max-IIIC, Japan) with Ni-filtered, $Cu K_\alpha$ radiation with a goniometer speed of $1 s^{-1}$.

3. Results and discussion

3.1. The effects of current density

The effect of CD was investigated by conducting the EC of cheese whey wastewater. Current densities of 30, 35 and

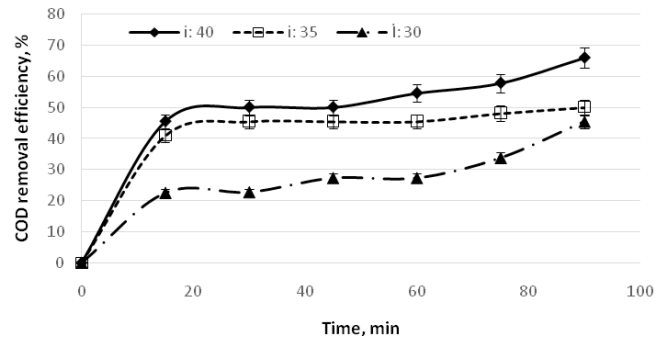


Fig. 2. Effect of CD on COD removal efficiency (pH 5; $0.15 M Na_2SO_4$).

$40 mA/cm^2$ were applied to the process in different runs while initial pH was adjusted to 5 and $0.15 M Na_2SO_4$ was used as supporting electrolyte. COD removal efficiencies of 45.50%, 50.04%, and 65.94% were obtained after 90 min at the current densities of 30, 35, and $40 mA/cm^2$ respectively, as shown in Fig. 2. An increase of CD favors COD removal efficiency as expected based on Eq. 1. Higher electron supply rate accelerates dissolution of iron to form Fe^{2+} in the solution. The dissolved amount can be estimated using Faraday equation (Eq. (9)).

$$C_{Fe} = \frac{M \cdot I \cdot t}{n \cdot F \cdot V} \quad (9)$$

where C_{Fe} is the theoretical concentration of Fe (g/L) in the solution, M is the molecular weight of Fe (g/mol), I is the applied current (A), t is the electrolysis time (s), n is the number of electrons involved in the dissolution reaction ($n = 2$ for Fe), F is the Faraday constant ($96,500 C/mol$) and V is the volume of liquid (L) in the reactor at time t .

Fe^{2+} precipitates as $Fe(OH)_2$ that forms flocs and adsorbs organic materials (Eq. (2)). According to Holt et al. [24], the current not only determines the coagulant dosage rate, but also the bubble production rate and fluid regime (mixing) within the reactor. Therefore, the collision between particles, floc growth and the potential for material removal, both pollutant and coagulant, are determined by the current. A similar result was reported by Hanafi et al. [25].

An increase of CD also increases the energy consumption rate (Fig. 3). Although the cumulative energy consumptions increased with increasing the applied voltage for current supply, the energy consumption per unit mass of removed COD showed different trend because of different removal efficiencies. For the operational CD of 30, 35 and $40 mA/cm^2$, the energy consumptions, respectively, were 16.15, 20.44 and $17.77 kWh/kg$ COD after 90 min of reaction. The power applied to an EC, overcomes the ohmic resistance for moving ions through the solution and the faradaic resistances for the anodic and cathodic reactions. It can be estimated by the following equations [26]:

$$P_{d\Omega} \left(\frac{\mu W}{cm^2} \right) = i^2 \Omega \quad (10)$$

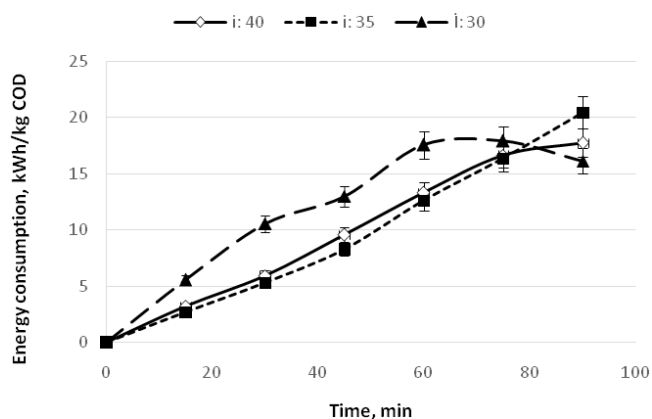


Fig. 3. Energy consumption of EC for different current densities (pH 5, 0.15 M Na₂SO₄).

$$P_{\text{dF}} \left(\frac{\mu\text{W}}{\text{cm}^2} \right) \approx i [k_1 \ln(i) + k_2] \quad (11)$$

where P_{dF} , P_{dR} , i and Ω are ohmic power dissipation, faradic power dissipation, CD and ohmic resistance, respectively. k_1 and k_2 are empirical constants. From Eqs. (10) and (11), it is clear that an increase in CD will increase both the ohmic and faradic power dissipations.

As shown in Figs. 2 and 3, the CD of 40 mA/cm² resulted in the highest removal efficiency with a moderate rate of consumed energy. The least energy per unit of removed COD was recorded for CD 30 mA/cm² but its removal efficiency was very low (45.5%). Comparing the results for CD of 35 and 40 mA/cm² at the end of reaction reveals that at 40 mA/cm², COD removal efficiency improved with almost the same energy consumption rate per unit removed COD. It was concluded that 40 mA/cm² is the more favorable value for CD but to avoid high temperatures inside the reactor, the rest of experiments was conducted with a CD of 35 mA/cm².

3.2. The effects of initial pH

Initial pH is an important operating factor influencing the performance of the EC process. Normally, buildup of hydroxide ion (Eqs. (3) and (5)) not only increases pH during the process, but also some times process shows buffer characteristics based on the working pH and electrode material [23]. pH values of 3, 5, 7 and 9 were examined with CD being fixed at 35 mA/cm² and 0.15 M Na₂SO₄. The final COD removal efficiency after 90 min was 59.12%, 50.04%, 48.39% and 42.58% for the pH 3, 5, 7 and 9, respectively (Fig. 4). Our findings revealed that acidic pH 3 resulted in the greatest removal capacity of COD. Therefore, further experiments were performed at pH 3. İrdemez et al. [27] reported a similar value for the best performing pH while investigating the effects of initial pH on phosphate removal from wastewater using iron plate electrodes. Although acidic pH enhances EC efficiency, setting up lower pH values for large-scale treatment would require large quantities of acids, which may not be economically feasible.

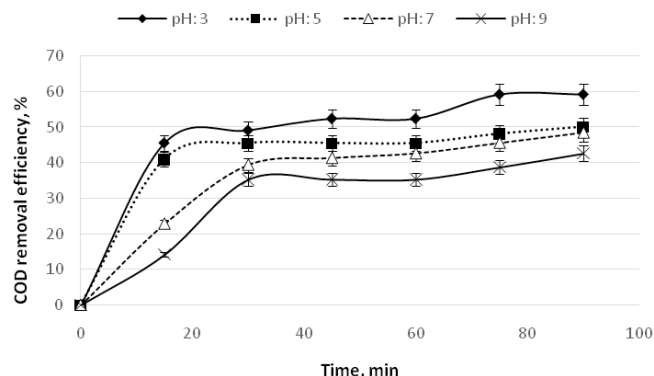


Fig. 4. Effect of pH value on COD removal efficiency ($i = 35 \text{ mA/cm}^2$; 0.15 M Na₂SO₄).

3.3. The effects of supporting electrolyte type

Six different supporting electrolytes, including NaNO₃, KNO₃, KCl, NaCl, Na₂SO₄ and K₂SO₄ were tested. On average, 0.15 M concentrations of supporting electrolytes were prepared and CD 35 mA/cm² and initial pH 3 were applied. The results for COD removal efficiency and energy consumption are summarized in Figs. 5 and 6. Na₂SO₄ was the most effective supporting electrolyte and, at the same time, shows the greatest rate of energy consumption. These results agree with the results of a previous work [28] for iron electrode. They identify the effectiveness of the type of the supporting electrolytes as Na₂SO₄ > NaCl > NaNO₃. One reason is that iron dissolves more easily when using sodium sulfate and less when using a nitrate anion electrolyte. This was mentioned by Izquierdo et al. [28]. Here, after 90 min of reaction, removal efficiency was 59.12%, 48.90%, 48.90%, 45.5%, 45.5% and 42.92%, for Na₂SO₄, K₂SO₄, NaCl, NaNO₃, KNO₃ and KCl, respectively (Fig. 5). This shows that generally, sodium-containing electrolytes are more effective than potassium cation electrolytes for this treatment. Moreover, the nitrate anion for both sodium and potassium is the least effective electrolyte. In the case where reaction continues for 90 min the difference in energy consumption is varied between 22.23 and 17.01 kWh/kg COD (Fig. 6). With KCl, the least amount of energy is consumed, because of its strong electrolytic characteristic. The results show that although KCl and K₂SO₄ are less effective as supporting electrolyte materials to reach high removal capacity, they are the most appropriate salts economically with regard to lower consumed energy per unit mass of removed COD.

3.4. The effects of supporting electrolyte concentration

To find the effect of supporting electrolyte concentration, tests were performed for 0.1, 0.15 and 0.20 M Na₂SO₄ while CD 35 mA/cm² and initial pH 3 being adjusted. The results are shown in Figs. 7 and 8 for COD removal and energy consumption against time, respectively. After 90 min, 48.90%, 59.12% and 60.26% of COD was removed at 0.1, 0.15 and 0.20 M Na₂SO₄, respectively. According to the graph, an increase in Na₂SO₄ concentration from 0.1 to 0.15 M showed a clear improvement in efficiency, but further increase from 0.15 to 0.2 M, did not result in any meaningful improvement in COD removal efficiency (Fig. 7). Similar result was

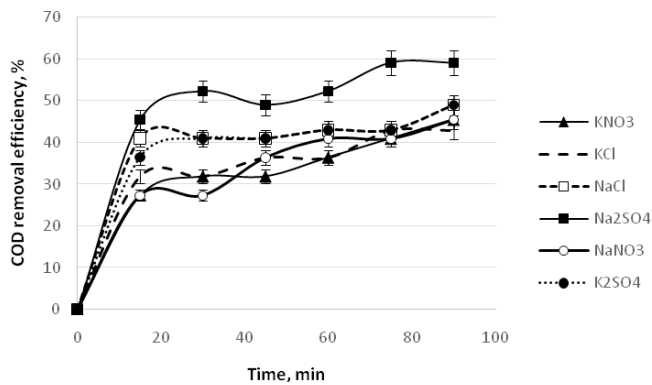


Fig. 5. Effect of different electrolyte type on COD removal efficiency ($i = 35 \text{ mA/cm}^2$; pH 3).

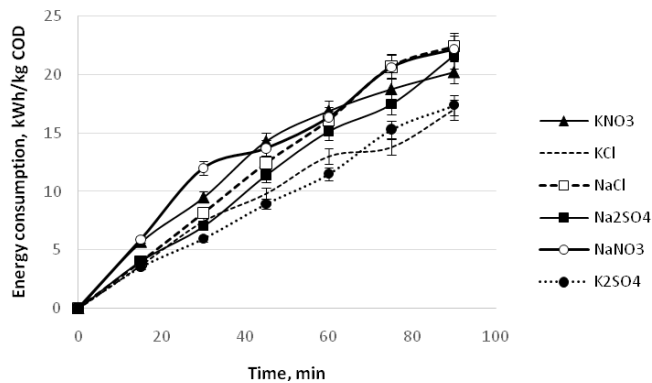


Fig. 6. Energy consumption of EC for different electrolytes ($i = 35 \text{ mA/cm}^2$; pH 3).

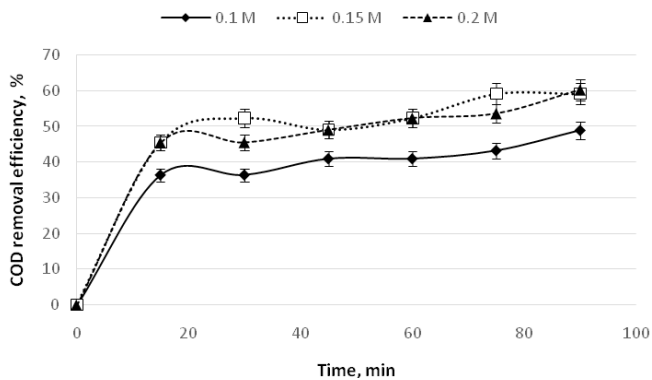


Fig. 7. Effect of Na₂SO₄ concentration on COD removal efficiency ($i = 35 \text{ mA/cm}^2$; pH 3).

reported elsewhere [29] and the increase of removal efficiency was mainly attributed to more available coagulant delivered to the medium resulting to the higher conductivity of the solution and thereby increasing the rate of metal dissolution. Some researchers also suggested that the supporting electrolyte anions plays a role in destroying the passivated anode layer and increase the anodic dissolution rate of metal [30]. However, a higher concentration of supporting electrolyte lowers the consumed energy per kilogram of removed COD (Fig. 8). In general, an increase of electrolyte concentration causes a reduction in energy consumption rate, which is

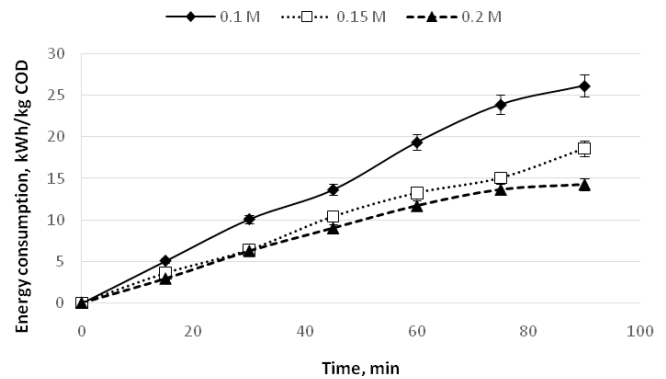


Fig. 8. Energy consumption of EC for different Na₂SO₄ concentrations ($i = 35 \text{ mA/cm}^2$; pH 3).

actually expected because of the increase in solution conductivity. Technically, 0.20 M concentration of sodium sulfate is recommended as the best performing value, but an economic feasibility study will determine its practical use on a larger scale.

3.5. The effect of hydrogen peroxide (electro-Fenton)

The co-application effect of EC and Fenton-based reactions on the removal of COD was investigated with addition of different concentrations of hydrogen peroxide including 0.05, 0.10 and 0.20 M while CD of 35 mA/cm², 0.15 M Na₂SO₄ and initial pH 3 being applied. After 90 min of reaction, COD removal efficiencies were 77.29%, 81.83% and 88.65% at 0.05, 0.10 and 0.20 M H₂O₂ concentrations, respectively. The results summarized in Fig. 9 clearly show that higher concentrations of hydrogen peroxide significantly assist COD removal. Similar result was reported elsewhere [31].

In addition to the effect of concentration of H₂O₂, the effect of addition mode on the performance of the process was also evaluated (Fig. 10). In the first run, all the 0.2 M H₂O₂ were added at once at the beginning. In the second run, 0.2 M H₂O₂ was added as four equal parts at $t = 0, 4, 8$ and 12 min. The addition of all the H₂O₂ at the start ensured a rapid removal of COD until 45 min but this effect over a longer reaction time did not show any significant difference (Fig. 10). Electro-Fenton effects are stronger at acidic pH and, consequently, the addition of a bulk amount of H₂O₂ at the start causes a considerable increase in EC removal efficiency. However, interestingly, there is no principal difference between two modes at a higher pH.

3.6. EC performance at the best operating condition

Finally, all the best obtained operational conditions were adjusted in a separate run to achieve the maximum COD removal. Therefore, the treatment was carried out at CD 40 mA/cm², initial pH 3, 0.20 M Na₂SO₄, and 0.20 M H₂O₂. The results for COD removal and energy consumption are presented in Figs. 11 and 12. This condition brought about almost 90.92% COD removal by reducing the initial COD of 15,500 to 1,408 mg/L after 90 min. Further reaction time did not improve the efficiency (Fig. 11). The total consumed

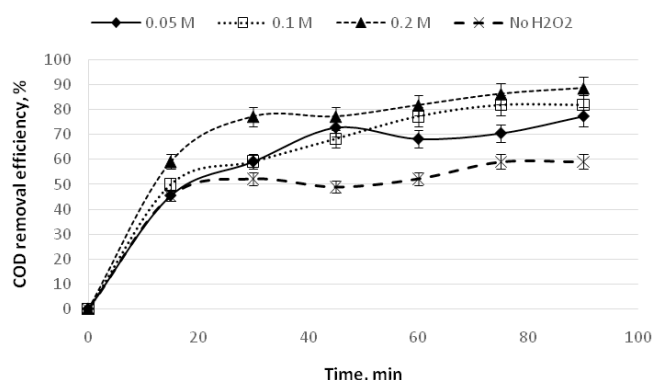


Fig. 9. Effect of H_2O_2 addition on COD removal efficiency ($i = 35 \text{ mA/cm}^2$; pH 3; $0.15 \text{ M Na}_2\text{SO}_4$).

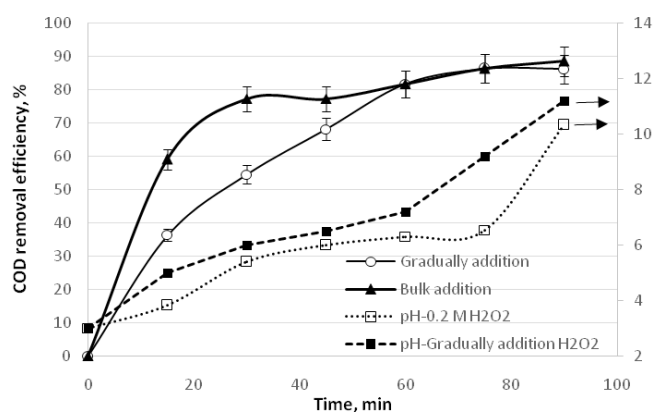


Fig. 10. Effect of H_2O_2 addition mode on COD removal efficiency ($i = 35 \text{ mA/cm}^2$; pH 3; $0.15 \text{ M Na}_2\text{SO}_4$).

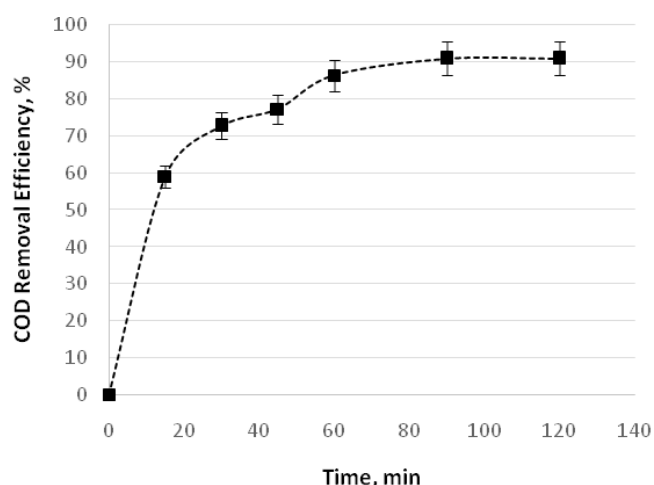


Fig. 11. Performance of reaction at best operating conditions ($i = 40 \text{ mA/cm}^2$; pH 3; $0.2 \text{ M Na}_2\text{SO}_4$; $0.20 \text{ M H}_2\text{O}_2$).

energy was 10.6 kWh/kg COD removed at 90 min (Fig. 12). According to the previous reports, total energy requirement of a conventional activated sludge treatment facility [32,33] with an assumed influent of 500 mg/L COD for a normal domestic wastewater [33] was about 1.2 kWh/kg COD removed. Kushwaha et al. [34] used a synthetic dairy

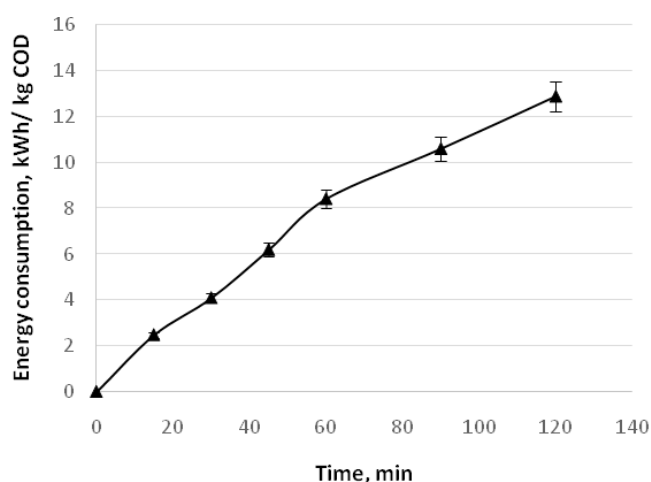


Fig. 12. Energy consumption of EC working at best operating conditions ($i = 40 \text{ mA/cm}^2$; pH 3; $0.20 \text{ M Na}_2\text{SO}_4$; $0.20 \text{ M H}_2\text{O}_2$).

wastewater and found energy consumption of 2.76 kWh/kg of COD where the initial COD was $3,900 \text{ mg/L}$ with 70% removal efficiency. The conventional activated sludge facilities are not able to treat such polluted wastewater as in this work. The reported low energy consumption rate by other researchers was achieved when a low initial COD was treated. The 90.92% removal efficiency in this study comparing with 82% for a conventional activated sludge plant [32] is very significant especially with regard to much less reaction time for an EC process. The final obtained residual COD of $1,408 \text{ mg/L}$ in the present work cannot be discharged directly to surface waters and requires additional treatment to reach standard of 170 mg/L . The permitted COD load for discharge to treatment plant in industrial zone in Turkey is $4,000 \text{ mg/L}$. Therefore, the designed EC setup successfully satisfies the legal limits as a pretreatment attempt in a single step.

3.7. Characterization of EC treatment sludge using XRD and XRF analyses

XRF analysis was used to quantitatively determine the elemental composition of solid waste. For process specifications of 40 mA/cm^2 , pH 3, $0.20 \text{ M Na}_2\text{SO}_4$ as supporting electrolyte and $0.20 \text{ M H}_2\text{O}_2$ as an enhancing agent, the obtained sludge was subjected to centrifuge and then dried at 100 C . XRF analysis showed that iron and oxygen contribute, respectively, for 52.14% and 33.44% of the dried sludge mass (Table 2). According to Eqs. (2) and (3), iron precipitates in the form of $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$. These compounds are not stable and when subjected to heat or even in water could undergo dehydration or oxidization to different iron oxides [35]. XRD analysis (XRD; Rigaku, D/Max-III C, Japan) was done to determine the different iron oxide phases. Result for XRD in Fig. 13 reveals that both hematite (Fe_2O_3) and magnetite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) phases present in the dried sludge. Amorphous structure of sludge is the reason for widened peaks and too much noise in XRD pattern.

In addition to iron and oxygen, sodium and sulfur, exist in significant amount contributing to 7.80% and 5.24% of mass, respectively. High amount of sodium and sulfur is directly

Table 2
XRF elemental analysis of obtained solid waste

Element	Mass, %
Fe(II and III)	52.14
O	33.44
S	5.24
Na	7.80
Mn	0.41
K	0.24
Ca	0.19
Si	0.11
Cl	0.17
Other	0.25

Note: pH 3, $i = 40 \text{ mA/cm}^2$; pH 3; 0.20 M Na_2SO_4 ; 0.20 M H_2O_2 .

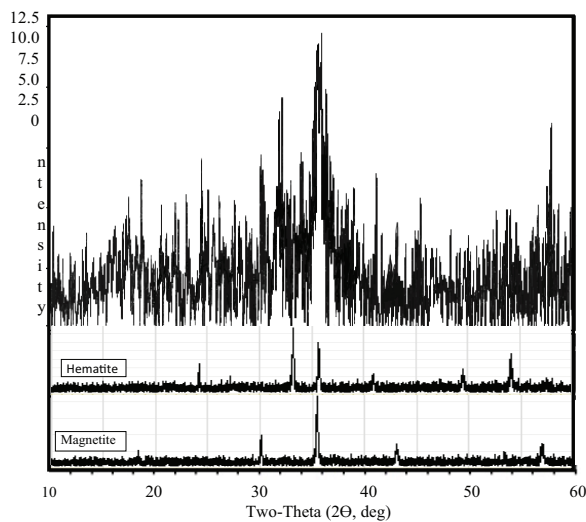


Fig. 13. XRD analysis of dried solid ($i = 40 \text{ mA/cm}^2$; pH 3; 0.20 M Na_2SO_4 ; 0.20 M H_2O_2).

related to adsorbed or trapped supporting electrolytic ions of Na_2SO_4 in the sludge. Based on XRF analysis, sodium to sulfur proportion is 1.49 which is interestingly lower than stoichiometric mass proportion of 2.87 in Na_2SO_4 . This is because sulfur also comes from other source, for instance, protein content of dairy wastewater. There are other elements in much lesser amount as presented in Table 2.

4. Conclusion

Our findings show that EC with the proposed reactor configuration is a highly effective process for treating cheese whey wastewater. Proposed batch-type reactor with its uniquely designed screw type iron anode impeller along with an iron shell as cathode is confirmed to be very efficient. Effective operational parameters such as CD, initial pH, supporting electrolyte type and its concentration and the addition of hydrogen peroxide (electro-Fenton effects) are concluded to have significant impacts on removal efficiency and changes in process demand for electrical energy as well. A summary of findings is as follows:

- Current densities of 30, 35 and 40 mA/cm^2 were examined. The 40 mA/cm^2 was the most efficient CD with 65.94% COD removal efficiency
- Initial pH values of 3, 5, 7 and 9 were tested. Acidic pH 3 resulted in the greatest removal capacity of COD.
- Six different supporting electrolytes, including NaNO_3 , KNO_3 , KCl , NaCl , Na_2SO_4 and K_2SO_4 were used. Na_2SO_4 is found to be the most effective supporting electrolyte.
- Three supporting electrolyte concentrations including 0.1, 0.15 and 0.20 M Na_2SO_4 were examined. Technically, 0.20 M concentration of Na_2SO_4 is recommended.
- Hydrogen peroxide addition (electro-Fenton effect) in 0.05, 0.10 and 0.20 M concentrations showed significant improvement in COD removal efficiency while 0.20 M to be the best choice.
- A separate run for the best performing conditions at CD 40 mA/cm^2 ; pH 3; 0.20 M Na_2SO_4 and 0.20 M H_2O_2 resulted in 90.92% COD removal by reducing the initial COD of 15,500 to 1,408 mg/L after 90 min of reaction.
- XRF analysis showed that 74.52% of the dried sludge mass was composed of iron oxide. Further XRD analysis showed presence of magnetite phase in the solid. It is concluded that the obtained sludge can be used as an iron source in other applications.

The legal limits for the direct discharge of cheese industries wastewater to the surface waters in Turkey is 170 mg/L COD and the permitted COD load for discharge to treatment plant in industrial zone is 4,000 mg/L . Therefore, the designed EC setup in this work with final COD of 1,408 mg/L , successfully satisfies the legal limits as a pretreatment attempt in a single step.

Acknowledgment

This study was supported by the Research Fund of Anadolu University, Turkey. Project No: 1101F007.

References

- [1] B. Sarkar, P.P. Chakrabarti, A. Vijaykumar, V. Kale, Wastewater treatment in dairy industries – possibility of reuse, *Desalination*, 195 (2006) 141–152.
- [2] C. Tocchi, E. Federici, L. Fidati, R. Manzi, V. Vincigurerra, M. Petruccioli, Aerobic treatment of dairy wastewater in an industrial three-reactor plant: effect of aeration regime on performances and on protozoan and bacterial communities, *Water Res.*, 46 (2012) 3334–3344.
- [3] F. Carta-Escobar, J. Pereda-Marin, P. Alvarez-Mateos, F. Romero-Guzman, M. Duran-Barrantes, F. Barriga-Mateos, Aerobic purification of dairy wastewater in continuous regime: Part I: analysis of the biodegradation process in two reactor configurations, *Biochem. Eng. J.*, 21 (2004) 183–191.
- [4] J. Luo, L. Ding, Y. Wan, P. Paullier, M.Y. Jaffrin, Application of NF-RDM (nanofiltration rotating disk membrane) module under extreme hydraulic conditions for the treatment of dairy wastewater, *Chem. Eng. J.*, 163 (2010) 307–316.
- [5] W.K. Lafi, M. Al-Anber, Z.A. Al-Anber, M. Al-shannag, A. Khalil, Coagulation and advanced oxidation processes in the treatment of olive mill wastewater (OMW), *Desal. Wat. Treat.*, 24 (2010) 251–256.
- [6] X. Tang, H. Zheng, H. Teng, Y. Sun, J. Guo, W. Xie, Q. Yang, W. Chen, Chemical coagulation process for the removal of heavy metals from water: a review, *Desal. Wat. Treat.*, 57 (2016) 1733–1748.

- [7] P. Saranya, S.T. Ramesh, R. Gandhimathi, Effectiveness of natural coagulants from non-plant-based sources for water and wastewater treatment—A review, *Desal. Wat. Treat.*, 52 (2014) 6030–6039.
- [8] M. Al-Shannag, Z. Al-Qodah, K. Bani-Melhem, M.R. Qtaishat, M. Alkasrawi, Heavy metal ions removal from metal plating wastewater using electrocoagulation: kinetic study and process performance, *Chem. Eng. J.*, 260 (2015) 749–756.
- [9] K. Cheballah, A. Sahmoune, K. Messaoudi, N. Drouiche, H. Lounici, Simultaneous removal of hexavalent chromium and COD from industrial wastewater by bipolar electrocoagulation, *Chem. Eng. Process.*, 96 (2015) 94–99.
- [10] M. Al-Shannag, Z. Al-Qodah, K. Alananbeh, N. Bouqellah, E. Assirey, K. Bani-Melhem, COD reduction of baker's yeast wastewater using batch electrocoagulation, *Environ. Eng. Manage. J.*, 13 (2014) 3153–3160.
- [11] M. Al-Shannag, W. Lafi, K. Bani-Melhem, F. Gharagheer, O. Dhaimat, Reduction of COD and TSS from paper industries wastewater using electro-coagulation and chemical coagulation, *Sep. Sci. Technol.*, 47 (2012) 700–708.
- [12] W. Lemlikchi, S. Khaldi, M. Mecherrri, H. Lounici, N. Drouiche, Degradation of disperse red 167 azo dye by bipolar electrocoagulation, *Sep. Sci. Technol.*, 47 (2012) 1682–1688.
- [13] B. Palahouane, N. Drouiche, S. Aoudj, K. Bensadok, Cost-effective electrocoagulation process for the remediation of fluoride from pretreated photovoltaic wastewater, *J. Ind. Eng. Chem.*, 22 (2015) 127–131.
- [14] B. Zeboudji, N. Drouiche, H. Lounici, N. Mameri, N. Ghaffour, The influence of parameters affecting boron removal by electrocoagulation process, *Sep. Sci. Technol.*, 48 (2013) 1280–1288.
- [15] M. Al-Shannag, K. Bani-Melhem, Z. Al-Anber, Z. Al-Qodah, Enhancement of COD-nutrients removals and filterability of secondary clarifier municipal wastewater influent using electrocoagulation technique, *Sep. Sci. Technol.*, 48 (2013) 673–680.
- [16] K. Eryuruk, U. Tezcanun, U. Bakir Ogutveren, Electrocoagulation in a plugflow reactor: the treatment of cattle abattoir wastewater by iron rod anodes, *Int. J. Environ. Res.*, 8 (2014) 461–468.
- [17] B. Ensing, F. Buda, E.J. Baerends, Fenton-like chemistry in water: oxidation catalysis by Fe(III) and H_2O_2 , *J. Phys. Chem. A*, 107 (2003) 5722–5731.
- [18] G. Güven, A. Perendeci, A. Tanyolaç, Electrochemical treatment of deproteinated whey wastewater and optimization of treatment conditions with response surface methodology, *J. Hazard. Mater.*, 157 (2008) 69–78.
- [19] G.F.S. Valente, R.C. Santos Mendonça, J.A.M. Pereira, L.B. Felix, The efficiency of electrocoagulation in treating wastewater from a dairy industry, Part I: iron electrodes, *J. Environ. Sci. Health B*, 47 (2012) 355–361.
- [20] J. Prakash Kushwaha, V. Chandra Srivastava, I. Deo Mall, Studies on electrochemical treatment of dairy wastewater using aluminum electrode, *AIChE J.*, 57 (2011) 2589–2598.
- [21] U.T. Un, E. Ozel, Electrocoagulation of yogurt industry wastewater and the production of ceramic pigments from the sludge, *Sep. Purif. Technol.*, 120 (2013) 386–391.
- [22] A. Aitbara, M. Cherifi, S. Hazourli, J.-P. Leclerc, Continuous treatment of industrial dairy effluent by electrocoagulation using aluminum electrodes, *Desal. Wat. Treat.*, 57 (2016) 3395–3404.
- [23] 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.
- [24] 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.
- [25] F. Hanafi, O. Assobhei, M. Mountadar, Detoxification and discoloration of Moroccan olive mill wastewater by electrocoagulation, *J. Hazard. Mater.*, 174 (2010) 807–812.
- [26] Z. Gu, Z. Liao, M. Schulz, J.R. Davis, J.C. Baygents, J. Farrell, Estimating dosing rates and energy consumption for electrocoagulation using iron and aluminum electrodes, *Ind. Eng. Chem. Res.*, 48 (2009) 3112–3117.
- [27] Ş. İrdemez, N. Demircioğlu, Y.Ş. Yıldız, The effects of pH on phosphate removal from wastewater by electrocoagulation with iron plate electrodes, *J. Hazard. Mater.*, 137 (2006) 1231–1235.
- [28] C.J. Izquierdo, P. Canizares, M.A. Rodrigo, J.P. Leclerc, G. Valentin, F. Lapique, Effect of the nature of the supporting electrolyte on the treatment of soluble oils by electrocoagulation, *Desalination*, 255 (2010) 15–20.
- [29] U. Tezcan Un, A.S. Koparal, U. Bakir Ogutveren, Electrocoagulation of vegetable oil refinery wastewater using aluminum electrodes, *J. Environ. Manage.*, 90 (2009) 428–433.
- [30] W.-L. Chou, C.-T. Wang, S.-Y. Chang, Study of COD and turbidity removal from real oxide-CMP wastewater by iron electrocoagulation and the evaluation of specific energy consumption, *J. Hazard. Mater.*, 168 (2009) 1200–1207.
- [31] Ü.T. Ün, S. Uğur, A. Koparal, Ü.B. Ögütveren, Electrocoagulation of olive mill wastewaters, *Sep. Purif. Technol.*, 52 (2006) 136–141.
- [32] A. Fenu, J. Roels, T. Wambecq, K. De Gussem, C. Thoeye, G. De Guedre, B. Van De Steene, Energy audit of a full scale MBR system, *Desalination*, 262 (2010) 121–128.
- [33] P.L. McCarty, J. Bae, J. Kim, Domestic wastewater treatment as a net energy producer—can this be achieved?, *Environ. Sci. Technol.*, 45 (2011) 7100–7106.
- [34] J.P. Kushwaha, V.C. Srivastava, I.D. Mall, Organics removal from dairy wastewater by electrochemical treatment and residue disposal, *Sep. Purif. Technol.*, 76 (2010) 198–205.
- [35] R.M. Cornell, U. Schwertmann, *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses*, 2nd ed., John Wiley & Sons, Germany, 2003.