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Electrochemical treatment of aqueous oxalic acid solution by using solid polymer electrolyte (SPE) reactor

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ABSTRACT

In this study, the feasibility of electrochemical oxidation of the aqueous oxalic acid solution has been investigated in an electrochemical reactor with SPE and simultaneous hydrogen production has been observed.

Experiments were conducted to examine the effects of applied current density, flow rate of solution, pH of the solution, the concentration of supporting electrolyte, the temperature of the solution, types of the electrode and membrane material on removal efficiency.

As a result of the studies oxalic acid as COD at the original pH can be treated to meet discharge limits at ambient temperature without any pH adjustment with low energy consumption. COD removal efficiency of 97% has been achieved by using titanium oxide coated with iridium oxide as anode. Since there is no need to use liquid electrolyte in this type of reactor, aqueous oxalic acid solution can be oxidized without adding any supporting electrolyte such as Na_2SO_4.

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1. Introduction

Organic compounds in the wastewater originate from decomposition of the plant and animal waste, industrial activities, domestic and agricultural wastewaters and the reaction between the natural organics and halogens during the treatment of wastewater.

Organics are termed "recalcitrant" if they are resistant to biological treatment. Because these organic compounds are chemically or metabolically unreactive, they are toxic to microorganisms. Oxalic acid which is one of these types of compounds is a common pollutant found in industrial wastewater, especially in textile or metallurgical industry and it is used as a model pollutant in wastewater applications [1,2].

Oxalic acid known as ethandioic acid with the structure of HOOC–COOH includes 2 carboxylic acid groups and is one of the most strong organic acids due to this carboxyl structure. Chemical structure of this compound can be seen in Fig. 1.

Oxalic acid combines with sodium, ferrous, calcium, magnesium or potassium ions to form oxalate salts which have low solubility. This organic compound is also an important intermediate in the complete mineralization of many organic pollutants. For example, oxalic acid and the other carboxylic acids are formed as intermediate products in the catalytic oxidation of benzene compounds in wastewater [3].

Biological treatment, incineration, adsorption, advanced oxidation and chemical or electrochemical treatment are used in the treatment of industrial wastewater which contains organic compounds. These methods are the most economic processes and are usually used for the treatment of readily degradable biocompatible organic pollutants present in the wastewater [4].

The situation is completely different when the wastewater contains toxic or/and refractory non-biocompatible organic pollutants [4]. For example, carboxylic acids such as oxalic acid in industrial wastewater accumulate in surface and ground waters, so biological treatment of this wastewater cannot be possible.

AOPs are particularly useful and produce very reactive agents such as OH radicals which are responsible for the powerful oxidation [5]. On the other hand these methods have low energy efficiency, especially in the production and utilization of photons. Many AOPs include the use of reactive and dangerous chemicals (O_3, H_2O_2), or the use of high temperature and pressure.

Most physicochemical methods such as flocculation, coagulation, filtration, open evaporating ponds and incineration (with or without concentration) give only a partial solution to the problem and should be followed by a biological treatment method which creates secondary pollutants. Other treatments which deal with more sophisticated technologies like reverse osmosis and ultra-
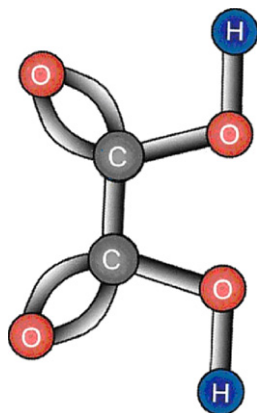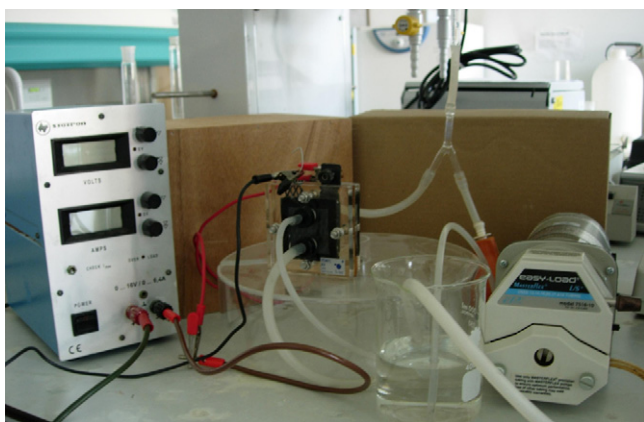

Fig. 1. Structure of oxalic acid.

Fig. 2. Electrochemical treatment setup.

filtration have the disadvantages of high cost and low efficiency [6].

Electrochemical techniques have an important role among the advanced treatment technologies and offer a good opportunity to prevent and remediate pollution problems [7–9]. The main reagent used here is electron which is a clean reagent, and therefore, it has advantages such as requirement of no chemicals before and after the treatment, producing no sludge, requiring small area and low investment cost. These methods are environment friendly, and they do not form new toxic wastes [7,10]. Therefore, electrochemical
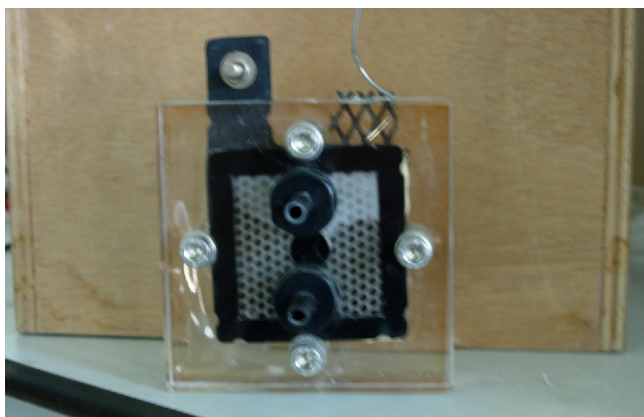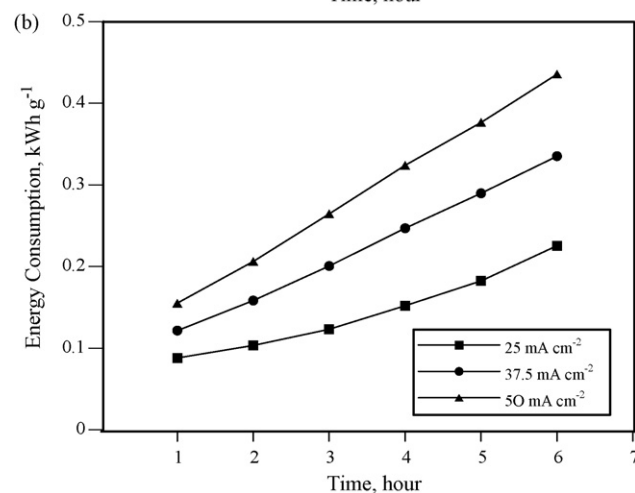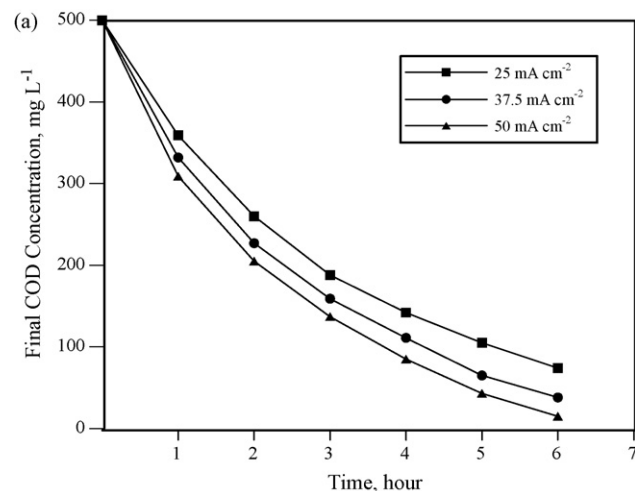

Fig. 3. Electrochemical reactor.

Fig. 4. Variation of final COD concentration and energy consumption with time for different applied current densities (Flow rate: 150 mL min^{-1}).

oxidation is one of the promising techniques in the treatment of wastewaters containing refractory organic compounds [11].
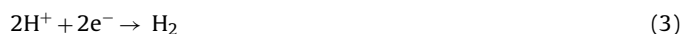
In this study, the feasibility of electrochemical oxidation of the aqueous solution of oxalic acid has been investigated in an electrochemical reactor with a solid polymer electrolyte and simultaneous hydrogen production has been observed.

Oxalic acid has been electrochemically oxidized to CO_2 and H_2O at the anode and hydrogen gas has been produced by the reduction of hydrogen ion at the cathode:

At the anode:

$$H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^- \tag{1}$$

$$C_2H_2O_4 + \tfrac{1}{2}O_2 \rightarrow 2CO_2 + H_2O \tag{2}$$

At the cathode:

$$2H^+ + 2e^- \rightarrow H_2 \tag{3}$$

The overall reaction:

$$C_2H_2O_4 \rightarrow 2CO_2 + H_2 \tag{4}$$

Parameters that can affect the performance of the process, such as current density, flow rate, pH of the solution, the concentration of supporting electrolyte, temperature of the solution, types of the electrode and membrane material have been examined.
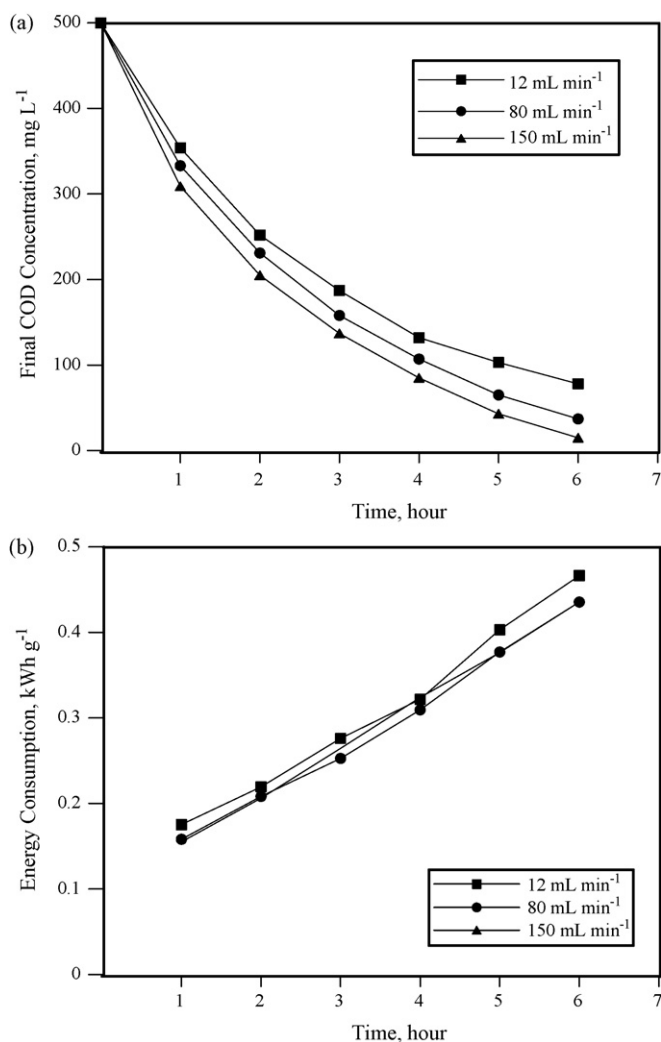
Fig. 5. Variation of final COD concentration and energy consumption with time for different flow rates (Current density: $50\,mA\,cm^{-2}$).

Fig. 6. Effect of pH on final COD concentration and energy consumption during electrochemical treatment (Current density: $50\,mA\,cm^{-2}$; flow rate: $150\,mL\,min^{-1}$).

2. Experimental

2.1. Chemicals

All chemicals used in the experiments were analytical grade. Fresh aqueous solutions of oxalic acid were used for each electrolysis. 3.782 g solid oxalic acid with purity of 99.5% was solved in 1 L of distilled water. This aqueous solution refers to 500 mg COD/L.

Potassium hydrogen phosphate (KH_2PO_4, MERCK) ($66\,mg\,L^{-1}$), magnesium sulfate ($MgSO_4\cdot7H_2O$, Merck) ($30\,mg\,L^{-1}$), ferric chloride ($FeCl_3.6H_2O$, MERCK) ($4\,mg\,L^{-1}$), sodium hydrogen carbonate ($NaHCO_3$, MERCK) ($80\,mg\,L^{-1}$) and oxalic acid (0.03 M) were used to prepare model solution in laboratory.

Sodium sulfate (Na_2SO_4, MERCK) and sodium hydroxide (NaOH, MERCK) have also been used for determining the supporting electrolyte effect and for adjusting the pH, respectively, in relevant experiments.

2.2. Materials

A power supply (Statron, 3240.2), a digital multimeter (Fluke 26-III True RMS), a peristaltic pump (Masterflex, 755-375), an analytical balance (OHAU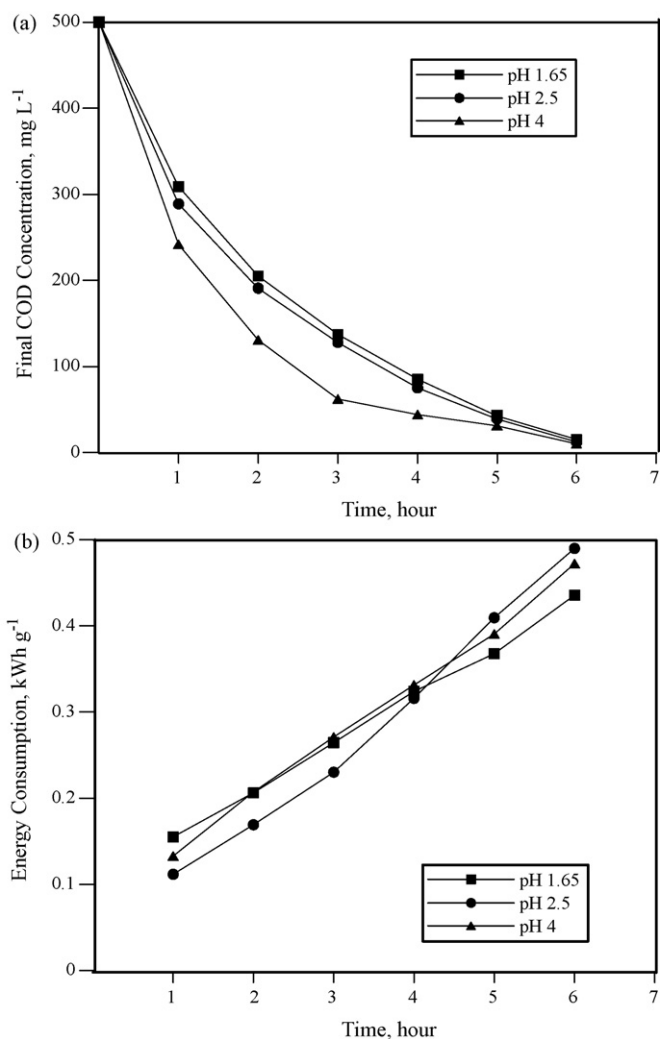S, Explorer Pro), a pH meter (Orion 710 A), a heater (IKA) and a water bath (Polyscience 9605) have been used in the experiments.

Nafion 117 (4 cm × 4 cm) and Nafion 111 (4 cm × 4 cm) cationic exchange membranes as SPE have been used. They have been supplied from fuelcellstore.com (USA).

Titanium oxide coated with iridium oxide expanded mesh ($16\,cm^2$) and carbon fibre with Pt catalyst ($16\,cm^2$) as gas diffusion electrode have been supplied from Magneto Special Anodes B.V. (Schiedam, The Netherlands) and fuelcellstore.com, respectively.

A COD reactor (HACH, 45600) has been used for COD analysis according to the standard methods for the examination of water and wastewater. Also, TOC apparatus (Elementer, Liquid TOC) and HPLC apparatus (Agilent 1100 with Supelcogel H column which has dimensions of 0.009 mm × 30 cm × 7.8 mm) have been used for determination of TOC and oxidation products, respectively.

2.3. Procedure

In this study, electrochemical oxidation of the aqueous oxalic acid solution has been carried out using an electrochemical reactor, a peristaltic pump, a reservoir and a power supply. Electrochemical treatment setup is illustrated in Fig. 2.
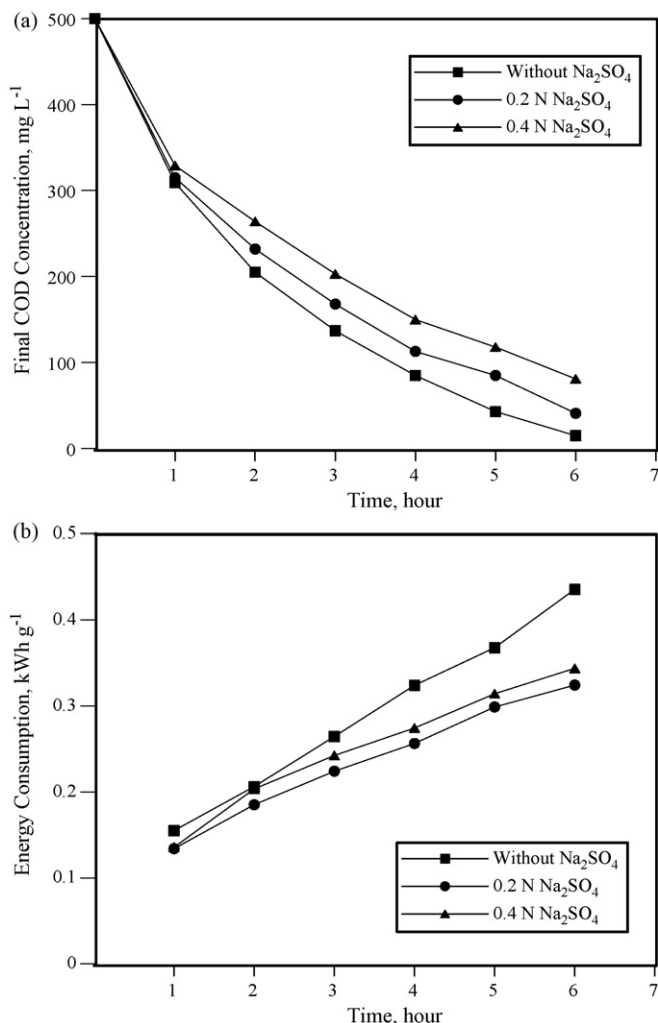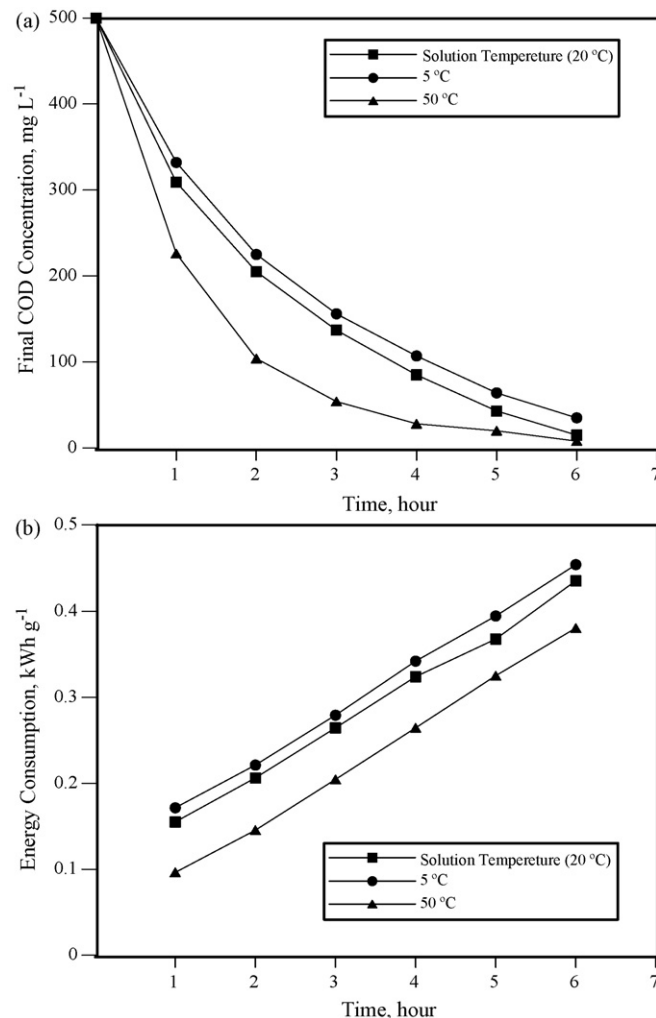
Fig. 7. Effect of supporting electrolyte concentration on the removal efficiency and energy consumption during electrochemical treatment (Current density: 50 mA cm^{-2}; flow rate: 150 mL min^{-1}).

Fig. 8. Effect of temperature on final COD concentration and energy consumption during electrochemical treatment (Current density: 50 mA cm^{-2}; flow rate: 150 mL min^{-1}).

Aqueous oxalic acid solution was recirculated from reservoir to anode side of the electrochemical reactor by peristaltic pump at ambient temperature. Batch and recycled mode of electrolysis were performed during 6 h. Samples were taken from the electrochemical reactor with the intervals of 1 h.

Since current density is an important factor affecting the removed fraction of oxalic acid and energy consumption of an electrochemical system, three different current densities of 25, 37.5 and 50 mA cm^{-2} were applied. Aqueous oxalic acid solution was recirculated through the electrochemical reactor with the flow rates of 12, 80 and 150 mL min^{-1}. The higher flow rates have not been used, because there was no significant increase in removal efficiency at higher flow rates.

Oxidation of oxalic acid to carbon dioxide and hydrogen has been achieved in an electrochemical reactor with SPE shown in Fig. 3. Oxalic acid was introduced into the anode side and then oxidized at the SPE/anode interface. Hydrogen ions generated by the oxidation reactions were transported through the SPE to the cathode side where hydrogen gas was produced.

In this study, the anode was separated from the cathode by Nafion 117 as a copolymer of polytetrafluoroethylene (PTFE) and polysulfonylfluoride containing pendant sulfonic acid groups. Since the electrolyte is solid and completely insoluble, wastewa-ter can be treated directly without an expendable liquid electrolyte [12].

Nafion 111 has also been used to determine the effect of the membrane thickness on removed fraction of oxalic acid and energy consumption of an electrochemical system. Since the Nafion 111 has very thin structure and is decomposed easily at higher current densities, two lower current densities of 25 and 37.5 mA cm^{-2} were applied.

The anode and cathode took place at the each sides of the SPE. Titanium oxide coated with iridium oxide as anode and carbon fibre with Pt catalyst as cathode were used in most of the experiments.

Platinum electrode and carbon fibre electrode with Pt catalyst as anode have also been used to observe the effect of the type of electrode on the removal efficiency and energy consumption. Since the carbon fibre electrode with Pt catalyst can be decomposed at higher current densities, only the current density of 25 mA cm^{-2} was applied in this case.

Temperature and pH of the solution were measured continuously during the experiments. Significant change in temperature and pH of the solution were not been observed during the experiment. To obtain the effect of temperature of the solution on the efficiency and energy consumption of the electrochemical system, 5, 50 °C and ambient temperature (approximately 20 °C) were examined.
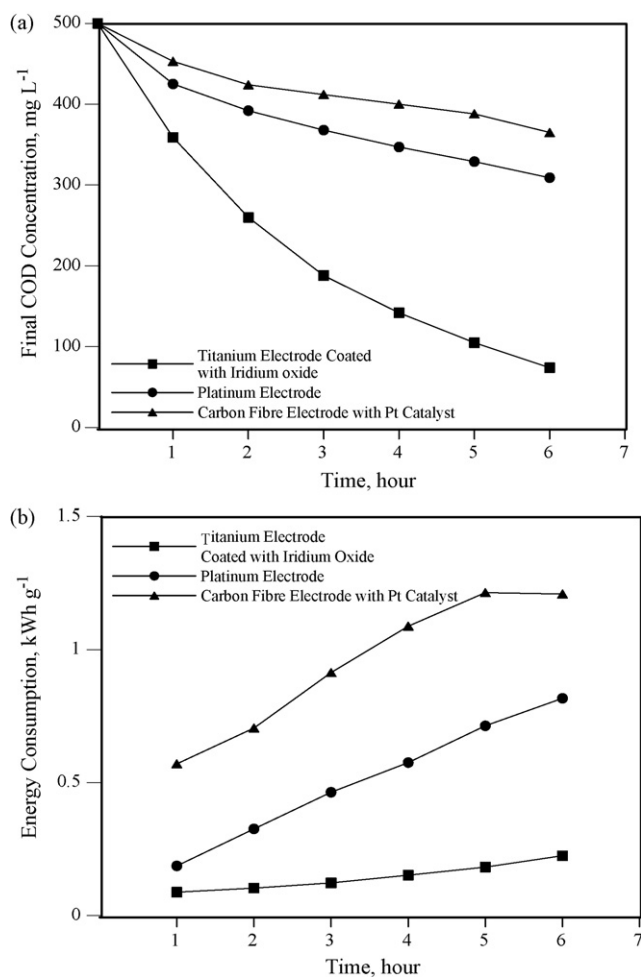
Fig. 9. Effect of type of electrode on final COD concentration and energy consumption (Current density: 25 mA cm^{-2}; flow rate: 150 mL min^{-1}).

pH values of 1.65 (original), 2.5 and 4 were studied to investigate the effect of initial pH of the solution. During the study, pH of 1.65 and 2.5 increased to 2.5 and 2.75, respectively. There was no significant pH change in the case of initial pH of 4. To obtain the effect of supporting electrolyte on the electrochemical system efficiency, 0.2 N and 0.4 N Na$_2$SO$_4$ were also added into the solution in certain experiments.

Electrochemical oxidation of oxalic acid solution at the anode has been determined by analyzing COD and energy consumption values have been calculated. Purity of hydrogen gas produced has been analyzed in an accredited Sentez Quality Control laboratory, İstanbul, Turkey. Hydrogen gas with purity of 99.999% at constant flow rate has also been observed at the cathode of the electrochemical reactor.

TOC analysis has been carried out at the optimum conditions of the electrochemical system to check the potential of the technique towards complete conversion to CO$_2$ and water.

HPLC has also been performed to obtain the intermediates formed after the electrochemical treatment of aqueous oxalic acid solution at the optimum conditions. The degradation of oxalic acid was monitored by high performance liquid chromatography (HPLC) using an Agilent 1100 system equipped with a diode array detector (DAD) and an autosampler. A Supelcogel H (9 μm, Ø = 7.8 mm × 300 mm) column was used in the experiments. The column was thermostated at 40 °C. The pressure was 40 bar during the analysis. 20 μL samples were injected. The column was eluted with 4 mM H$_2$SO$_4$ with a flow rate of 0.5 mL min^{-1}. Detection was performed at 210 nm.

3. Results

3.1. Effect of current density

The efficiency of an electrochemical system depends largely on the energy consumption per unit amount of organic removed. Energy consumption is directly affected by the current density applied to the system. Optimum conditions have been obtained at the current density of 50 mA cm^{-2} at the flow rate of 150 mL min^{-1} during the electrochemical treatment.

The effect of applied current density on the final COD concentration and energy consumption for this study is shown in Fig. 4(a). An increase in applied current density has resulted in an increase in the transport of the oxalic acid to the anode surface, therefore, in removal efficiency. The removal efficiency of 85% was achieved with an energy consumption of 0.225 kWh g^{-1} at a flow rate of 150 mL min^{-1} and a current density of 25 mA cm^{-2}. When a current density of 50 mA cm^{-2} was applied, a removal efficiency of 97% was achieved with an energy consumption value of 0.435 kWh g^{-1} at the same flow rate. As expected, applied voltage is increased due to increase in current density. An increase in applied voltage resulted in an increase in energy consumption as shown in Fig. 4(b).

3.2. Effect of flow rate

An increase in flow rate has resulted in an increase in COD removal as it can be seen in Fig. 5(a). When the systems are mass transfer controlled, there is a decrease in the film thickness, which resists to mass transfer, due to the increase in the flow rate. This case is typical for the mass transfer controlled systems [13].

Final COD concentration of 37 mg L^{-1} has been achieved at 80 mL min^{-1} at the current density of 50 mA cm^{-2} whereas 15 mg L^{-1} was obtained at flow rate of 150 mL min^{-1} at the same current density after electrochemical treatment of 6 h. There was no significant difference in energy consumption values at different flow rates as it can be seen in Fig. 5(b).

3.3. Effect of pH

The effect of pH on the final COD concentration and energy consumption is shown in Fig. 6. High removal efficiencies were obtained at all pHs. The final COD concentration of the oxalic acid solution at pH 2.5 and pH 4 were achieved as 12 and 10 mg L^{-1}, respectively, at the end of 6 h electrolysis. Energy consumption values were obtained 0.472 and 0.490 kWh g^{-1}, respectively, at the same duration.

Since almost equal final COD concentration of 15 mg L^{-1} and lower energy consumption of 0.435 kWh g^{-1} value have been obtained, the original pH of the solution (pH 1.65) can be preferred due to no need of chemical addition.

3.4. Effect of supporting electrolyte

The effect of supporting electrolyte on the final COD concentration is shown in Fig. 7(a). Supporting electrolyte has no positive effect on the removal efficiency. Final COD concentrations of 41 and 81 mg L^{-1} were achieved with 0.2 N and 0.4 N Na$_2$SO$_4$, respectively.

However, energy consumption has slightly decreased according to the decrease in voltage due to increasing conductivity as shown
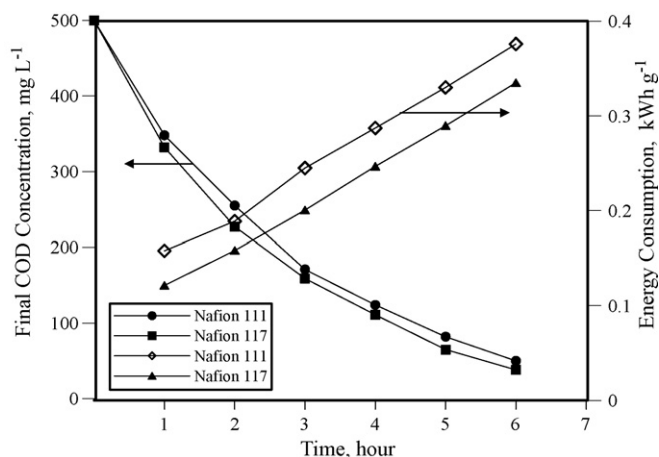
Fig. 10. Effect of membrane thickness on final COD concentration and energy consumption (Current density: 37.5 mA cm^{-2}; flow rate: 150 mL min^{-1}).

in Fig. 7(b). It has also been reported by Simond and Comninellis [14] that supporting electrolyte was not required to remove the organic matters effectively in the electrolysis system where solid polymer electrolyte was used in its cathode.

3.5. Effect of temperature

The effect of the solution temperature on the final COD concentration and energy consumptions are shown in Fig. 8. Final COD concentrations of 15 and 8 mg L^{-1} have been obtained at ambient temperature and at 50 °C, respectively, whereas it was 35 mg L^{-1} at lower temperature of 5 °C.

On the other hand lower energy consumption of 0.380 kWh g^{-1} has been observed at higher temperature as shown in Fig. 8(b). It has also been reported by Nagai et al. [15] that an increase in the temperature resulted in a decrease at applied potential causing a reduction of energy consumption.

Since the COD removal efficiencies are slight difference at ambient temperature and 50 °C and additional energy requirement will be needed to increase temperature of the solution, electrochemical treatment of the oxalic acid solution at ambient temperature is more applicable.
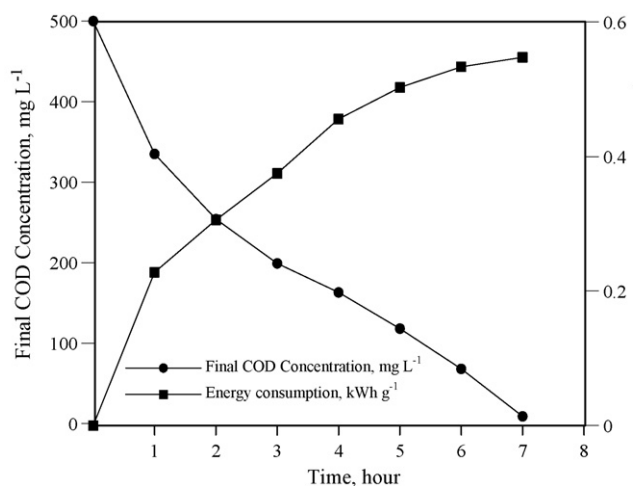
Fig. 11. Variation of final COD concentration and energy consumption with time for the model wastewater solution (Current density: 50 mA cm^{-2}; flow rate: 150 mL min^{-1}).
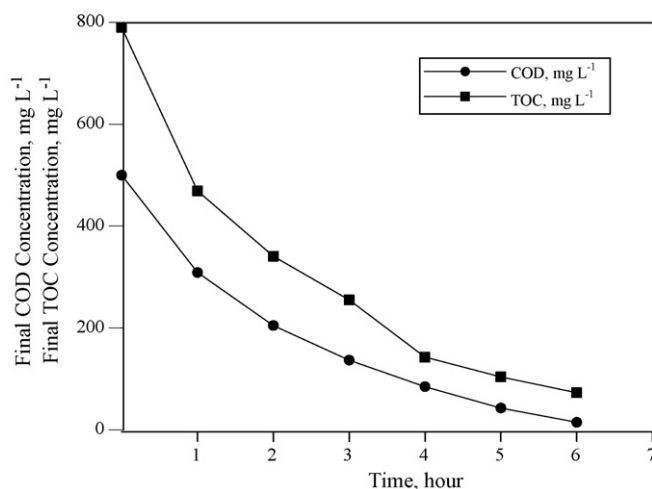
Fig. 12. Variation of TOC and COD concentration with time (Current density: 50 mA cm^{-2}; flow rate: 150 mL min^{-1}).

Table 1
TOC and COD analysis values

Time (h)	COD (mg L^{-1})	TOC (mg L^{-1})
0	500	790
1	309	469
2	205	341
3	137	255
4	85	143
5	43	104
6	15	73

3.6. Effect of electrode

To observe the effects of the type of electrode on COD removal efficiency and energy consumption, platinum electrode and carbon fibre electrode with Pt catalyst have also been used.

It can be seen in Fig. 9(a) that COD removal of 85% and 38% was achieved by using titanium electrode coated with iridium oxide and platinum electrode as anode, respectively, at the current density of 25 mA cm^{-2} after the electrochemical treatment of 6 h. Respective energy consumption values were 0.225 and 0.817 kWh g^{-1} as shown in Fig. 9(b).

When using the carbon fibre electrode with Pt catalyst as anode, lower COD removal of 27% with a higher energy consumption
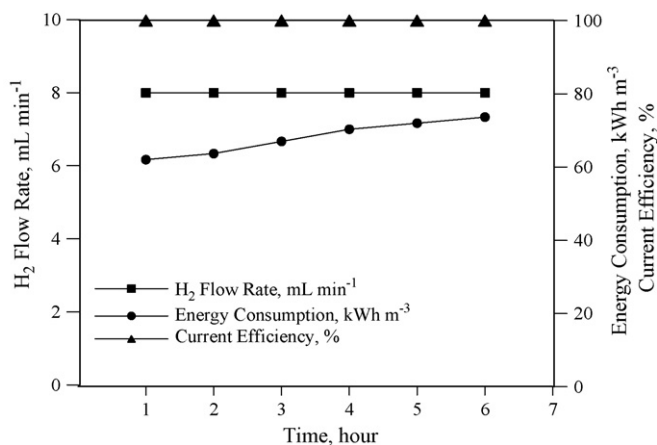
Fig. 13. Variation of current efficiency, energy consumption and flow rate of hydrogen with time (Current density: 50 mA cm^{-2}; flow rate: 150 mL min^{-1}).

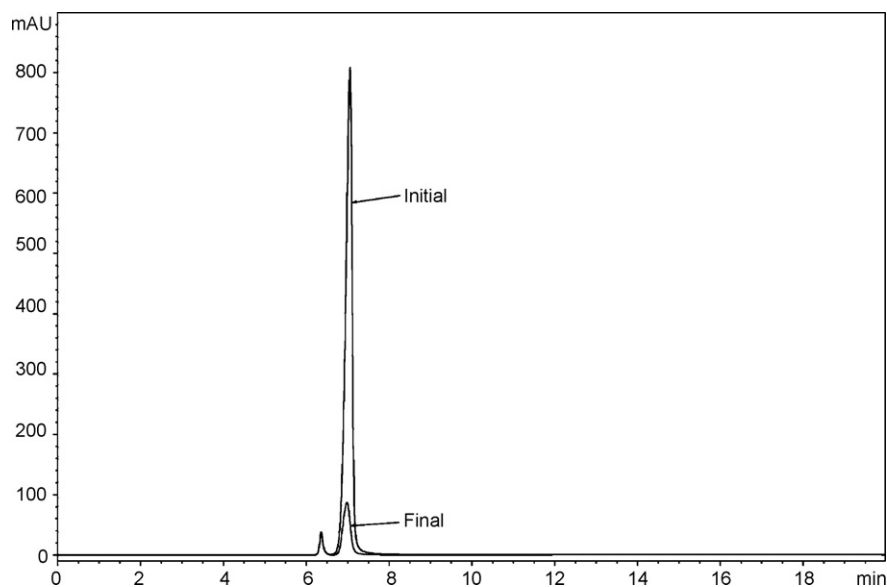**Fig. 14.** HPLC analysis result of aqueous oxalic acid solution (Current density: $50\,mA\,cm^{-2}$; flow rate: $150\,mL\,min^{-1}$).

of $1.209\,kWh\,g^{-1}$ at $25\,mA\,cm^{-2}$ has been obtained as shown in Fig. 9(b).

3.7. Effect of membrane thickness

The variation of final COD concentration and energy consumption for two types of membrane, Nafion 117 and Nafion 111, is shown in Fig. 10. Nafion 117 is slightly better regarding COD removal and lower energy consumption. The results suggest that oxalic acid can be successfully removed using both membranes.

Model solution containing oxalic acid and some of the other wastewater compounds was prepared in laboratory conditions and 98% of COD removal efficiency with energy consumption of $0.547\,kWh\,g^{-1}$ was obtained after electrochemical treatment of 7 h as it can be seen in Fig. 11.

TOC analysis has been carried out in the optimum conditions of the electrochemical system to check the potential of the complete conversion of oxalic acid to CO_2 and water. After this analysis, final COD concentration of $15\,mg\,L^{-1}$ and final TOC concentration of $73\,mg\,L^{-1}$ were obtained as shown in Fig. 12. Results of the TOC and COD analysis are illustrated in Table 1.

As aqueous oxalic acid solution can be treated to meet discharge limits at the optimum conditions by applying electrochemical oxidation, hydrogen gas with purity of 99.999% at constant flow rate with current efficiency of 99% can also be produced as shown in Fig. 13.

Electrochemical oxidation of oxalic acid to CO_2 and H_2O without production of any intermediate has been observed by HPLC analysis as it can be seen in Fig. 14.

4. Conclusion

In this study, the removal of oxalic acid as organic compound in the electrochemical reactor with SPE can be achieved efficiently by applying electrochemical oxidation. The results suggest that aqueous oxalic acid solution can be treated by using titanium oxide coated with iridium oxide as anode with COD removal efficiency of 97%. Hydrogen gas with purity of 99.999% with the current efficiency of 99% has also been produced, with this method.

Studies with model solution containing oxalic acid and some of the other wastewater compounds prepared in laboratory have shown that COD removal efficiency of 98% has been achieved after electrochemical treatment of 7 h. Complete electrochemical oxidation of oxalic acid to CO_2 and H_2O without production of intermediate has been proved by HPLC analysis.

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