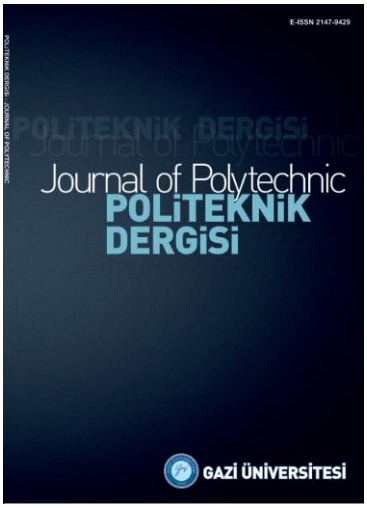

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Investigation of hydrogen production via black water electrolysis

Karasu elektrolizi yoluyla hidrojen üretiminin incelenmesi

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Investigation of Hydrogen Production via Black Water Electrolysis

Highlights

- *As an alternative to electrolysis of water, electrolysis of olive oil wastewater was discussed.*
- *Waste management was carried out by preventing black water accumulation.*
- *The effects of catalytic additive, temperature, electrode type, electrolyte, membrane were examined.*

Graphical Abstract

Hydrogen production was carried out by electrolysis of black water, which is a waste generated in olive oil production. In the electrolysis of black water with $FeSO_4$ and acidic electrolyte (H_2SO_4) using a pretreated Nafion XL membrane on the Zn/Zn electrode pair, pure H2 formation at the cathode was determined.

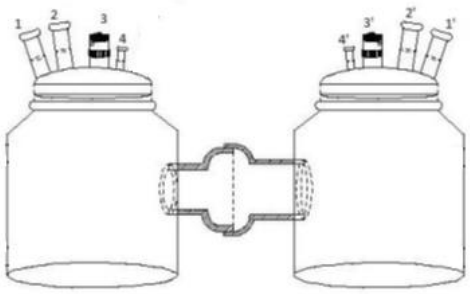

Figure. Schematic representation of experiment system

Aim

To contribute to waste management and hydrogen technology by producing hydrogen from blackwater, which is olive oil wastewater.

Design & Methodology

Electrochemical measurements were performed in the experiments. In order to optimize the working conditions, potential values versus current density were recorded in black water electrolysis.

Originality

Experiments were carried out in a unique two-compartment electrolysis cell.

Findings

The formation of pure hydrogen has been recorded at the cathode. 1.9 mA/cm^2 current density was obtained at 1 V potential and room temperature.

Conclusion

It has been proven that black water, which is a process waste, can be successfully utilized to produce hydrogen under conditions obtained from the results of this study.

Declaration of Ethical Standards

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Investigation of Hydrogen Production via Black Water Electrolysis

Araştırma Makalesi / Research Article

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ABSTRACT

As an alternative to hydrogen production by electrolysis of water, using as raw material waste valorization and organic pollutants in wastewater are crucial issues. In this context, electrolysis of black water, produced as waste in olive oil production and high energy source potential due to the aromatic compounds in its content, was carried out in this study. Parametric studies were carried out by examining the effect of working conditions on hydrogen production. The experiments using a two-chamber electrolysis cell examined the effects of catalytic additive ($Fe^{2+/3+}$), temperature (26ºC-60ºC-70ºC-80ºC), type of electrode (Cu/Cu, Zn/Zn and Pd/Pt) and electrolyte (H_2SO_4, H_3PO_4, HCl, $C_2H_2O_4$ and $C_2H_4O_2$), membrane and pretreatment applied to the membrane. In the electrolysis of black water with $FeSO_4$ and acidic electrolyte (H_2SO_4) using a pretreated Nafion XL membrane on the Zn/Zn electrode pair, pure H_2 formation at the cathode was determined. Under these conditions, 1.9 mA/cm^2 current density was obtained at 1 V potential and room temperature.

Keywords: Hydrogen, black water, olive oil wastewater, electrolysis, electrochemical reaction

Karasu Elektrolizi Yoluyla Hidrojen Üretiminin İncelenmesi

ÖZ

Suyun elektrolizi yoluyla hidrojen üretimine alternatif olarak atıkların değerlendirilmesi ve atık sudaki organik kirleticilerin hammadde olarak kullanılması önemli konulardır. Bu bağlamda, bu çalışmada zeytinyağı üretiminde atık olarak ortaya çıkan ve içeriğindeki aromatik bileşikler nedeniyle enerji kaynağı potansiyeli yüksek olan karasuyun elektrolizi gerçekleştirilmiştir. Çalışma koşullarının hidrojen üretimine etkisi incelenerek parametrik çalışmalar yapılmıştır. İki bölmeli bir elektroliz hücresi kullanılarak yapılan deneylerde, katalitik katkı maddesinin ($Fe^{2+/3+}$), sıcaklığın (26ºC-60ºC-70ºC-80ºC), elektrot tipinin (Cu/Cu, Zn/Zn ve Pd/Pt), elektrolit (H_2SO_4, H_3PO_4, HCl, $C_2H_2O_4$ ve $C_2H_4O_2$), membran ve membrana uygulanan ön işlemin etkisi parametrik olarak incelenmiştir. Zn/Zn elektrot çifti ve ön işleme tabi tutulmuş Nafion XL membranı kullanılarak karasuyun $FeSO_4$ katkısı ve asidik elektrolit (H_2SO_4) ile elektrolizinde katotta saf H_2 oluşumu belirlenmiştir. Bu koşullar altında 1 V potansiyelde ve oda sıcaklığında 1,9 mA/cm^2 akım yoğunluğu elde edilmiştir.

Anahtar Kelimeler: Hidrojen, karasu, zeytinyağı atıksuyu, elektroliz, elektrokimyasal reaksiyon.

1. INTRODUCTION

Most of the olive oil production processes take place in Mediterranean countries. These countries produce more than 15 M m3/year or about 98% of the world's olive oil production [1, 2]. In addition to the main products such as olive and olive oil, solid and liquid wastes and by-products such as "pomace" and "black water" are produced in olive oil factories. There are various processes in the production of olive and olive oil including batch, continuous and filtering. Although it varies depending on the production method, 20% olive oil, 30% semi-solid waste and 50% black water are obtained. In countries such as Australia and Spain, olive oil production is carried out in two phases modern process. For this reason, a large part of the waste generated after the process is released as pomace. In Turkey, traditional and three-phase modern processes are commonly used during olive oil production. In these processes, larger volumes of black water are formed compared to two-phase systems [3]. Figure 1 shows two production process in detail [4, 5].

Since black water in other words, olive mill wastewater (OMWW) cannot be used directly after it is obtained, it causes environmental pollution by discharging it to soil or water. All the olive producing countries in the world accept black water as a problem in olive oil production and use different alternatives for its solution [6].

N evertheless, black water should not be considered a waste and a problem; on the contrary it is an output that should be seen as a resource. Within this context, it can be seen as important regarding energy content and bioenergy. It is generally dark brown-black colored wastewater with a very high organic matter, polyphenol and solid content [7]. Black water is acid (pH 4–5.8), due to the self-oxidation reactions and polymerization of phenolic compounds [8].

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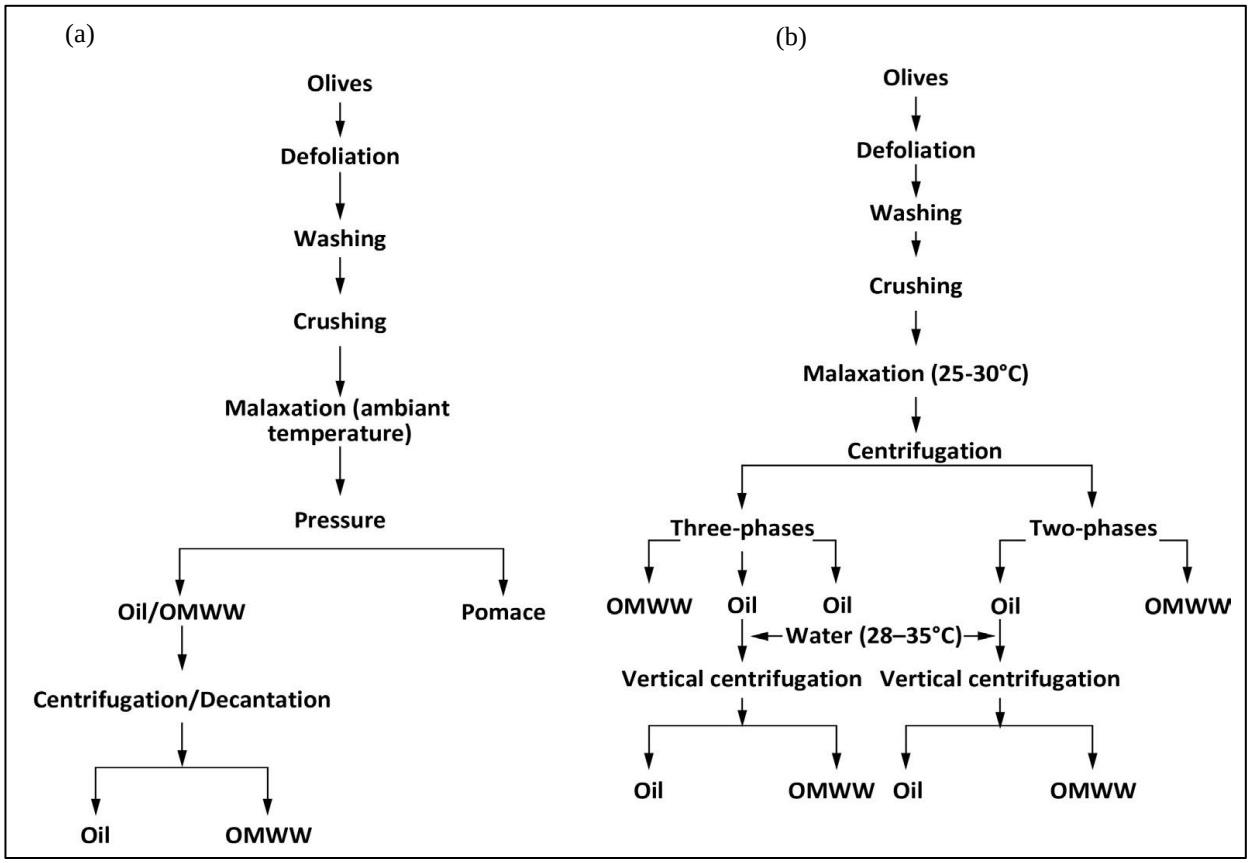


Figure 1. Production and extraction process of olive oil (a) traditional process, (b) modern process

A comparison of the components of various black water samples is given in Table 1. Black water is a complex mixture with a varying composition. This variation depends on several factors, including the method used to extract it, the specific type of olive used, and the biological properties of the olives themselves [13, 14]. An important factor to consider is the high level of Chemical Oxygen Demand (COD) often found in black water. COD indicates a high concentration of organic pollutants, which can have negative consequences for the environment. Discharging black water directly into soil or waterways can harm plant life and pollute clean water sources [15-17].

Black water is a waste that should be treated a resource of valuable components that should be recovered. Firstly many treatments of black water studies have been carried out. These are categorized as physico-chemical treatment (thermal, coagulation-flocculation, electro-coagulation, membrane process), biological treatment (aerobic, anaerobic, co-composting), oxidation treatment (wet oxidation, Fenton advanced oxidation, ozonation, photocatalysis) [18].

For example, when considering thermal treatment, the high moisture content of black water makes its direct thermochemical conversion not economically viable [19, 20]. Some of these techniques have several drawbacks such as groundwater contamination, bad smell, evaporation duration (limited by the formation of residual oil layer) and high cost requirement.

Table 1. Various black water components in the literature

Parameters	Ahmadi et al., 2005 [9]	Kestioğlu et al., 2005 [10]	Bettazi et al., 2006 [11]	Oz et al., 2013 [12]
pH	5.38	4.7	4.4-4.8	5.14
COD*, g/L	167-181	186	262-301	40.51
TSS**, g/L	36-39	65	-	12.59
Phenol, g/L	-	9.7	9.6-10.6	5.06
Oil-Grease, g/L	-	35	-	-
Total N, g/L	0.08	0.67	-	0.22
Total P, mg/L	5.2	0.18	-	0.24

*COD= Chemical Oxygen Demand, **TSS=Total Suspended Solids

On the other hand valorization seems to be better choice. There are studies on biofuels (methane and bioethanol) [21], bio-coal [22] and bio-fertilizer production from black water [23].

Generally, black water contains (by weight) 83-96% water, 3.5-15% organics, 0.5-2% mineral salts, 1.0-8.0% sugars, 0.5-2.4% nitrogenous compounds, 0.5-1.5% organic acids, 0.02-1.0% oils, 1.0-1.5% phenol and pectin [24]. It is likely to be utilized due to its rich organic structure. Black water also contains phenolic compounds such as tyrosol, hydroxytyrosol, protocatechnic acid, syringic acid, gallic acid, p-coumaric acid, caffeic acid, ferulic acid, vanillic acid and vanillin. It contains a high organic load and low biodegradability due to the high content of phenols. Phenol extraction can be performed by applying methods such as solvent extraction, adsorption on resins, supercritical fluid extraction and membrane separation. Polyphenolic compounds in its structure are used in the medical industry due to their antioxidant and anti-allergic properties [25]. Additionally, black water can be used to produce natural antimicrobials [26]. In addition, the phenolic structure provides functionality in the hydrogen formation of -OH groups in the structures of these phenolic compounds. This situation makes black water a subject to be studied on hydrogen production [27]. The transformation of waste black water into value-added products such as hydrogen with electrochemical process is a remarkable issue.

Electrochemical methods have been successfully applied to purify and valorize several industrial wastewater [28, 29]. A previous study on black water electrolysis electrolytic oxidation of black water containing a 4% (w/v) concentration of NaCl and using a Ti/Pt electrode as an anode was examined. They analyzed the black water content after electrolysis and commented on the efficiency of the process. They claimed complete degradation of polyphenols and total discoloration of black water [30]. In another study, they have investigated electrochemical treatment of diluted and raw black water in batch scale. Furthermore, they reported high polyphenol removal efficiency and no toxic by-products were generated [31]. In another study, it was reported that under the used electrochemical conditions, COD (chemical oxygen demand) and TOC (total organic carbon) reductions were nearly 55% [32].

All of these electrochemically applied methods are studies aimed at reducing the pollution caused by black water. There is no evidence of high value-added product and/or hydrogen production from black water using the electrochemical method from the literature. In this study, in line with the aims of environmentally friendly disposal of black water and obtaining valuable products from black water, it will be used to produce hydrogen with electrolysis, and waste management will be contributed by reducing the waste volume. Generally, the direct electro-oxidation rate of organic pollutants is dependent on the catalytic activity of the anode, on the diffusion rate of organic compounds in active area of the anode and applied potential. The indirect electro-oxidation rate depends on the diffusion rate, temperature and pH. Therefore, the effect of catalytic additive, electrode and electrolyte type, membrane and temperature were systematically investigated in the study.

The primary motivation of the study is to both reduce the pollution caused by the direct discharge of black water to the environment and to produce hydrogen by utilizing black water. Approximately 7 M m^3 of black water is generated as waste per year in olive oil production. When black water is released into the water, the light transmittance and oxygen amount in the environment decrease. This situation both negatively affects aquatic life and causes uncontrolled pollution of water resources. On the other hand, releasing black water into agricultural lands negatively affects the physical, chemical properties and quality of the soil, thus negatively affecting plant growth. With this study, black water was used as a raw material in hydrogen production, thus preventing the accumulation of black water as waste. Thanks to the phenol and various organic components in the structure of black water, it has been considered as a promising compound for hydrogen production.

2. MATERIAL and METHOD

In order to optimize the working conditions during the black water electrolysis, the current density values against the potential applied to the electrodes were recorded. GW Instek brand PSP-405 model programmable power supply was used at this stage. Since the current density values obtained are directly related to hydrogen formation, an opinion about hydrogen formation was obtained from these results [33]. The experiments were carried out in a unique electrolysis cell designed from pyrex glass, consisting of two-chambers, anode and cathode, and the chambers can be separated from each other by a membrane [34]. The total system volume is 1500 mL and the solution in the system was stirred continuously at 240 RPM (revolutions per minute) (25.13 rad/s). The mixing process was carried out on a heated magnetic stirrer (Are brand FB15001 model). Cu/Cu, Zn/Zn and Pd/Pt electrodes were used in the experiments. The distance between the electrodes is 12 cm. Different electrolytic media consisting of H_2SO_4, H_3PO_4, HCl, $C_2H_2O_4$ and $C_2H_4O_2$ were used to examine the electrolyte effect in the experiments. By using different acids, 0.04 M acidic environments were created. In addition, the effect of Fe2+/3+ ions used as additives in the system was investigated. For this purpose, 0.1 M FeSO4 solution was added to the system as a catalytic additive. The effect of this additive was determined by current density-potential change in the electrolysis cell and cyclic voltammetry (CV) method performed in a three-electrode cell. The flow chart containing main experimental steps is given in Figure 2.

In the CV method, Pt was used as the working electrode. During the experiment, the working electrode surface is contaminated due to adsorption and surface oxidation. This causes a decrease in the peak current and a shift in the peak potential.

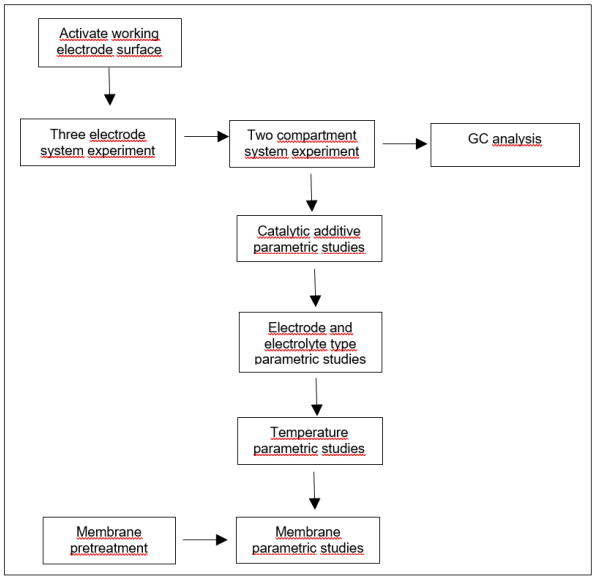


Figure 2. Flow chart of experimental steps

Therefore, the electrodes must be cleaned before the experiment. There are various pretreatment methods for cleaning the electrode surface, in other words for activating it. With the activation or cleaning process, the adsorbed substances that prevent the transfer of the electrode are removed from the surface and the microstructure of the electron surface is changed. For this purpose, the electrode surface is first made shiny and smooth. The electrode surface was polished with fine alumina in circular motions. In order to remove the alumina dust remaining on the surface of the electrode after polishing, the electrode was treated with an ultrasonic cleaner (Cole-Parmer brand, 8848 model) in a mixture of distilled water and then 50% acetonitrile and 50% isopropanol. 1.00×10^{-3} M ferricyanide solution was used to control the cleanliness of the Pt electrode. For this, the difference between the anode and cathode potentials in the alternating voltammetry experiment was taken as basis. On a clean electrode surface, the difference between the anode and cathode peak potentials should decrease at a scanning speed of 10 mV/s at CV of ferricyanide. This difference gives us an idea about the pollution of the electrode [35]. After the working electrode surface is cleaned, the three-electrode system was installed. The experiments were carried out without mixing since the reaction is diffusion-controlled during the CV measurement. Before starting the experiment, the black water solution was mixed and homogenized.

In two-chamber electrolysis cell system to determine the effect of temperature, the electrolysis of the black water solution with H_2SO_4 as the electrolyte and $FeSO_4$ as the catalytic additive was carried out at four different temperatures: room temperature (26ºC), 60ºC, 70ºC and 80ºC. In another experimental setup, experiments were carried out without a membrane and using a membrane that separates the anode-cathode compartments from each other. Nafion membrane, which is characterized by proton permeability and thermal stability, was used in the membrane system. Nafion XL (27.5 μm) membrane of Ion Power brand is used in the system. Since the cathode compartment, where hydrogen formed in the system, was separated by a membrane, it became a clean solution zone. In this way, the production and separation of pure hydrogen took place in a single step. The number of protons attached to the sulfonic acid group in the membrane structure was increased by pretreatment process applied to the membranes. In this way, the transition of protons from the anode to the cathode is facilitated and membrane performance is increased. Nafion XL membrane was pretreated according to the procedure described below in which membrane was consecutively kept in different solutions for different times [36].

- 3% H_2O_2 solution at 80ºC for 1 hour.
- Distilled water at 80ºC for 1 hour.
- 0.05 M H_2SO_4 solution at 80ºC for 1 hour.
- Distilled water at 80ºC for 1 hour.
- 2 M H_2SO_4 solution for 24 hours.
- Distilled water for 24 hours.

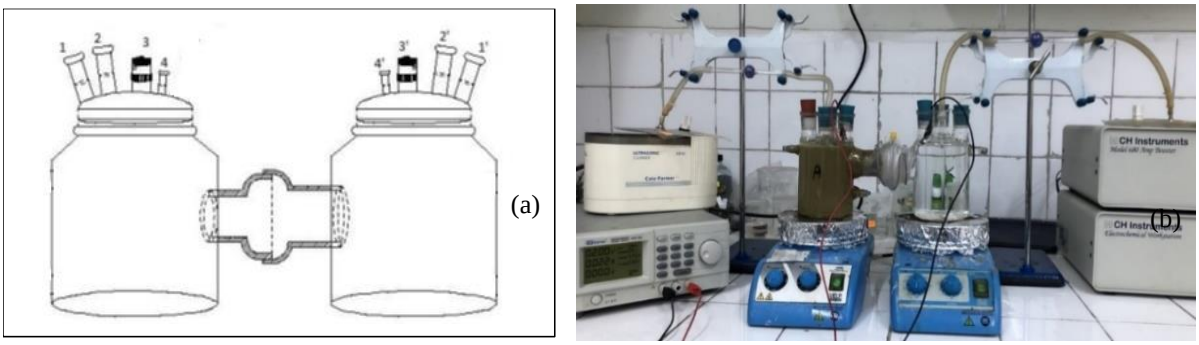


Figure 3. (a) Schematic representation (1/1': pH meter input, 2/2': electrode input, 3/3': gas outlet, 4/4': thermometer input) and (b) image of experiment system

The long-term electrolysis of black water in acidic medium at room temperature was investigated in a two-chamber membrane electrolysis system. The image of the experimental system is given in Figure 3. The gas products obtained in the anode and cathode compartments were analyzed in SRI-310C model gas chromatography (GC) with TCD detector.

3. RESULTS and DISCUSSION

3.1. Effect of Catalytic Additive

Before starting the experiment, it was subjected to CV analysis in ferricyanide solution to check the cleanliness of the Pt working electrode. The graph of the CV measurement taken before and after the electrode is cleaned is given in Figure 4a and Figure 4b, respectively.

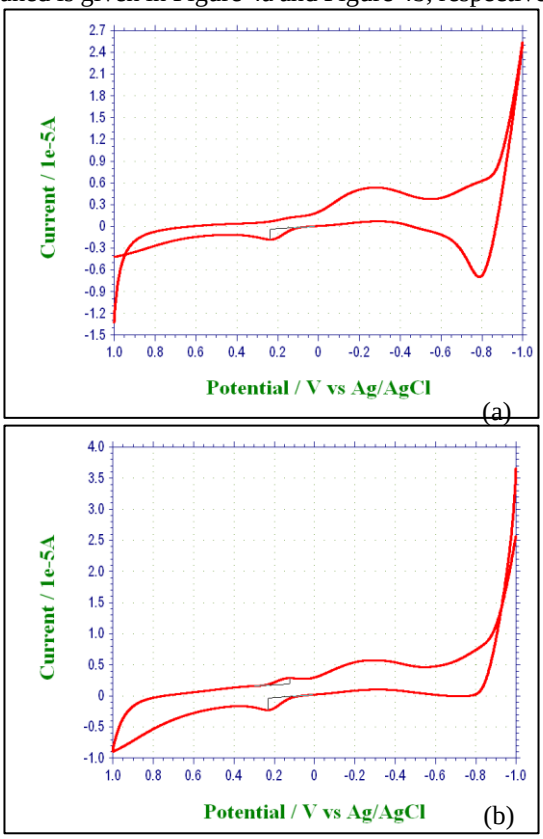


Figure 4. CV graph of Pt electrode in ferricyanide solution (a) before, (b) after cleaning process

In Figure 4a, it is seen that the cathodic peak occurs at about -0.3 V and the anodic peak at 0.24 V. There is 0.54 V (540 mV) difference between the two peak values. In Figure 4b, after cleaning the electrode, the cathodic peak occurred at 0.23 V and the anodic peak at 0.12 V. The difference has decreased to 0.11 V (110 mV). This is an indication that the electrode needs to be cleaned and that cleaning has been accomplished with this process.

Black water concentration is expressed in g/L. CV is not a very preferred method in solutions where the concentration value cannot be expressed in molar terms such as black water. The results obtained cannot be used in general electrochemistry equations since there is no solution concentration expression. However, CV method was used in black water because it is a fast method to obtain general information. In the case of using clean Pt as the working electrode, the effect of the catalytic additive on black water is given in the CV image in Figure 5. When Figure 5 is examined, the positive effect of $FeSO_4$ is seen especially at the negative potential limit. The increase in current density in the cathodic region is due to $Fe^{2+/3+}$ ions.

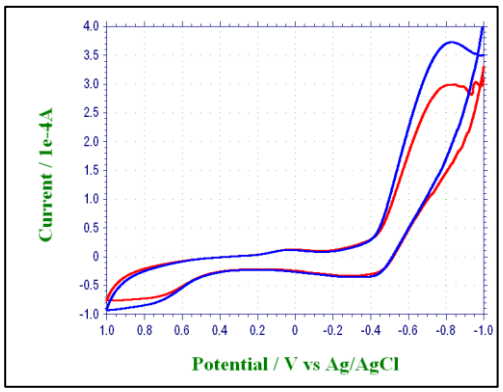


Figure 5. Investigation of $FeSO_4$ effect in acidic black water electrolysis for Pt working electrode by CV method (blue line: with additive, red line: without additive)

With this foresight, the effect of the catalytic additive on the current density-potential was determined in the two compartment system in the experiment using Cu/Cu electrodes. The current density-potential graph formed during the electrolysis of acidic black water samples with and without the added catalytic additive at 80°C is given in Figure 6.

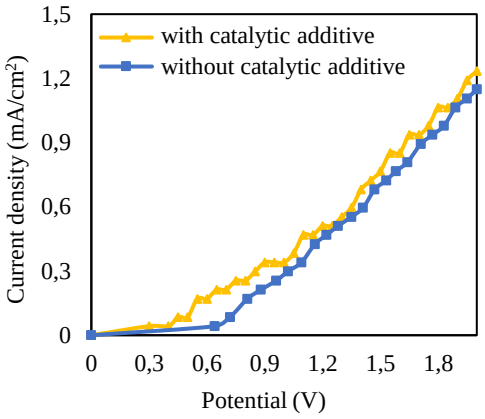


Figure 6. Effect of catalytic additive on current density-potential graph

It has been observed that the addition of $Fe^{2+/3+}$ has a positive effect on the current density. With the addition of $Fe^{2+/3+}$, the current density for 1 V at 80°C increased by 17% compared to the case without the addition of $Fe^{2+/3+}$. It is well-known that $Fe^{2+/3+}$ maybe utilized for oxidations of organic compounds in aqueous phase [37]. $FeSO_4$ was used as a catalytic additive in the following stages of the study, since it was seen that the current density values obtained increased with the addition of $FeSO_4$ both in CV experiments and in the current density-potential relationship.

3.2. Effect of Electrode and Electrolyte Type

In the previous studies graphite, titanium, platinum, ruthenium can applied as electrocatalyst for electrolysis of wastewater [38-40]. Within the scope of the study, affordable electrode alternatives that can be used in black water electrolysis are discussed. In addition to the effect of three different electrode pairs (Cu/Cu, Zn/Zn and Pd/Pt), five different electrolytic media (H_2SO_4, HCl, H_3PO_4, $C_2H_4O_2$, $C_2H_2O_4$) were also investigated. Only two studies directly related to black water electrolysis

have been found in the literature. Neutral electrolyte was used in both studies [30, 41]. In addition, in the previous studies, the treatment of black water was mostly discussed and comparisons were made regarding TOC and COD values. No data is included regarding the formation of hydrogen as a result of electrolysis.

The current density-potential graphs obtained during black water electrolysis are given in Figure 7 comparatively.

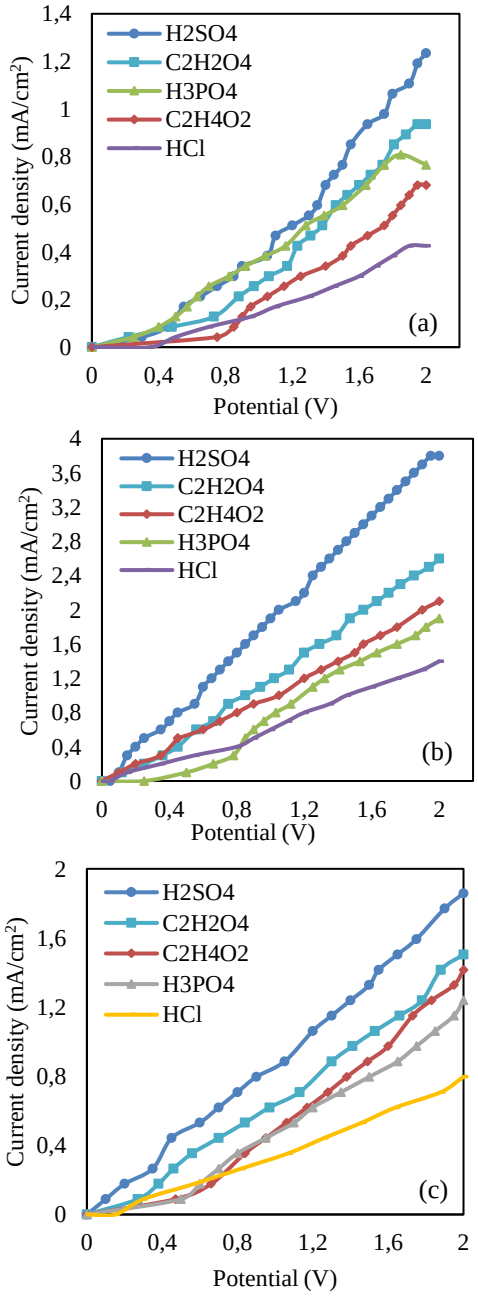


Figure 7. Current density-potential graph obtained in black water experiments at 80°C using different electrolyte solutions and (a) Cu/Cu, (b) Zn/Zn, (c) Pd/Pt electrode pairs

Since the acidity will increase as the K_a value increases, the current density values are expected to increase with the effect of H^+ ions given to the medium. The fact that the highest current density values are obtained when H_2SO_4 electrolyte was used for all electrodes confirms this case [41]. Therefore, current density-potential graphs obtained by using Cu/Cu, Zn/Zn and Pd/Pt electrodes in black water electrolysis with H_2SO_4 are given in Figure 8.

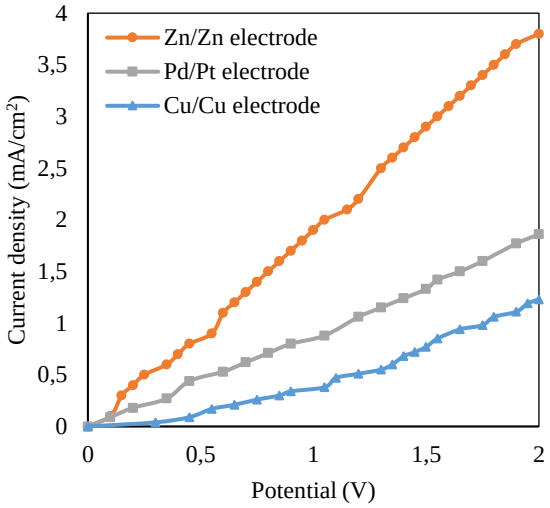


Figure 8. Electrode comparison for black water electrolysis with H_2SO_4

In the H_2SO_4 electrolyte medium, the highest current density value was reached when Zn/Zn electrode pair was used. When the current density values obtained at 1 V potential were compared, 4.2 times higher current density was obtained with Zn/Zn electrode pair compared to Cu/Cu electrode pair. Similarly, 2.2 times higher current density was obtained with Zn/Zn electrode pair compared to Pd/Pt electrode pair.

3.3. Effect of Temperature

In this study, the effect of temperature in the Zn/Zn electrode, H_2SO_4 electrolyte medium was investigated in the light of the results obtained in the experiments to determine the electrode and electrolyte type for black water electrolysis. The current density-potential graph obtained during the black water electrolysis at different temperatures is given in Figure 9.

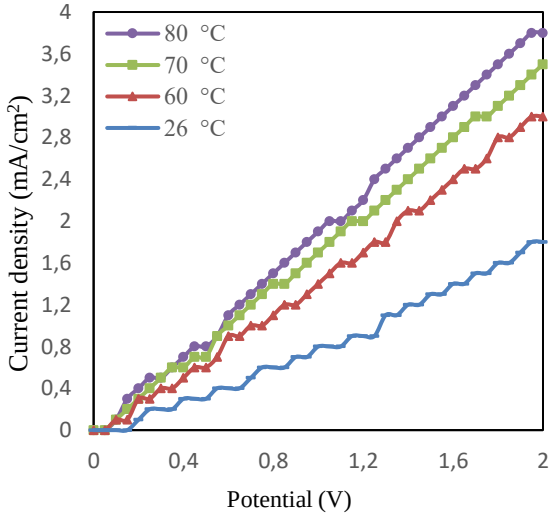


Figure 9. Current density-potential graph of black water electrolysis at different temperatures

The increase in temperature positively affects many electrochemical reactions due to reaction kinetics [42]. For 1 V potential, the current density value increased 2.4 times as the system was heated and the temperature increased from room temperature to 80°C.

3.4. Effect of Membrane and Pretreatment

Experiments were performed in the presence of Nafion XL membrane, using Zn/Zn electrode pair and 0.04 M H_2SO_4 electrolytic environment. The graph of the current density-potential obtained in the experiments performed in the black water electrolysis at room temperature and 80°C in the system with and without membrane is given in Figure 10.

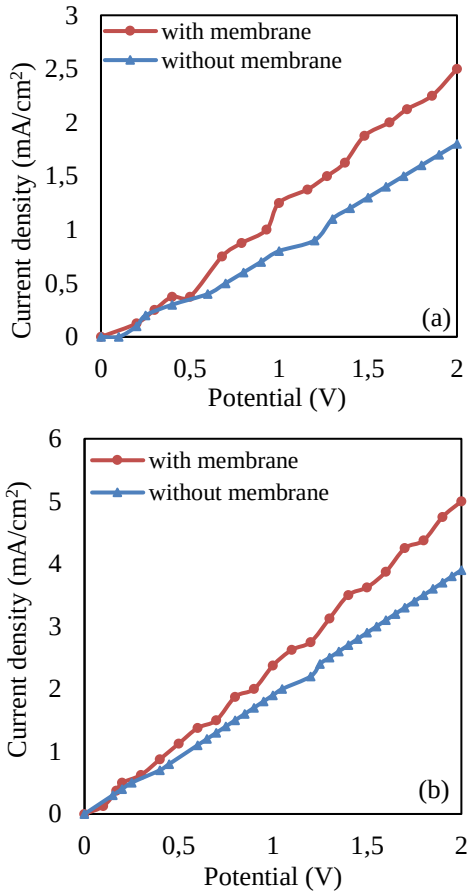


Figure 10. Current density-potential graph with and without membrane system (a) at room temperature and (b) at 80°C

When the results are compared, higher current density values were obtained in the system with the membrane. This is due to the selective permeable structure of the membrane. The structure of the membrane provides a positive effect on the direct transition of H^+ ions to the cathode.

The water molecules in the Nafion membrane form weak bonds with the proton, allowing the hydrogen ion to move from the anode compartment to the cathode compartment. It is treated with acid to activate the membrane and to increase the amount of water molecules per sulfonic group. After pretreatment, the water content and conductivity of the membrane increase [43]. The pretreatment applied to the membrane does not affect the surface morphology and functional groups of the Nafion membrane, but increases the proton permeability.

The current density-potential graph of the black water electrolysis at room temperature and at 80°C using activated and non-activated membrane by the given in Figure 11.

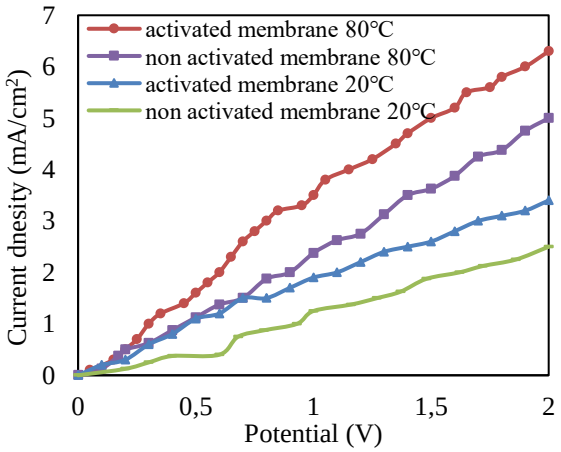


Figure 11. Current density-potential graph obtained in electrolysis at room temperature and 80°C when the pretreated membrane is used

It is known that the conversion increases as the applied potential increases [41]. Moreover with the effect of pretreatment applied to the membrane, the current density values increased by 36% and 26% for the experiment performed at room temperature and at 80°C, respectively. Gas chromatography results of gas products formed during the performance test are given in Figure 12 and 13. Under these conditions, the formation of pure H_2 at the cathode and CO formation at the anode were recorded.

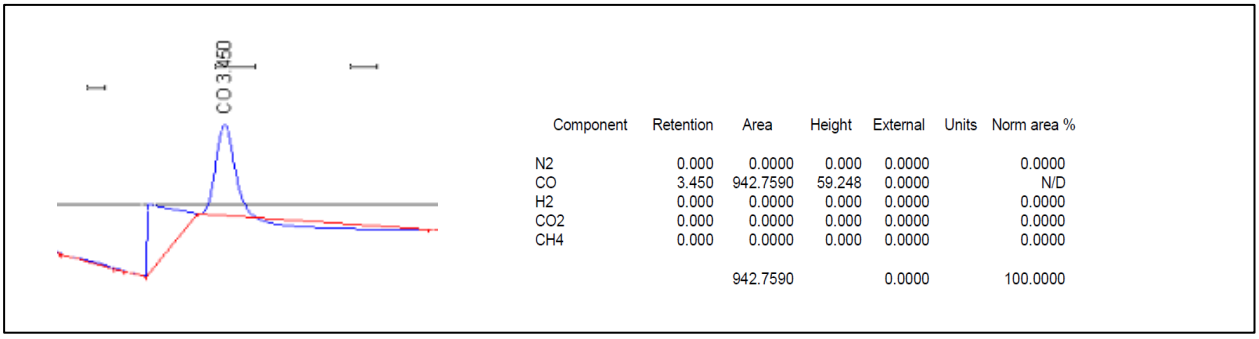
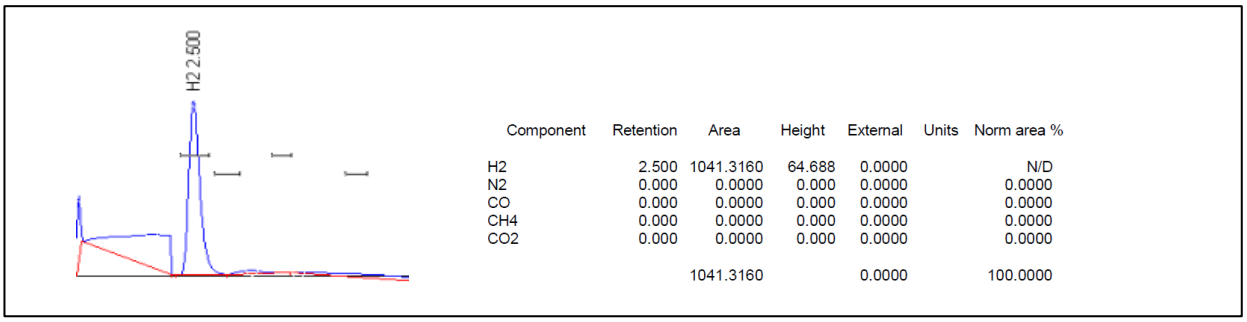


Figure 12. GC analysis of gas formed in the anode compartment



Component	Retention	Area	Height	External	Units	Norm area %
H2	2.500	1041.3160	64.688	0.0000		N/D
N2	0.000	0.0000	0.000	0.0000		0.0000
CO	0.000	0.0000	0.000	0.0000		0.0000
CH4	0.000	0.0000	0.000	0.0000		0.0000
CO2	0.000	0.0000	0.000	0.0000		0.0000
		1041.3160		0.0000		100.0000

Figure 13. GC analysis of gas formed in the cathode compartment

4. CONCLUSION

In the study, hydrogen production by electrochemical reforming method using black water, which is the waste produced during olive oil production, was investigated. Electrochemical methods have been successfully used in the purification or treatment of several industrial wastewater [44-46]. However, studies on hydrogen production by black water electrolysis are not common in the literature.

The direct electro-oxidation rate of wastewater is dependent on the catalytic activity of the anode and on the diffusion rate of organic compounds in the active points of the anode. On the other hand the indirect electro-oxidation rate is dependent on the diffusion rates of oxidant, temperature and pH. Here, parameters affecting the electro-oxidation rate were examined. For this purpose the most suitable operating condition for hydrogen production was determined by considering parameters such as catalytic additive, temperature, electrode materials and electrolyte type, membrane and pretreatment applied to the membrane. In H_2SO_4 medium current density values obtained 1 V potential were compared, 4.2 times and 2.2 times higher current densities were obtained with Zn/Zn electrode pair compared to Cu/Cu and Pd/Pt electrode pair respectively. These results show that electrode-electrolyte medium selection plays an critical role for electro-oxidation of black water. Additionally, pure hydrogen formation was achieved in the cathode section by separating the anode and cathode solutions from each other by using a membrane in the system. And also activating the membrane used with pretreatment procedures, increased the current density values obtained from the system by approximately 30%.

According to the current density values, use black water with $FeSO_4$ in H_2SO_4 electrolytic medium, using Zn/Zn electrode pair and activated Nafion XL membrane was determined as the most suitable condition for black water electrolysis. Under these conditions, pure H_2 formation was recorded at the cathode, according to the GC analysis results of the product gases obtained from the anode and cathode compartments. Hence, it has been proven that black water, which is a process waste, can be successfully utilized to produce hydrogen under conditions obtained from the results of this study.

SYMBOLS and ABBREVIATIONS

COD= Chemical Oxygen Demand

CV=Cyclic Voltammetry
GC=Gas Chromatography
OMWW=Olive Mill Wastewater
RPM=Revolutions Per Minute
TCD= Thermal Conductivity Detector
TOC=Total Organic Carbon
µm= micrometre

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DECLARATION OF ETHICAL STANDARDS

The authors of this a rticle declare that the materials and methods used in this study do not require ethical committee permission and/or legal- special permission.

AUTHORS' CONTRIBUTIONS

Merve GÖRDESEL YILDIZ: Conceptualization, Methodology, Formal analysis, Investigation, Writing - Original Draft, Visualization.

Özgü YÖRÜK: Conceptualization, Methodology, Formal analysis, Investigation, Visualization

Duygu UYSAL: Conceptualization, Methodology, Validation, Writing - Review & Editing, Supervision

Özkan Murat DOĞAN: Conceptualization, Methodology, Validation, Writing - Review & Editing, Supervision

CONFLICT OF INTEREST

There is no conflict of interest in this study.

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