



Hybrid processes for the treatment of cattle-slaughterhouse wastewater using aluminum and iron electrodes

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ABSTRACT

Electrocoagulation (EC) of cattle-slaughterhouse wastewater, which is characterized by (i) high turbidity (up to 340 Nephelometric turbidity units), (ii) increased chemical oxygen demand (COD) concentration (4200 mg L^{-1}), and (iii) a dark color, was investigated with the purpose of lowering the turbidity and COD concentration to levels below the permitted direct-discharge limits. Iron and aluminum were used as electrode materials. Experiments were conducted to evaluate the effects of current density, initial pH, and supporting electrolyte (Na_2SO_4) dosage on the performance of the system. COD removal increased with increase in current density. The original pH of wastewater (7.8) was found to be preferable for both the electrode materials. Higher concentrations of Na_2SO_4 caused an increase in COD removal efficiency, and energy consumption was considerably reduced with increasing conductivity. Hybrid processes were applied in this work to achieve higher COD removal efficiencies. In the case of aluminum electrode, polyaluminum chloride (PAC) was used as the coagulant aid for the aforesaid purpose. COD removal of 94.4% was obtained by adding 0.75 g L^{-1} PAC. This removal efficiency corresponded to effluent COD concentration of 237 mg L^{-1} , which meets the legal requirement for discharge from slaughterhouses in Turkey. In the case of iron electrode, EC was conducted concurrent with the Fenton process. As a result, 81.1% COD removal was achieved by adding 9% H_2O_2 . Consequently, hybrid processes are inferred to be superior to EC alone for the removal of both COD and turbidity from cattle-slaughterhouse wastewater.

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1. Introduction

Slaughtering of animals and the production of related products are coupled with the need for plenty of clean water and the emission of polluted water that has to be purified before it can be discharged into the drainage system. Therefore, slaughterhouse processes in industrialized countries are governed by strict legislation to protect public health and environment. Wastewater from a cattle slaughterhouse is a mixture of the processing water from both the slaughtering line and the cleaning of the guts, which causes a large variation in the concentration of organic matter. The main pollutant in slaughterhouse effluents is organic matter. The contributors of organic load to these effluents are paunch, feces, fat and lard, undigested food, blood, suspended material, urine, loose meat, soluble proteins, excrement, and colloidal particles [1].

The treatment of slaughterhouse wastewater by anaerobic methods [2–4] and hybrid systems [5] have been intensively studied. Coagulation of slaughterhouse wastewater has also been studied by adding aluminum salts and polymer compounds, and a maximum chemical oxygen demand (COD) removal efficiency of 45–75% has been reported [1].

Recently, electrochemical methods such as electrooxidation [6] and electrocoagulation (EC) [7] have been widely used for the treatment of wastewaters and flue gases [8,9]. The EC of poultry-slaughterhouse wastewater in a plexiglass reactor using four parallel monopolar aluminum and iron electrodes was studied by Kobya et al. [10]. Electrolysis of fowl-slaughterhouse wastewater using cast iron electrodes to minimize odors and organic matter was studied by Marconato et al. [11].

The formation of highly effective coagulants is made possible by the reaction of aluminum or iron ions (resulting from the dissolution of the anode) with the hydroxyl ions produced at the cathode. The reactions occurring within the experimental setup may be summarized in Table 1. As seen from Table 1 amorphous $\text{Al}(\text{OH})_{3(s)}$ flocs having large surface areas formed in aluminum anode are active in rapid adsorption of soluble organic compounds and trapping of colloidal particles and are easily separated from

Abbreviations: AOPs, advanced oxidation processes; EC, electrocoagulation; EF, electro-Fenton; NTU, Nephelometric turbidity unit; PAC, polyaluminum chloride.

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Nomenclature

| | |
|-------------------------------------------|--------------------------------------------------------------------|
| C | COD concentrations after electrocoagulation (mg L ⁻¹) |
| C ₀ | COD concentrations before electrocoagulation (mg L ⁻¹) |
| C _{Na₂SO₄} | concentration of the Na ₂ SO ₄ (M) |
| COD | chemical oxygen demand (mg L ⁻¹) |
| EEC | electrical energy consumptions (kWh m ⁻³) |
| I | current (A) |
| j | current density (mA cm ⁻²) |
| RE | removal efficiency (%) |
| t | time (h) |
| v | volume of solution (m ³) |
| V | potential (V) |

aqueous medium by sedimentation or H₂ flotation [12]. However, depending on the pH of the aqueous medium other ionic species, such as Al(OH)²⁺, Al₂(OH)₂⁴⁺ and Al(OH)₄⁻ may also be present in the system [13]. In the iron electrode two mechanisms have been proposed for the production of Fe(OH)_n where n=2 or 3 as seen from Table 1. The Fe(OH)_{n(s)} formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation [13].

EC of wastewater from a cattle slaughterhouse using a sacrificial anode made either from iron or aluminum is described in this article. The purpose of this work was to investigate the feasibility of treating cattle-slaughterhouse wastewater by EC to achieve the required legal direct-discharge limit of COD which is 250 mg L⁻¹ in Turkey for the slaughterhouse industry effluents [14]. The influence of the operating variables such as pH, current density, and supporting electrolyte (Na₂SO₄) dosage on the removal efficiencies of COD and turbidity were also determined. Hybrid systems (i.e. an electro-Fenton (EF) process in the case of iron anode and addition of polyaluminum chloride (PAC) as coagulant aid in the case of aluminum electrode) were also investigated to compare the efficiencies of the processes. The electrical energy consumed per unit volume of treated wastewater (EEC) has been calculated for different experimental conditions.

2. Experimental studies

The wastewater used in this work was taken from the local cattle-slaughterhouse processing plant located in Eskisehir, Turkiye. Although the quality of the effluent was variable, it was highly colored and typically had a pH of 7.8, COD of 4200 mg L⁻¹,

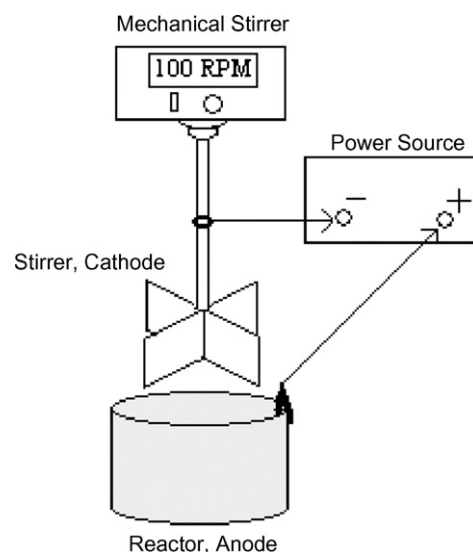


Fig. 1. Experimental setup.

turbidity of 340 Nephelometric turbidity units (NTU), and conductivity of 3.2 m S cm⁻¹.

The pH was adjusted to a desired value using 1N H₂SO₄ and 1N NaOH solutions. A specific amount of supporting electrolyte (0.1, 0.05, 0.025 and 0.01 M Na₂SO₄) was added to the wastewater to increase the conductivity and to facilitate EC. PAC (0.1, 0.3, 0.5 and 0.75 g L⁻¹ PAC) obtained from the local wastewater-treatment facility was used as the coagulant aid with an aluminum electrode whereas H₂O₂ (3, 6 and 9%) was used for the same purpose with an iron electrode.

The electrochemical system consists of a reactor, a mechanical stirrer, and a direct current (dc) power supply (Statron Type 3234.4); its schematic representation is shown in Fig. 1. In the experiments, the iron anode was used with an iron cathode, and the aluminum anode was used with an aluminum cathode. The aluminum and iron cylindrical reactors that operated as anodes were of 6.6 cm height and had an internal diameter of 10.8 cm. The mechanical stirrer (Heidolph RZR 2102) consisted of two blades and operated as the cathode; it was dipped into the reactor containing wastewater. It was also used to maintain uniform composition and to enable the agglomeration of flocs in the solution by rapidly stirring the mixture at 100 rpm. The performance of the reactor was evaluated in the batch mode.

In each run, wastewater (0.3 L) was poured into the electrolytic cell, and the pH, conductivity, and current density were adjusted to the desired value. The reaction was started by switching the dc

Table 1
The reactions occurred at aluminum and iron electrode and in the solution [13]

| Aluminum electrode | | |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Anode | | $\text{Al} \rightarrow \text{Al}_{(\text{aq})}^{3+} + 3\text{e}^-$ |
| In the solution | | $\text{Al}_{(\text{aq})}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + 3\text{H}_{(\text{aq})}^+$ $n\text{Al}(\text{OH})_3 \rightarrow \text{Al}_n(\text{OH})_{3n}$ |
| Iron electrode | | |
| Mechanism 1 | Anode | Mechanism 2 |
| $4\text{Fe}_{(\text{s})} \rightarrow 4\text{Fe}_{(\text{aq})}^{2+} + 8\text{e}^-$ | | $\text{Fe}_{(\text{s})} \rightarrow \text{Fe}_{(\text{aq})}^{2+} + 2\text{e}^-$ |
| $4\text{Fe}_{(\text{aq})}^{2+} + 10\text{H}_2\text{O}_{(\text{l})} + \text{O}_{2(\text{g})} \rightarrow 4\text{Fe}(\text{OH})_{3(\text{s})} + 8\text{H}_{(\text{aq})}^+$ | In the solution | $\text{Fe}_{(\text{aq})}^{2+} + 2\text{OH}_{(\text{aq})}^- \rightarrow \text{Fe}(\text{OH})_{2(\text{s})}$ |
| $8\text{H}_{(\text{aq})}^+ + 8\text{e}^- \rightarrow 4\text{H}_{2(\text{g})}$ | Cathode | $2\text{H}_2\text{O}_{(\text{l})} + 2\text{e}^- \rightarrow \text{H}_{2(\text{g})} + 2\text{OH}_{(\text{aq})}^-$ |

power supply on, and the entire EC process lasted about 1 h. At the end of the run, the stirrer and inside reactor were washed thoroughly with 0.1 M HCl and then with distilled water to remove any solid residues on the surfaces and dried. Samples from the effluent were taken at 10-min intervals and centrifuged (Hettich EBA 20) at 5000 rpm for 3 min; after digestion of the resulting supernatant using the Hach COD Digestion Reagent, the solution was analyzed for COD using a Hach DR/2000 spectrophotometer. Turbidity, conductivity, and pH were determined in supernatant liquid by means of turbidimeter (Hach 2100 P), conductimeter (Inolab Cond., Level 1), and pH meter (Orion 420 A), respectively. All the samples were analyzed in duplicate to ensure data reproducibility, and an additional measurement was carried out, if necessary.

3. Results and discussion

The effects of parameters such as pH, current density, supporting electrolyte dosage, amount of coagulant aid, and H_2O_2 concentration have been evaluated under specific conditions for a constant reaction time.

The calculation of removal efficiency (RE%) after EC and the electrical energy consumed per unit volume of treated wastewater (EEC) was calculated using the Eqs. (1) and (2), respectively.

$$\text{RE}\% = \left(\frac{C_0 - C}{C_0} \right) \times 100, \quad (1)$$

where C_0 and C are the concentrations of COD before and after EC, respectively, in mg L^{-1} and

$$\text{EEC} = \frac{VIt}{v}, \quad (2)$$

where EEC is the electrical energy consumption (kWh m^{-3}), V is the potential (V), I is the current (A), t is the time (h), and v is the volume of solution (m^3).

3.1. Effect of initial pH

The pH of raw wastewater can have either a positive or a negative influence on the treatment efficiency as it affects the stability of various hydroxide species that are formed. Likewise, a change in pH can modify the surface charge of particles and greatly influence the removal of colloidal dispersed organics from solution [15]. Al^{3+} ions on hydrolysis may generate hydroxyaluminum species. At pH < 4 aqueous complex $\text{Al}(\text{H}_2\text{O})_6^{3+}$ is predominant. Between pH 5 and 6 the predominant hydrolysis products are $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_2^+$; between pH 5.2 and 8.8 the solid $\text{Al}(\text{OH})_3$ is most prevalent; and above pH 9 the soluble species $\text{Al}(\text{OH})_4^-$ is the predominant and the only species present above pH 10. [16,17].

Similarly, ferric ions generated by electrochemical oxidation of iron electrode may form monomeric species ($\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_6^{3+}$, $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$, $\text{Fe}(\text{H}_2\text{O})_4\text{OH}_2^+$, $\text{Fe}(\text{OH})_3$, and $\text{Fe}(\text{OH})_4^-$), and polymeric species ($\text{Fe}_2(\text{H}_2\text{O})_8\text{OH}_2^{4+}$, $\text{Fe}_2(\text{H}_2\text{O})_6\text{OH}_4^{2+}$), depending on the pH of the aqueous medium in the EC process. The complexes (i.e. hydrolysis products) have a pronounced tendency to polymerize at pH 3.5–7.0. Under very acidic conditions (pH < 2.0), $\text{Fe}(\text{OH})_6^{3+}$ remains in solution, but as the pH or the coagulant concentration rises, hydrolysis occurs to form $\text{Fe}(\text{OH})_{3(s)}$ [18].

The effect of initial pH on COD removal at 20 mA cm^{-2} in the presence of $0.05 \text{ M Na}_2\text{SO}_4$ was examined at the pH values of 7.8 (original pH), 5.0, and 9.0 for the aluminum electrode and at pH values of 7.8, 4.0 and 9.0 for the iron electrode. In all experiments, pH was not controlled but monitored throughout the electrolysis. Generally, similar trends were observed using both the electrodes, as observed in Fig. 2. The removal efficiency clearly increased with

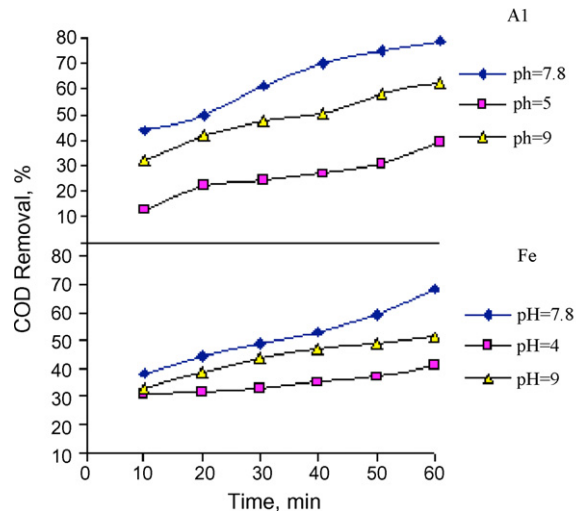


Fig. 2. Effect of initial pH on COD removal for iron and aluminum electrodes. j : 20 mA cm^{-2} , $C_{\text{Na}_2\text{SO}_4}$: 0.05 M .

an increase of pH from an acidic pH to 7.8 and subsequently dropped at pH 9.0. Because the coagulant could not be produced efficiently at low and high pH values as described above, the adsorption of organic pollutants could not take place. The maximum COD removal efficiency was 78.8% for the aluminum electrode and 68.5% for the iron electrode at pH 7.8 after a period of 60 min. Similar results were obtained with an iron electrode by Daneshvar et al. [19] and with an aluminum electrode by Yilmaz et al. [20].

Furthermore, the final pH of wastewater was increased during the EC process as observed by previous research [7] because of hydroxyl anions generated in the cathode as shown in Eq. (3). As seen in Fig. 3 the final pH of the treated wastewater was seen to increase with an increase in the initial pH and a sharp increase occurred in a very short period in case of lower initial pH's. Final pH of 8.76 and 9.05 were obtained at initial pH of 7.8 for Al and Fe electrode, respectively. According to Turkish Directive on Water Pollution Control [14], the discharge limit is between 6 and 9 pH for the slaughterhouse and meat processing plants. Consequently, the treated wastewater can directly discharged into natural aquatic streams without any pH adjustment.



Turbidity was effectively removed from the electrocoagulated and flocculated wastewater through charge neutralization using the Fe^{2+} or Fe^{3+} and Al^{3+} ions produced during electrolysis, followed by the agglomeration of colloidal particles. The pH dependency of turbidity removal is represented in Fig. 4. As seen from Fig. 4, turbidity change with initial pH was less sensitive at Al electrode compared to the Fe electrode. Treated wastewater with iron electrodes appeared greenish first, and then turned yellow and turbid due to the Fe^{2+} and Fe^{3+} while with aluminum electrodes the effluent was found very clear and stable [21]. The best performance was obtained at pH 7.8 for both electrode materials. The turbidity of the solution (340 NTU) was reduced dramatically, down to 3 NTU with aluminum electrode and to 33.6 NTU with the iron electrode, within 10 min of reaction at the original pH of 7.8. In conclusion, pH 7.8 is preferable for COD removal using both electrode materials, which is also beneficial for turbidity removal. Thus, the initial pH of wastewater need not be adjusted for the EC process as well as the final pH of treated wastewater to discharge the aquatic streams; thus, the additional cost of adjusting pH can be avoided.

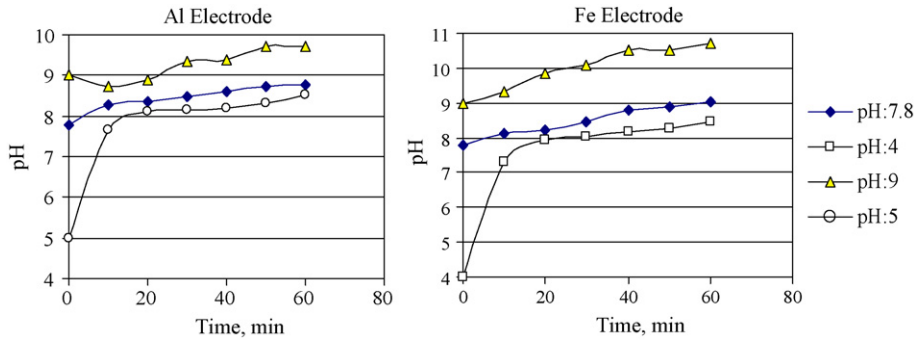


Fig. 3. The changes in the pH's according to the treatment times. j : 20 mA cm^{-2} , $C_{\text{Na}_2\text{SO}_4}$: 0.05 M .

3.2. Effect of current density

The supply of current to the EC system determines the amount of Al^{3+} or Fe^{2+} ions released from the respective electrodes and the amount of resulting coagulant. Thus, more Al^{3+} and Fe^{2+} ions get dissolved into the solution and the formation rate of $\text{M}(\text{OH})_n$ is increased. The influence of current density on the COD removal rates was investigated at the original pH with $0.05 \text{ M Na}_2\text{SO}_4$. COD removal rapidly increases on increasing the current density during the first 10 min; after this time, the removal efficiency scarcely increases (Fig. 5). This effect is also observed during the EC of

wastewater from vegetable-oil refineries using iron electrode [7]. Using an aluminum electrode at 25 mA cm^{-2} , COD removal of 81.7% was achieved whereas COD removal was 65.4% at 10 mA cm^{-2} . In the case of iron electrode, COD removal increased from 63.8 to 70.2% by increasing the current density from 15 to 25 mA cm^{-2} . For the aluminum electrode, the effect of current density was more pronounced on COD removal. In both cases, the current density had almost no effect on the turbidity removal, yielding efficiencies of between 99.1 and 99.4% for the aluminum electrode and between 94.4 and 97.6% for the iron electrode within 10 min. Increasing the current supplied to a fixed electrode configuration reduces the time required to treat a specific quantity of effluent to obtain the desired quality.

The effect of the current density on the EEC during the EC process is presented in Fig. 6. For both the electrode materials, electrical energy consumption increased more rapidly as the current density increased. Because the applied potential increased by increasing

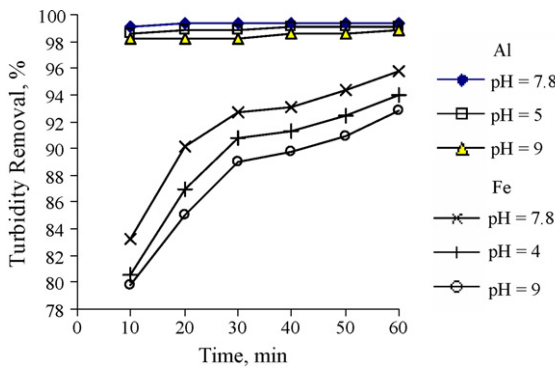


Fig. 4. Effect of initial pH on turbidity removal for iron and aluminum electrodes. j : 20 mA cm^{-2} , $C_{\text{Na}_2\text{SO}_4}$: 0.05 M .

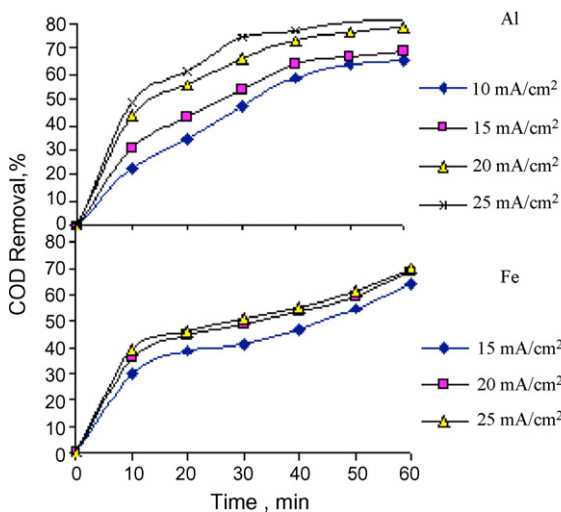


Fig. 5. Effect of current density on COD removal for iron and aluminum electrodes. pH: 7.8, $C_{\text{Na}_2\text{SO}_4}$: 0.05 M .

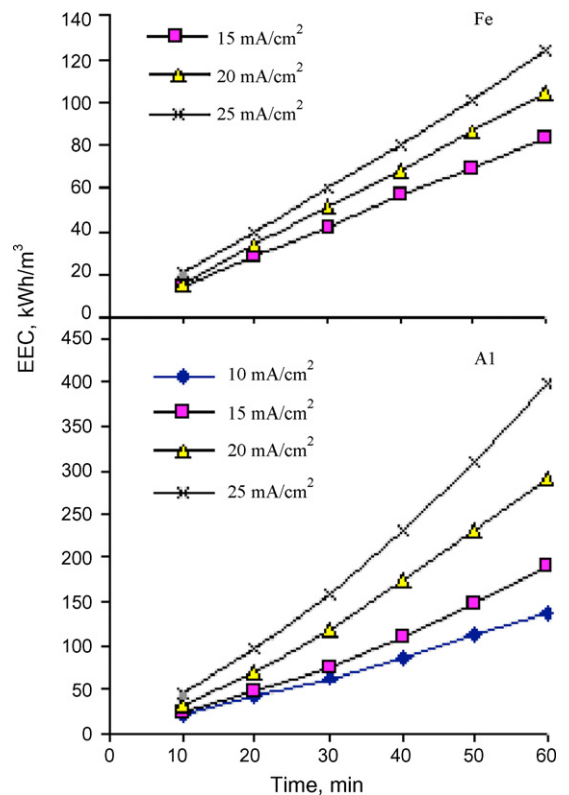


Fig. 6. Effect of current density on EEC for iron and aluminum electrodes. pH: 7.8, $C_{\text{Na}_2\text{SO}_4}$: 0.05 M .

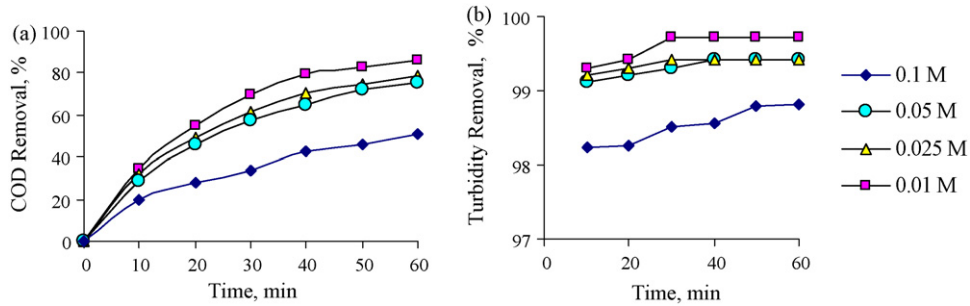


Fig. 7. Effect of salt concentration on COD removal (a) and turbidity removal (b) at aluminum electrode. pH: 7.8, j : 20 mA cm^{-2} .

the current density, EEC also increased. However, EEC increased exponentially whereas the potential and current increased linearly. Thus, when the optimal current density and potential have been selected, either higher removal rate or lower energy consumption can be preferred.

In the case of aluminum electrode, COD removal of 81.7% was achieved within 1 h, with maximum EEC of 399 kWh m^{-3} at 25 mA cm^{-2} . However, at 10 mA cm^{-2} , a maximum COD removal of 65.4% was achieved with lower EEC of about 138 kWh m^{-3} . In the case of iron electrode, a COD removal of 70.2% was achieved with electrical energy consumption of 124 kWh m^{-3} at 25 mA cm^{-2} whereas COD removal was 63.8% with an EEC of 83 kWh m^{-3} at 15 mA cm^{-2} .

3.3. Effect of supporting electrolyte concentration

The conductivity of wastewater can influence the electrochemical treatment because it facilitates the passage of current. To evaluate the effect of the supporting electrolyte concentration on removal of COD and turbidity at 20 mA cm^{-2} by an aluminum electrode, different quantities of Na_2SO_4 were added. The results are shown in Fig. 7. As the Na_2SO_4 concentration increased, the conductivity of the electrolyte was expected to increase correspondingly. The COD removal efficiency decreased from 86.4 to 50.5% after 60 min when the salt concentration was increased from 0.01 to 0.1 M. This decrease in the COD removal efficiency may be due to the fact that the excess SO_4^{2-} ions interact with hydroxyl ions under high salt concentrations. Furthermore, excess SO_4^{2-} ions may inhibit the localized corrosion of aluminum electrodes, leading to a lower COD removal efficiency. Similarly, turbidity removal slowly increased from 98.82 to 99.71% (corresponding to effluent turbidities of 4 and 1 NTU, respectively) by decreasing the salt concentration from 0.1 to 0.01 M.

The effect of Na_2SO_4 concentration on EEC is shown in Fig. 8. As the conductivity increased, the EEC was considerably reduced. With the aluminum electrode, the EEC of 547 kWh m^{-3} at 0.01 M Na_2SO_4 decreased to 158 kWh m^{-3} , with increasing Na_2SO_4 concentration up to 0.1 M. However, COD removal decreased with increase in the salt concentration. As the necessary voltage to achieve the fixed current density is diminished, the electrical energy consumed is decreased. When the conductivity of the solution increases, the reduction of IR (IR: ohmic voltage losses in all components of the electrochemical system) drop decreases, therefore the voltage necessary to reach a certain current density is correspondingly diminished, and consequently, the electrical energy consumed is also decreased. Similar effects on the EEC with increase in conductivity were previously reported by Tezcan Ün et al. [17] and Daneshvar et al. [22].

Consequently, excess electrolyte imposes energy demands on the system without any significant effect on the performance (%

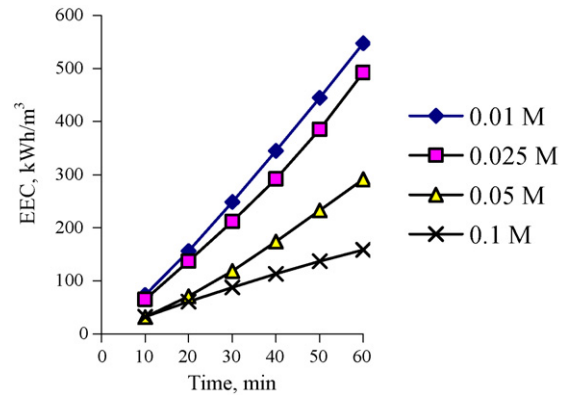


Fig. 8. Effect of salt concentration on EEC for aluminum electrode. pH: 7.8, j : 20 mA cm^{-2} .

COD removal). Furthermore, the costs attributed to sludge disposal increases correspondingly due to volume augmentation. To avoid heat generation and high energy consumption, 0.05 M Na_2SO_4 was chosen as the supporting electrolyte concentration for further experiments. Similarly, 0.05 M Na_2SO_4 was also used as the supporting electrolyte for the iron electrode.

3.4. Effect of PAC concentration

To increase the performance of the aluminum reactor and to obtain dischargeable effluents, PAC was intended to be used as the coagulant aid. Therefore, PAC was added to the wastewater to achieve particle instability and increase in the particle size, consequently achieving effective removal of organic substances present as COD.

Electrochemical treatment was started immediately after addition of PAC in to the wastewater. The results obtained from processing at 20 mA cm^{-2} are shown in Fig. 9. For an operating time of 60 min, 81.1%, 84.0%, 92.1%, and 94.4% COD removal were obtained for 0.1, 0.3, 0.5, and 0.75 g L^{-1} PAC, respectively, in the presence of 0.05 M Na_2SO_4 . The removal efficiency of 94.4% corresponds to COD concentration of 237 mg L^{-1} in the effluent, which meets the legal requirement of 250 mg L^{-1} for COD discharge by the slaughterhouse industry in Turkey. Similar results were obtained in previous reports concerning the EC of wastewater from vegetable-oil refinery using aluminum electrodes [17]. An effluent turbidity of 1 NTU was obtained (corresponding to 99.7% turbidity removal) for both 0.3 and 0.5 g L^{-1} PAC. Moreover, any further increase in PAC concentration caused no improvement in the removal of effluent turbidity. The color change of cattle-slaughterhouse wastewater during EC in relation to time was observed with the naked eye, as shown in Fig. 10.

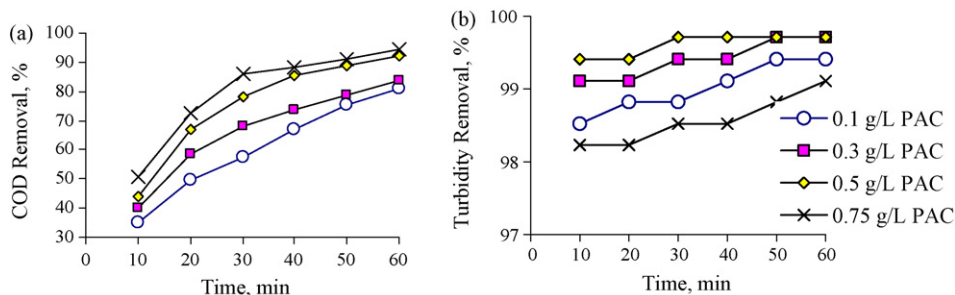


Fig. 9. Effect of PAC concentration on COD removal (a) and turbidity removal (b) at aluminum electrodes. pH: 7.8, j : 20 mA cm^{-2} , $C_{\text{Na}_2\text{SO}_4}$: 0.05 M .

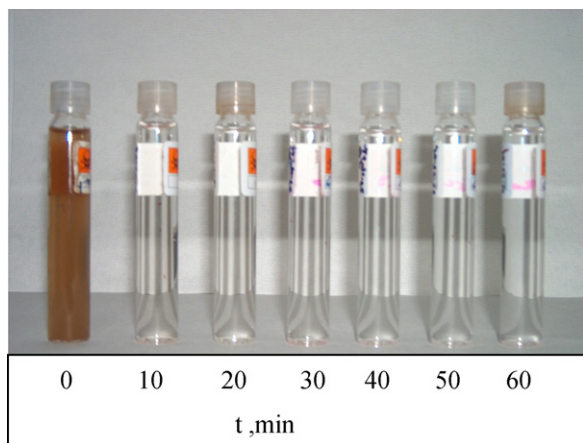
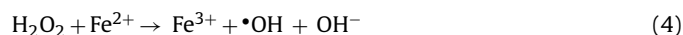


Fig. 10. Color change in the effluent with electrolysis time. pH: 7.8, j : 20 mA cm^{-2} , $C_{\text{Na}_2\text{SO}_4}$: 0.05 M , 0.75 g L^{-1} PAC. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3.5. Electro-Fenton process

Recently, more efficient processes, such as advanced oxidation processes (AOPs), for different kinds of wastewater have been extensively investigated. Among these AOPs, Fenton oxidation is particularly attractive because of its high efficiency of removal of organics and its simplicity, without requiring any special equipment. The ferrous or ferric ions react with H_2O_2 to generate hydroxyl radicals ($\cdot\text{OH}$), which is a nonselective strong oxidant [23].



Various EF oxidation processes such as EF-FeRe, EF-FeO_x; EF-H₂O₂-FeRe, and EF-H₂O₂-FeO_x have been defined (Re implies regeneration in the oxidation process) [24]. In EF-FeRe, both H_2O_2 and Fe^{2+} are externally applied while, simultaneously, Fe^{2+} is continuously regenerated at the cathode. In EF-FeO_x; H_2O_2 is

externally applied whereas a sacrificial Fe anode is used as the Fe^{2+} source. Moreover, Fe^{2+} may be continuously regenerated at the cathode depending on the setup of the electrolytic cell. In EF-H₂O₂-FeRe, both H_2O_2 and Fe^{2+} are concurrently generated at the cathode, with the primary focus on H_2O_2 generation. In EF-H₂O₂-FeO_x, H_2O_2 is generated at the cathode whereas a sacrificial Fe anode supplies Fe^{2+} [24].

Although there are many reports on using the electro-Fenton process for treatment of both wastewater containing organic pollutants such as landfill leachate [25], pesticides (atrazine [26]), herbicides [27] (picloram [28]) and wastewater from alcohol distilleries [29], no study has paid attention to the application of this process for the treatment of slaughterhouse wastewater.

In this portion of the study, to further capitalize on the dissolved Fe ion present in the bulk phase, H_2O_2 was added externally to the electrolytic reactor whereas a sacrificial iron anode was used as the ferrous ion source (EF-FeO_x). The addition of hydrogen peroxide at the beginning of the experiments resulted in the rapid and efficient production of hydroxyl radicals. The effect of different amounts of H_2O_2 on wastewater processing was investigated, and the results are shown in Fig. 11. COD removal efficiencies of 73.8%, 78.7%, and 81.1% were obtained by adding 3%, 6%, and 9% H_2O_2 , respectively, whereas COD removal was 68.6% without H_2O_2 addition. The turbidity removal efficiency was over 91% corresponding to all concentrations of H_2O_2 , as for example, an outlet turbidity of 18 NTU was achieved by adding 9% H_2O_2 . The effects of hydroxyl radicals originated from H_2O_2 produced rapidly caused the rapid removal of COD and turbidity at the beginning of the experiments. As the concentration of COD and turbidity decrease with time, removal rate also decreased as expected as seen from Fig. 11(a) and (b). Thus, the electro-Fenton method can be concluded to have a synergistic effect on COD removal because higher COD removal was achieved in comparison with the COD removal obtained from a previous study by the EC of wastewater from olive-oil processing [23]. Thus, this investigation verified that the removal efficiency could be promoted by coupling the Fenton reaction with EC.

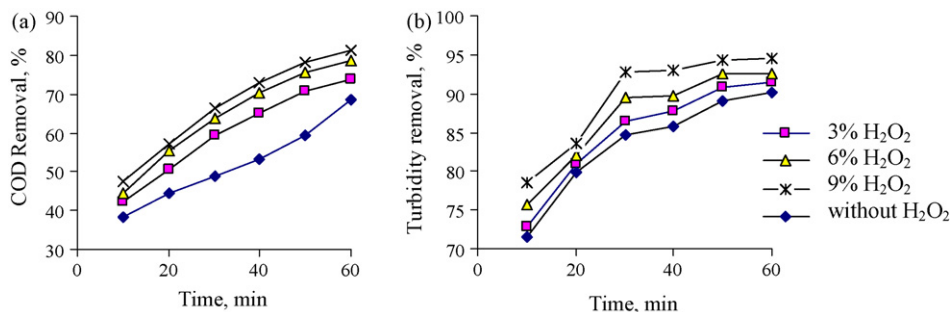


Fig. 11. Effect of H_2O_2 concentration on COD removal (a) and turbidity removal (b) at iron electrodes. pH: 7.8, j : 20 mA cm^{-2} .

4. Conclusions

In this study, the electrochemical treatment of cattle-slaughterhouse wastewater by EC using aluminum and iron electrodes was investigated. The effects of the different operational parameters on the removal of COD and turbidity were analyzed. The following conclusions can be drawn from the experimental results:

- A pH of 7.8 (the original pH of the wastewater) is preferable for a high COD removal using both electrode materials, which is additionally beneficial for turbidity removal.
- According to the results obtained from the above experiments, the removal efficiencies increased by increasing the current density for both aluminum and iron electrodes. Moreover, the energy consumption increased by increasing the current density. Al electrodes showed a higher efficiency of COD removal than Fe electrodes.
- Different Na_2SO_4 concentrations were used to increase the ionic conductivity of the wastewater and to minimize EEC. An increase in conductivity caused a decrease in EEC. On the contrary, it was found that higher concentration of Na_2SO_4 caused a reduction in the removal of COD from wastewater.
- To obtain a higher COD removal efficiency, the feasibility of hybrid processes were investigated. In the case of aluminum electrode, EC was carried out with PAC as the coagulant aid. From the results, removal of COD from wastewater was shown to be effective with a PAC dosage in the range of the current investigation. COD removal of 94.4% was obtained at 0.75 g L^{-1} PAC corresponding to 237 mg L^{-1} effluent COD concentration, which met the legal discharge requirement for slaughterhouse industries in Turkey. Consequently, dischargeable effluent was obtained by applying EC together with the addition of 0.75 g L^{-1} PAC.
- In the case of iron electrode, EC was carried out along with the Fenton process. COD removal of 81.1% was obtained by adding 9% H_2O_2 . This investigation verified that the removal efficiency could be promoted by coupling the Fenton reaction with EC.
- Consequently, it can be inferred that EC is a comparatively suitable process for removal of both COD and turbidity using either aluminum or iron electrodes to effectively treat slaughterhouse wastewater. However, the aluminum electrode is found to be more suitable than the iron electrode considering the removal efficiencies of each with respect to both COD and turbidity.

References

- [1] N.Z. Al-Mutairi, M.F. Hamoda, I. Al-Ghusain, Coagulant selection and sludge conditioning in a slaughterhouse wastewater treatment plant, *Bioresource Technology* 95 (2004) 115–119.
- [2] L. Masse, D.I. Massé, Effect of soluble organic, particulate organic, and hydraulic shock loads on anaerobic sequencing batch reactors treating slaughterhouse wastewater at 20C, *Process Biochemistry* 40 (3–4) (2005) 1225–1232.
- [3] A. Torkian, A. Egbali, S.J. Hashemian, The effect of organic loading rate on the performance of UASB reactor treating slaughterhouse effluent, *Resources, Conservation and Recycling* 40 (1) (2003) 1–11.
- [4] C.E.T. Caixeta, M.C. Cammarota, A.M.F. Xavier, Slaughterhouse wastewater treatment: evaluation of a new three-phase separation system in a UASB reactor, *Bioresource Technology* 81 (1) (2002) 61–69.
- [5] M. Merzouki, N. Bernet, J.P. Delgenès, M. Benlemlih, Effect of prefermentation on denitrifying phosphorus removal in slaughterhouse wastewater, *Biore-source Technology* 96 (12) (2005) 1317–1322.
- [6] Ü. Tezcan Ün, Ü. Altay, A.S. Kopalal, Ü. Bakır Ögütveren, Complete treatment of olive mill wastewaters by electrooxidation, *Chemical Engineering Journal* 139 (2008) 445–452.
- [7] Ü. Tezcan Ün, Treatment of vegetable oil refinery wastewater by electrocoagulation, *Fresenius Environmental Bulletin* 16 (9a) (2007) 1056–1060.
- [8] Ü. Tezcan Ün, A.S. Kopalal, Ü. Bakır Ögütveren, Electrochemical desulfurization of waste gases in a batch reactor, *Journal of Environmental Engineering (ASCE)* 133 (1) (2007) 13–19.
- [9] Ü. Tezcan Ün, A.S. Kopalal, Ü. Bakır Ögütveren, Sulfur dioxide removal from flue gases by electrochemical absorption, *Separation and Purification Technology* 53 (1) (2007) 57–63.
- [10] M. Kobya, E. Senturk, M. Bayramoglu, Treatment of poultry slaughterhouse wastewaters by electrocoagulation, *Journal of Hazardous Materials* 133 (1–3) (2006) 172–176.
- [11] J.C. Marconato, E.D. Bidoia, R.C. Rocha-Filho, Electrolytic treatment of wastewater from a fowl slaughterhouse using cast-iron electrodes, *Bulletin of Electrochemistry* 14 (6–7) (1998) 228–230.
- [12] D. Ghosh, H. Solanki, M.K. Purkait, Removal of Fe(II) from tap water by electrocoagulation technique, *Journal of Hazardous Materials* 155 (1–2) (2008) 135–143.
- [13] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC)—science and applications, *Journal of Hazardous Materials* 84 (1) (2001) 29–41.
- [14] Turkish Directive on Water Pollution Control, Table 5.6: Food Industry Slaughterhouse and Meat Processing Plants), 31 December, 2004.
- [15] P. Drogui, M. Asselin, S.K. Brar, H. Benmoussa, J.-F. Blais, Electrochemical removal of pollutants from agro-industry wastewaters, *Separation and Purification Technology* 61 (3) (2008) 301–310.
- [16] J.A.G. Gomes, P. Daida, M. Kesmez, M. Weir, H. Moreno, J.R. Parga, G. Irwin, H. McWhinney, T. Grady, E. Peterson, D.L. Cocke, Arsenic removal by electrocoagulation using combined Al–Fe electrode system and characterization of products, *Journal of Hazardous Materials* 139 (2) (2007) 220–231.
- [17] Ü. Tezcan Ün, A.S. Kopalal, Ü. Bakır Ögütveren, Electrocoagulation of vegetable oil refinery wastewater using aluminum electrodes, *Journal of Environmental Management* 90 (2009) 428–433.
- [18] M. Kobya, C. Ciftci, M. Bayramoglu, M.T. Sensoy, Study on the treatment of waste metal cutting fluids using electrocoagulation, *Separation and Purification Technology* 60 (3) (2008) 285–291.
- [19] N. Daneshvar, H. Ashassi-Sorkhabi, A. Tizpar, Decolorization of orange II by electrocoagulation method, *Separation and Purification Technology* 31 (2) (2003) 153–162.
- [20] A.E. Yilmaz, R. Boncukcuoğlu, M.M. Kocakerim, A quantitative comparison between electrocoagulation and chemical coagulation for boron removal from boron-containing solution, *Journal of Hazardous Materials* 149 (2) (2007) 475–481.
- [21] M. Kobya, S. Delipinar, Treatment of the baker's yeast wastewater by electrocoagulation, *Journal of Hazardous Materials* 154 (1–3) (2008) 1133–1140.
- [22] N. Daneshvar, A.R. Khataee, A.R. Amani Ghadim, M.H. Rasoulifard, Decolorization of C.I. Acid Yellow 23 solution by electrocoagulation process: Investigation of operational parameters and evaluation of specific electrical energy consumption (SEEC), *Journal of Hazardous Materials* 148 (3) (2007) 566–572.
- [23] Ü. Tezcan Ün, S. Uğur, A.S. Kopalal, Ü. Bakır Ögütveren, Electrocoagulation of olive mill wastewaters, *Separation and Purification Technology* 52 (1) (2006) 136–141.
- [24] Z. Qiang, J.-H. Chang, C.-P. Huang, Electrochemical regeneration of Fe^{2+} in Fenton oxidation processes, *Water Research* 37 (2003) 1308–1319.
- [25] H. Zhang, D. Zhang, J. Zhou, Removal of COD from landfill leachate by electro-Fenton method, *Journal of Hazardous Materials* 135 (1–3) (2006) 106–111.
- [26] A. Ventura, G. Jacquet, A. Bermond, V. Camel, Electrochemical generation of the Fenton's reagent: application to atrazine degradation, *Water Research* 36 (14) (2002) 3517–3522.
- [27] B. Boye, M.M. Dieng, E. Brillas, Anodic oxidation, electro-Fenton and photoelectro-Fenton treatments of 2,4,5-trichlorophenoxyacetic acid, *Journal of Electroanalytical Chemistry* 557 (2003) 135–146.
- [28] A. Özcan, Y. Şahin, A.S. Kopalal, M.A. Oturan, Degradation of picloram by the electro-Fenton process, *Journal of Hazardous Materials* 153 (2008) 718–727.
- [29] Y. Yavuz, EC and EF processes for the treatment of alcohol distillery wastewater, *Separation and Purification Technology* 53 (1) (2007) 135–140.