

Electrochemical treatment of deproteinated whey wastewater and optimization of treatment conditions with response surface methodology

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Received 27 July 2007; received in revised form 26 November 2007; accepted 21 December 2007

Available online 3 January 2008

Abstract

Electrochemical treatment of deproteinated whey wastewater produced during cheese manufacture was studied as an alternative treatment method for the first time in literature. Through the preliminary batch runs, appropriate electrode material was determined as iron due to high removal efficiency of chemical oxygen demand (COD), and turbidity. The electrochemical treatment conditions were optimized through response surface methodology (RSM), where applied voltage was kept in the range, electrolyte concentration was minimized, waste concentration and COD removal percent were maximized at 25 °C. Optimum conditions at 25 °C were estimated through RSM as 11.29 V applied voltage, 100% waste concentration (containing 40 g/L lactose) and 19.87 g/L electrolyte concentration to achieve 29.27% COD removal. However, highest COD removal through the set of runs was found as 53.32% within 8 h. These results reveal the applicability of electrochemical treatment to the deproteinated whey wastewater as an alternative advanced wastewater treatment method.

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Keywords: Electrochemical wastewater treatment; Optimization; Response surface methodology; Statistical experiment design; Whey wastewater

1. Introduction

Whey wastewater is a by-product of the dairy industry whose major components are lactose (44–52 g/L), proteins (6–8 g/L) and mineral salts (4–9 g/L) [1,2]. Whey wastewater is produced more than 145×10^6 tonnes per year in the world [3,4] and approximately half of the world whey production was disposed into rivers, lakes or other water bodies; treated in wastewater treatment plants or loaded onto land [1,5]. Whey wastewater disposal has become increasingly important due to more stringent legislative requirements for effluent quality [6] since whey is a heavy organic pollutant with high biological and chemical oxygen demand values (BOD and COD), 40–60 and 50–80 g/L, respectively [5,7,8].

Whey can be processed through valorization technologies such as protein and lactose recovery by ultrafiltration, spray drying for powder production or directly utilized for animal feed. However, because of high energy and process cost requirements and due to sanitary reasons, separation technologies or storage of whey are not applicable especially for medium- and small-scale cheese-making plants. Laboratory and pilot scale trials for treatment of whey have been conducted under anaerobic [9–15] or aerobic [9,12,16,17] conditions, but the majority of these treatment methods dealt with the relatively, easily trended or diluted whey at long hydraulic retention times (HRTs) [18]. Furthermore, lactose is largely responsible for the high BOD and COD contents and very low numbers of microorganisms are able to directly utilize lactose as carbon source [1]. Moreover these microorganisms may require adjusted conditions and supplemental chemicals such as ammonium salts [19,20], which are deficient in deproteinated whey wastewater.

Treatment of whey wastewater is essential before discharging the residue to receiving waterways. Electrochemical treatment

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may be considered as an alternative process under the conditions when conventional treatment methods fail to reduce pollution [21]. The electrochemical treatment is considered as one of the advanced oxidation processes, potentially a powerful method of pollution control, offering high removal efficiencies. Electrochemical processes generally have lower temperature requirement than those of other equivalent non-electrochemical treatments and usually there is no need for addition of chemicals. Electrochemical treatment generally requires compact reactors and simple equipments for control and operation of the process. The process would be relatively non-specific, that is, applicable to a variety of contaminants but capable of preventing the production of unwanted side-products [22]. In recent years there has been an increasing interest in the treatment of industrial effluents by electrochemical methods as an alternative to traditional biological treatments [23]. Many researchers had investigated the electrochemical oxidation of various types of wastewater containing phenol [24–26], cyanides [27], nuclear wastes [28], human wastes [29], cigarette industry wastewater [30], textile wastewater [31] and tannery wastewater [32].

Nevertheless, there is less research dealing with electrochemical treatment of food-processing industrial wastewater. Electrochemical oxidation was applied to the treatment of coke-plant wastewater [33], coffee curing wastewater [34], olive oil wastewater [35], olive mill wastewater [36–42], green table olive processing wastewater [43], starchy wastewater [44], distillery industry wastewater [45–47], beer brewery wastewater [48] and vinasse from beet molasses [49].

In recent years, studies have been carried out to determine the feasibility and to optimize the electrochemical treatment technologies with response surface methodology. Response surface methodology (RSM), is an important branch of experimental design and a critical technology in developing new processes, optimizing their performance, and improving design and formulation of new products. The most popular class of second-order design was the central composite design (CCD). The CCD was first introduced by Box and Wilson in 1951, and is suited for fitting a quadratic surface, which usually works well for the process optimization [50]. The CCD is an effective design that is ideal for sequential experimentation and allows a reasonable amount of information for testing lack of fit while not involving an unusually large number of design points [50–52]. In the optimization process, the responses can be simply related to chosen factors by linear or quadratic models. A quadratic model, which also includes the linear model, is given as

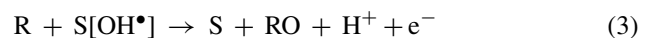
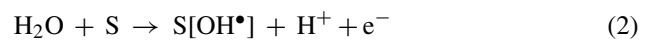
$$\eta = \beta_0 + \sum_{j=1}^k \beta_j x_j + \sum_{j=1}^k \beta_{jj} x_j^2 + \sum_{i < j=2}^k \beta_{ij} x_i x_j + e_i \quad (1)$$

where η is the response, x_i and x_j are variables ($i = 1$ to k), β_0 is the constant coefficient, β_j , β_{jj} and β_{ij} (i and $j = 1$ to k) are interaction coefficients of linear, quadratic and the second-order terms, respectively, k is the number of independent parameters ($=3$) and e_i is the error. RSM has already been used to optimize the electrochemical treatment of industrial paint wastewater [53], textile dye wastewater [54,55], electrochemical removal of mercury ions from wastewater [56], sodium from fermented

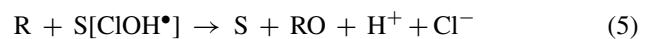
food composts [57], chromium from industrial wastewater [58] and chromium-contaminated waters [59]. Kaminari et al. [60] have used RSM to study the effects of the operational-parameters involved in designing fluidized-bed electrochemical reactors for the electrochemical removal of lead from industrial wastewater.

In this study, an attempt was made to achieve electrochemical treatment of deproteinated whey wastewater and optimization of operational conditions, being first in literature. Two mechanisms are thought to be responsible for electrochemical degradation of organic matter, R :

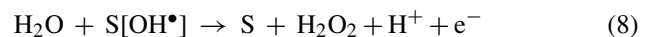
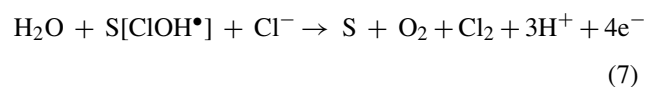
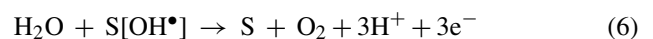
- Direct anodic oxidation where the pollutants are adsorbed on the anode surface, S , and destroyed by the anodic electron transfer reactions.
- Indirect oxidation in the liquid bulk, which is mediated by the oxidants formed electrochemically; such oxidants include chlorine, hypochlorite, hydroxyl radicals, ozone and hydrogen peroxide. Anodic water discharge results in the formation of hydroxyl radicals that are adsorbed on the anode surface and can then oxidize the organic matter [35]:



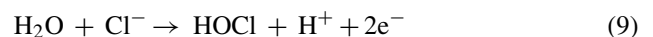
In the presence of NaCl , chlorohydroxyl radicals are also formed on the anode surface and then can oxidize the organic matter:



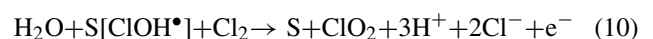
Reactions between water and radicals near the anode can yield molecular oxygen, free chlorine and hydrogen peroxide:

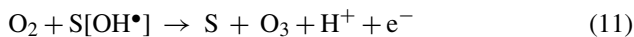


Furthermore, hypochloric acid can be formed by the reaction:



Therefore, direct anodic oxidation of deproteinated whey wastewater through reactions (3) and (5) results in reduced COD as well as the formation of primary oxidants such as oxygen, chlorine, hypochloric acid and hydrogen peroxide. Free chlorine and oxygen can further react on the anode-yielding secondary oxidants such as chlorine dioxide and ozone, respectively [35]:





Primary and secondary oxidants are quite stable and migrate in the solution bulk where they indirectly oxidize deproteinated whey wastewater constituents.

The objective of this work is to investigate the effects of operational parameters on electrochemical destruction of whey wastewater and to optimize the process in the presence of supporting electrolyte with adequate electrode material using RSM by Design-Expert® 6.0 (trial version). The runs were designed in accordance with the central composite design and carried out batch-wise. The whey wastewater was prepared from whey powder dissolved in distilled water for the standardization of the wastewater throughout the runs. Three factors—waste concentration, applied voltage and electrolyte concentration were selected as the operational (independent) variables, while COD removal percent was the response (dependent variable) of the treatment process in the design and optimization.

2. Materials and methods

2.1. Chemicals and materials

Whey powder used in the experiments was obtained from Pınar Milk Company (İzmir, Turkey) for the preparation of standard wastewater in batch runs. The standard whey wastewater was prepared with 50 g/L concentration of whey powder in 1 L distilled water and regarded as 100% waste concentration. The prepared whey wastewater contained 40 g/L lactose, 0.5 g/L fat, <5 g/L yeast, trace amount of proteins and had an overall COD value of 48–52 g/L. Different waste concentrations were prepared from standard wastewater (100% waste concentration) by dilution with distilled water. Simulated wastewater was autoclaved at 121 °C for 15 min with spa ZEUS (PBI International, Italy) autoclave to facilitate the precipitation of the proteins left in whey powder before the batch experiments. NaCl (Merck) in high purity was used as supporting electrolyte. Merck quality, K₂Cr₂O₇, (NH₄)₂Fe(SO₄)₂, HgSO₄, Ag₂SO₄ and H₂SO₄ were used for COD analysis. Carbon electrodes were obtained from Meteor, Germany. Iron and stainless steel (SS304) electrodes were manufactured in Ankara Mechanical Factory, Turkish Sugar Factories Corporation (Ankara, Turkey). All electrodes were of cylindrical shape with OD = 13 mm and 6 cm immersed length.

2.2. Experimental setup

The electrochemical reactor designed in our laboratory [61] was used batch-wise in all experiments. The reactor was made of glass having a net working volume of 2 L immersed in a temperature controlled water bath. The electrodes (in three pairs) were used as anode and cathode and placed tightly 8 cm apart on a Plexiglas® reactor cover. A glass stirrer with a single 4.5 cm diameter paddle was used for homogenization with a Heidolph-RZR1 (Germany) model mixer at constant 360 rpm, which provided adequate mixing. Temperature of the water bath

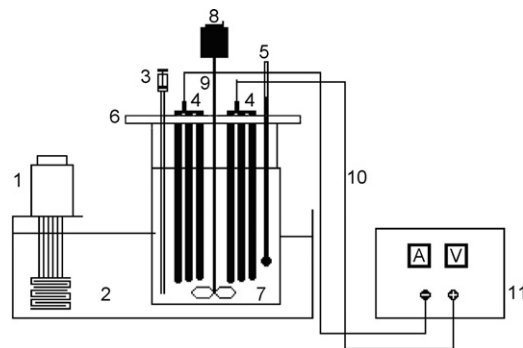


Fig. 1. Schematic diagram of the experimental setup. (1) Heating/cooling unit; (2) circulation water bath; (3) sampling outlet; (4) electrodes; (5) glass thermometer; (6) Plexiglas® reactor cover; (7) electrochemical reactor; (8) driving motor; (9) glass stirrer; (10) connection cables; (11) DC power source.

was controlled with a temperature-controlled heating–cooling unit (Selecta P Digiterm 100, Spain) to maintain a constant reaction temperature of 25 °C. The reaction temperature was monitored with a glass thermometer immersed. The current was applied by a constant voltage/current controlled DC power source; NETES NPS-1810 D (China). Experimental setup is shown in Fig. 1.

2.3. Analyses

The pH and turbidity were measured with a WTW 320 model pH meter (Germany) and a Hach 2100AN IS turbidimeter (USA), respectively. COD analyses were carried out by “Standard Methods for the Examination of Water and Wastewater” [62]. In COD analysis, 0.5–3 mL liquid sample was diluted to 50 mL with distilled water and 1 g of HgSO₄ was added to the diluted sample to overcome the chloride interference. Deproteinated whey wastewater was loaded into the reactor and the reaction under predetermined conditions started with the application of specified voltage and continuous agitation. At appropriate time intervals, samples of 10 mL were taken from the reactor and analyzed to determine the COD, turbidity and pH.

2.4. Experimental design and optimization

The CCD was used for the RSM in the experimental design. The CCD with three factors at three levels was applied using Design-Expert® 6.0 (trial version) with the bounds of the independent variables. Each independent variable was coded at three levels between –1 and +1 at the ranges determined by the preliminary experiments as well as by literature experience, where the independent variables changed in the ranges: waste concentration, 20–100%; applied voltage, 2–12 V; electrolyte concentration, 0–50 g/L.

The total number of experiments with three factors was obtained as 20 (=2^k + 2k + 6), where k is the number of factors (=3). Fourteen experiments were augmented with six replications at the design center to evaluate the pure error and were carried in randomized order as required in many design procedures. Experimental conditions of CCD runs of Design-Expert®

Table 1
Experimental conditions of central composite design (CCD) runs of Design-Expert® and the corresponding result, COD removal percent

Runs	Waste concentration (%)	Applied voltage (V)	Electrolyte concentration (g/L)	COD removal (%)
1	20	12	0	8.40
2	60	7	25	23.14
3	60	12	25	53.32
4	100	2	50	13.97
5	60	7	25	20.84
6	20	2	50	13.42
7	60	7	25	23.42
8	60	2	25	5.20
9	20	12	50	34.21
10	60	7	25	20.84
11	100	12	0	12.24
12	20	7	25	26.90
13	60	7	0	7.62
14	60	7	25	23.44
15	100	7	25	19.54
16	60	7	50	28.65
17	100	12	50	19.53
18	60	7	25	24.07
19	20	2	0	4.48
20	100	2	0	2.57

and corresponding results (responses) are presented in Table 1. First four columns of Table 1 show run number and experimental conditions of the runs arranged by the CCD. Performance of the process was evaluated by analyzing the response of COD removal percent.

The dependent variable, COD removal percent, was processed for Eq. (1) with Design-Expert® 6.0 program including ANOVA to obtain the interaction between the process variables and the response. The quality of the fit of polynomial model was expressed by the coefficient of determination R^2 and R^2_{adj} , and statistical significance was checked by the F -test in the program. For optimization, a module in Design-Expert® software searched for a combination of factor levels that simultaneously satisfy the requirements placed on each of the responses and factors. The desired goals were selected as maximum COD removal percent while applied voltage was preferred within the range, pollution load was kept maximum and electrolyte concentration was set to minimum. In Design-Expert® program goal settings are given with plus (+) symbols. Corresponding importances of goals were selected (+++++), the highest, in the program for all of the dependent and independent variables. These individual goals were combined into an overall desirability function by Design-Expert® software for maximization to find the best local maximum [63].

3. Results and discussion

3.1. Selection of electrode material

The efficiency and products of electrochemical oxidation of organic pollutants in wastewater is strongly dependent upon the nature of anodic material [64,65]. For electrode mate-

rials, iron, carbon and stainless steel SS304 were selected as they are relatively low cost and commercially used at large.

The COD, turbidity and pH time profiles of batch experiments were presented in Fig. 2 (a), (b) and (c), respectively, for carbon, stainless steel and iron electrodes at 25 °C, 8 V applied voltage, 100% waste concentration with 50 g/L NaCl concentration. After 8 h of reaction time, overall values of COD removal for iron, stainless steel and carbon electrodes were achieved as 35.6, 24.2 and 12.3%, respectively. Turbidity removals for iron and stainless steel electrodes were realized as 91.6 and 25.2%, respectively, while an increase in turbidity was experienced for carbon electrode most likely due to the slow erosion of the electrode during the reaction.

The efficiency of indirect oxidation depends on the diffusion rate of oxidants into the solution, temperature and the pH value of reaction medium [35]. The medium pH was stable around 6.60 for carbon electrode, while pH increased and remained constant at 11.7 for iron and steel electrodes as observed in all other runs with iron electrode. The pH rise was most likely due to Fenton reaction where hydroxyl ion is produced in the presence of Fe^{2+} and hydrogen peroxide both being available in the reaction medium [66]. Moreover, hydrogen production under alkaline conditions at the cathode also produces hydroxyl ions. Under acidic conditions, chlorine present in the form of hypochloric acid is the dominant oxidizing agent, while at alkaline conditions as established in this study, reactions involving hypochlorite, chloride ions, oxygen, hydrogen peroxide and hydroxyl radicals are effective [35].

Due to success with iron electrode in terms of turbidity and COD removals, iron was chosen as the most suitable electrode material for the electrochemical treatment reactions of deproteinated whey wastewater and utilized in the rest of the runs.

3.2. Experimental results

Twenty batch runs were conducted in CCD designed experiments to visualize the effects of independent factors on response and the results along with the experimental conditions were presented in Table 1. More than 20% COD removal was realized in 10 runs of the table. As a general trend, increase in electrolyte concentration and applied voltage resulted in enhanced COD removal in all runs. The precipitate volume measured was very low (3–5%, v/v) for all runs after 8 h and the precipitate was extracted with adequate amounts of sulphuric acid successively twice to desorb any contaminant adsorbed onto the precipitate. COD of the collected extracts was analyzed and found 2–5% more than the supernatant on volumetric base proving insignificant contribution of adsorption after 8 h of electrochemical destruction.

In Table 1, run 3 specifically gave the highest COD removal as 53.32%, after 8 h. Fig. 3 specifically shows COD and turbidity removals and pH profiles with the reaction time in this run. In Fig. 3, 98.0% of turbidity and 34.9% of COD removals were achieved in the first hour of reaction time indicating a relatively high COD initial removal rate and more efficient removal of

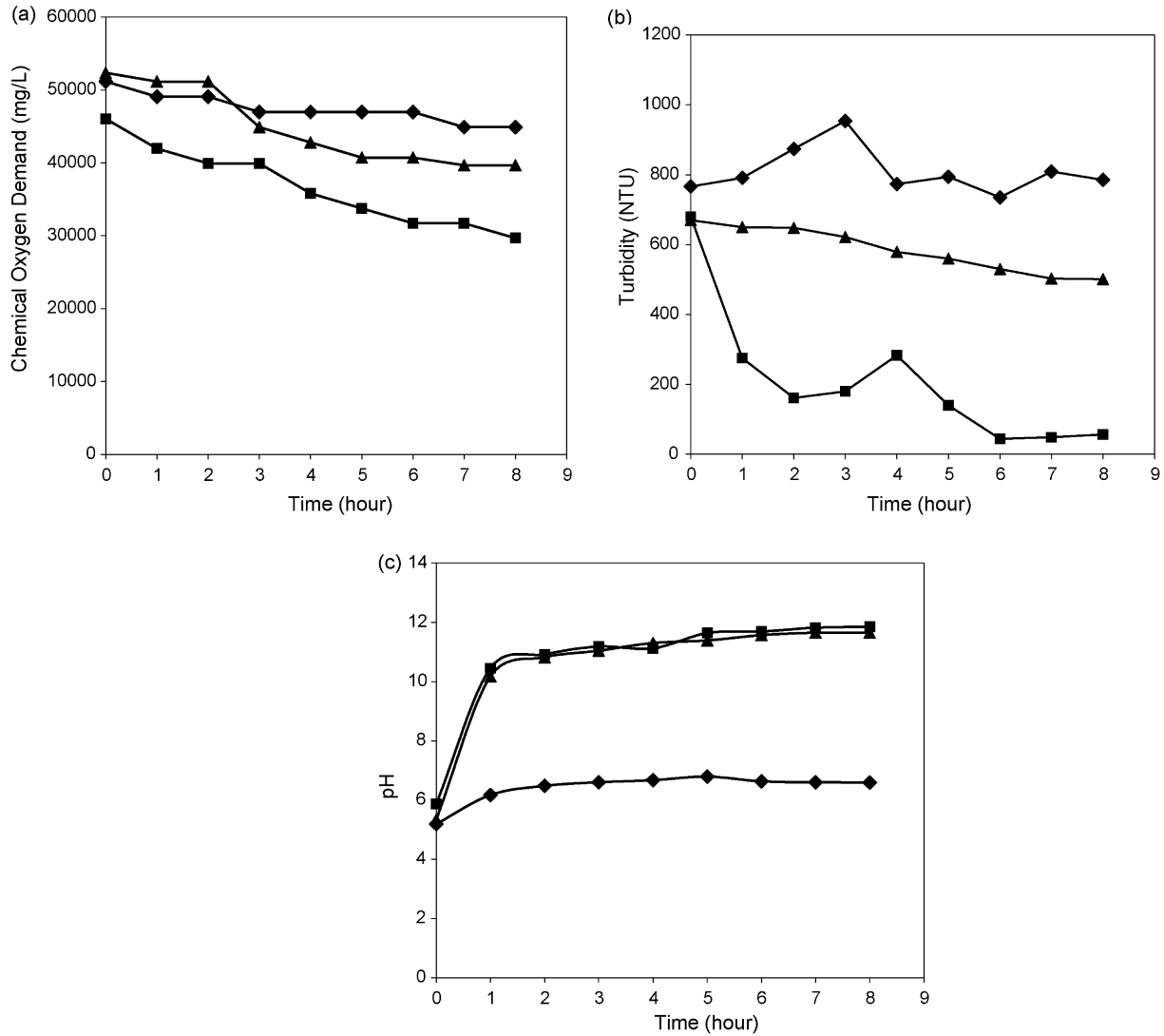


Fig. 2. (a) COD concentration–time profile (b) Turbidity–time profile (c) pH-time profile during batch experiments for carbon, stainless steel and iron electrodes at 25 °C reaction temperature, 50 g/L electrolyte concentration, 100% waste concentration and 8 V applied voltage (◆, carbon; ■, iron; ▲, stainless steel).

turbidity than that of COD. In Fig. 3, pH increased from 5.0 to 10.5 within the first hour of reaction due to production of hydroxyl ions [35].

3.3. Evaluation of experimental results with Design-Expert®

In Table 1, objective function (COD removal percent) responses range from 2.57 to 53.32, yielding a maximum to minimum ratio of 20.741. Design-Expert® program advises a response transformation for better approximation of objective function when this ratio is greater than 10. Therefore, all available response transformations were tried in the program to improve the model prediction power. The inverse transformation yielded the highest correlation coefficient ($R = 0.9696$) with a quadratic approximating function for the reverse of dependent variable COD removal percent, y , given in the following

equation:

$$\frac{1}{y} = +0.30623 + 1.92465E - 003x_1 - 0.046361x_2 - 7.01814E - 003x_3 - 3.31902E - 006x_1^2 + 2.24179E - 003x_2^2 + 5.37320E - 005x_3^2 - 1.11458E - 004x_1x_2 - 1.36880E - 005x_1x_3 + 3.45909E - 004x_2x_3 \quad (12)$$

In Eq. (12), x_1 , x_2 and x_3 correspond to independent variables of waste concentration, applied voltage and electrolyte concentration, respectively. ANOVA results for COD removal are presented in Table 2. In the table, F -value of the model was 17.46 which implied that the model is significant for inversed COD removal percent. Adeq Precision measures the signal to noise ratio and a ratio greater than 4 is desirable. Therefore, for the model of inversed COD removal percent, the ratio of 16.363

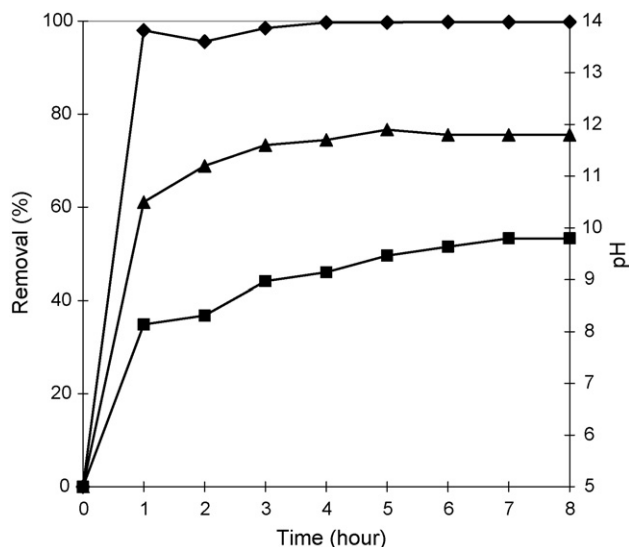


Fig. 3. COD, turbidity removal percents and pH profiles with the reaction time for run 3 at 25 °C reaction temperature, 25 g/L electrolyte concentration, 60% waste concentration and 12 V of applied voltage (■, COD removal (%); ◆, turbidity removal (%); ▲, pH).

indicated that adequate signals for the models could be used to navigate the design space. The values of $\text{Prob} > F$ less than 0.0500 showed that model terms are significant, whereas values greater than 0.1000 pointed that the model terms are not significant. For inversed COD removal percent $\text{Prob} > F$ is less than 0.0001 indicating that terms are significant in the model. The lack of fit F -value of 218.58 implies the lack of fit is also significant. Coefficient of determination ($R^2 = 0.9402$) and adjusted R -square ($R^2_{\text{adj}} = 0.8863$) found for the model of inversed COD removal percent were high, indicating a good fit for the inversed dependent variable.

3.4. Optimization of experimental conditions

The results were optimized by Design-Expert® software using the approximating function of inversed COD removal percent in Eq. (12). In optimization, a cost driven approach was preferred in the range of 2–12 V applied voltage, electrolyte concentration was minimized so as to save electrolyte, whereas inversed COD removal percent was minimized at maximized waste concentration. The optimization results with the responses in non-transformed scale are shown in Table 3 in the order of descending desirability.

Optimized conditions under specified cost driven constraints were obtained for highest desirability at 100% waste concen-

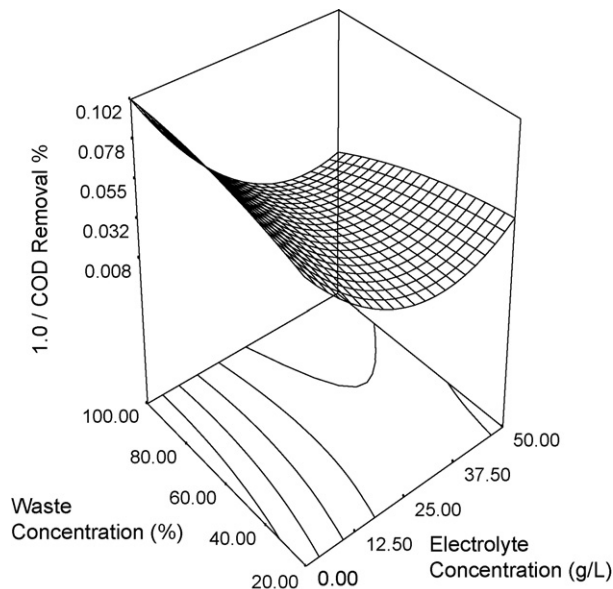


Fig. 4. The effects of waste and electrolyte concentrations on inversed COD removal percent at 25 °C reaction temperature and 11.29 V of applied voltage.

tration, 19.87 g/L electrolyte concentration and 11.29 V applied voltage at 25 °C. Under these optimized conditions, the program estimated 29.27% COD removal percent after 8 h of reaction time. In order to validate the optimization, a specific batch run was performed near these optimum conditions (20.27 g/L electrolyte concentration and 12 V applied voltage) at 25 °C. In this run, COD removal was realized as 25.90%, proving fair predictive power of the model approach.

3.5. Effects of operational parameters at optimum conditions

Eq. (12) has been used to visualize the effects of experimental factors on the inversed response under optimized conditions in 3D graphs of Figs. 4–6. The effects of waste and electrolyte concentration on inversed COD removal percent at 25 °C reaction temperature and 11.29 V applied voltage after 8 h of reaction time are shown in Fig. 4. In Fig. 4, the inversed COD removal percent decreased by increasing electrolyte concentration and was not significantly affected by the increase in waste concentration. Increasing electrolyte concentration raised the electrolytic conductivity, which in turn enhanced the reaction rate of electrochemical destruction. On the other hand, an increase in electrolyte concentration increased the secondary oxidants such as hypochlorite, oxygen and hydrogen peroxide under alkaline

Table 2
Regression analysis and response surface fitting (ANOVA) for inversed COD removal percentage

Source	Sum of squares	Degrees of freedom	Mean square	F -value	$\text{Prob} > F$
Model	0.14	9	0.016	17.46	<0.0001
Residual	9.033E–003	10	9.033E–004		
Lack of fit	8.992E–003	5	1.798E–003	218.52	<0.0001
Pure error	4.115E–005	5	8.230E–006		

$R^2 = 0.9402$, $R^2_{\text{adj}} = 0.8863$, Adeq precision = 16.363.

Table 3
Optimization results

Solution no.	Waste concentration (%)	Applied voltage (V)	Electrolyte concentration (g/L)	COD removal (%)	Desirability
1	100.00	11.29	19.87	29.27	0.938
2	100.00	11.32	19.72	28.97	0.937
3	100.00	11.35	19.32	28.19	0.937
4	100.00	11.22	20.53	30.63	0.936
5	100.00	11.94	20.34	29.32	0.555

conditions to oxidize wastewater indirectly [35,67]. In Fig. 4, inversed COD removal percent increased with decreasing electrolyte concentration due to decreasing current and diminished indirect oxidation rate with reduced amount of chloride in the reaction medium. On the other hand, inversed COD removal percent was not significantly affected by the waste concentration implying almost zero-order kinetics of destruction.

The effects of applied voltage and electrolyte concentration on inversed COD removal percent at 25 °C and 100% waste concentration are presented in Fig. 5. Inversed COD removal decreased by increasing the applied voltage because potential is the major driving force for the respective phenomena of interest in electrochemical reactors [68]. The increased voltage promotes the availability of new reactions by enabling higher half cell voltage for oxidation. In addition, enhanced voltage increases the current simultaneously, which directly amplifies the rate of the electrochemical destruction reaction. Under lower applied voltage, inversed COD removal percentage decreases profoundly with increasing electrolyte concentration due to the increased current but this effect became weak at higher applied voltages.

The effects of applied voltage and waste concentration on inversed COD removal percent at 25 °C and 19.87 g/L electrolyte concentration are given in Fig. 6. In Fig. 6, inversed COD removal percent decreased with increasing applied voltage pro-

portionally as observed before in Fig. 5. Waste concentration again had a little influence on inversed COD removal percent and causes a small drop at very high concentrations.

Although there has not been any literature work done yet to compare the results of this study, there are several ways to treat whey wastewater. The conventional method of whey wastewater treatment is based on biological methods; however, these methods generally need long HRT. Moreover, direct treatment of raw whey in highly loaded anaerobic reactors is considered not very reliable because of the difficulties frequently encountered in maintaining a stable operation. The majority of these difficulties were apparently due to rapid acidification of the waste [13]. An anaerobic rotating biological contact reactor fed with whey wastewater demonstrated a COD removal of 76% and organic loading rate, OLR, of 10.2 kg COD/(m³ day), however, reactor could not sustain a stable operation at HRT values shorter than 5 days [69]. Similarly, a minimum HRT of 5 days was needed in a pH controlled upflow fixed film loop reactor where the COD removal and OLR were 95% and 14 kg COD/(m³ day), respectively [70]. Yan et al. reported that the whey concentration between 25 and 30 g COD/L were optimal at HRT of 5 days for a stable operation of upflow anaerobic–sludge blanket reactor with a treatment efficiency of 97% COD removal [71]. On the other hand, at the influent concentration of 38.1 g COD/L, instability

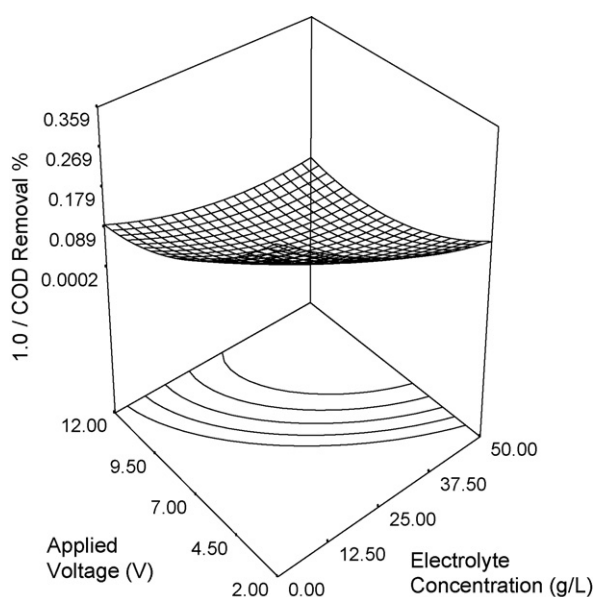


Fig. 5. The effects of applied voltage and electrolyte concentration on inversed COD removal percent at 25 °C reaction temperature and 100% waste concentration.

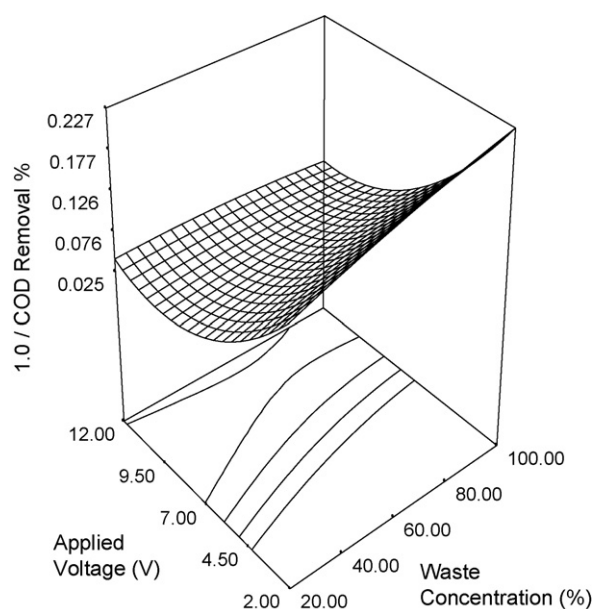


Fig. 6. The effects of applied voltage and waste concentration on inversed COD removal percent at 25 °C reaction temperature and 19.87 g/L electrolyte concentration.

of the reactor was observed most likely due to the accumulation of volatile fatty acids in the acidogenic stage beyond the assimilative capacity of the methanogenic stage [11,71]. Similar findings were also reported when treating whey wastewater with an anaerobic attached-film expanded-bed reactor [72]. In the case of two-phase systems such as the downflow–upflow hybrid reactor in which the acidogenic and methanogenic phases are separated within the reactor, 97% of COD removal was demonstrated with an inlet COD of 68 g COD/L and under OLR around 10 kg COD/(m³ day) but for a HRT around 7 days [73]. As is clear of biological treatment of whey wastewater, treatment duration has prolonged periods.

As an alternate to biological treatment methods, ozonation process was previously applied to the whey effluent with a load of 50–80 g COD/L as advanced oxidation. The efficiency of ozonation process was studied with different doses of ozone from 7 to 14 mg/L and different initial pH values of the effluent changing between 4 and 10. Studies demonstrated that ozonation is not an effective technique at all in none of the conditions for the treatment of whey wastewater due to high organic load [74,75].

There have been some electrochemical methods specifically employed for the dairy industry using direct current electrocoagulation with sacrificed iron anode which was affected by the initial pH, the current density, the amount of NaCl and the initial COD and oil–grease concentration in the work of Şengil and Özacar [76]. They reported that COD and oil–grease were effectively removed, 98% and 99% respectively, at initial pH 6–7 when the initial concentration of COD and oil–grease was 18300 and 4570 mg/L, respectively. In the same study optimal NaCl amount was found as 0.3 g/L whereas optimal current density was 0.6 mA/cm² [76]. Although these results seem to show better performance than those of ours, it has to be taken into account that the initial COD concentration of whey wastewater was approximately 2.8 times higher than that of dairy wastewater while the total area of the electrode plates used in electrocoagulation process were ca. twofold larger than the total submerged surface area of the six cylindrical electrodes used in this study. Moreover, electrocoagulation is merely a separation process, not an oxidation one, which requires successive treatment steps for the separated residue.

There are also applications of electrodialysis and dilution–concentration principle in the dairy industry for milk or milk by-products but these are towards mainly demineralization and neutralization of the whey, not treatment at all [77,78]. Apart from these studies, Boergardts et al. developed a three-stage process using bipolar membrane electrodialysis technique to purify dairy wastewater [79]. In this process, after pre-treatment with base in the first stage, the wastewater was introduced into a fermenter where the lactose present in the wastewater is fermented to form lactic acid, being the second stage. In the third stage, the purified broth was subjected to bipolar electrodialysis to yield concentrated lactic acid and base solutions from the purified broth. The decrease of the COD value in the wastewater during the bipolar electrodialysis of (pre-treated) fermentation broth fed in batch-wise was ca. 41 g COD/L in 5 h [79]. In addition to these processes, electroflotation alone [80] and together with electrocoagulation

and electrooxidation were applied for the treatment of dairy wastewater. A commercial product for the electrochemical treatment of whey wastewater with flow rates from 10 to 200 m³ day, namely PolipurTM (<http://www.polipur.com>), was developed by Envirogain Inc. (Canada) in collaboration with École Polytechnique de Montréal (Canada). It was demonstrated with PolipurTM that after a rough primary treatment, COD of the cheese dairy effluents decreased from 3780 to 530 mg/L whereas the decline for the BOD was from 1500 to 330 mg/L [81]. Again, in this combined process, the COD concentration of the dairy wastewater is almost 13.75-fold less than the one in our study and due to electrocoagulation and electroflotation, there remains a separated residue which needs further treatment steps.

With our study, it has been demonstrated that deproteinated whey wastewater could be treated by electrochemical oxidation and a final effluent with reduced pollution load can be obtained. For practical applications of the electrochemical treatment of deproteinated whey wastewater, further investigation is needed in order to achieve higher COD removals for the required environmental regulations.

4. Conclusion

The electrochemical treatment of deproteinated whey wastewater was investigated with iron electrodes in the presence of NaCl electrolyte, for the first time in literature. The effects of operating parameters of applied voltage, waste and electrolyte concentrations on COD removal were elucidated batch-wise and COD removal changed in the range 2.57–53.32%. The highest reduction of COD concentration was achieved 16751 mg/L in the electrochemical treatment of deproteinated whey wastewater which did not require a pre-treatment process. This removal value is relatively higher than many other electrochemical treatment processes and the electrolysis time of 8 h is the main advantage of this method over conventional biological treatments. For the use of electrochemical treatment in industrial applications, treatment process was experimentally designed and optimized through response surface methodology, where a cost driven approach was followed. In this respect, minimization of inversed COD removal percent was pursued while applied voltage was kept in the range, electrolyte concentration was minimized and waste concentration was maximized at 25 °C of reaction. The optimum conditions were satisfied at 100% waste concentration, 19.87 g/L external electrolyte concentration and 11.29 V applied voltage estimating 29.27% COD removal. Outcome of this study reveals the applicability of electrochemical treatment of whey wastewater as an alternative method to previous conventional solutions.

Acknowledgements

Authors are thankful to Pınar Milk Company (İzmir, Turkey) for free dried whey powder. Sugar Institute and Ankara Mechanical Factory of Turkish Sugar Factories Corporation (Ankara, Turkey) are greatly acknowledged for providing their facilities to carry out this work and for craftsmanship. This study was

also supported by the Project Management Unit of Akdeniz University, Antalya, Turkey.

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