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Treatment of Oilfield Produced Water Using Three Electrochemical Processes: Comparative Study

Wahbi Al-Ameri[1], Ahmed Elhassan[2], Ragaei Maher[3]

[1]University of Khartoum (Sudan) and University of Hadhramout (Yemen)
[2]University of Khartoum, Khartoum, Sudan
[3]Greater Nile Petroleum Operating Company (GNPOC), Sudan
(E-mail: wahbi737@gmail.com)

Abstract: Although various techniques exist for remediation of wastewater, electrochemical technology and electrochemical advanced oxidation processes are the most promising and innovating methods for destroying and eliminating a broad-range of organic and inorganic contaminants presented in the produced water effluents. This study presents integrated electrochemical treatment techniques including electrocoagulation process, electrooxidation process and electro-Fenton process for a real produced water, supplied by an oil company. The electrocoagulation method was conducted by iron and aluminum electrodes, electrooxidation method by graphite electrodes and the electro-Fenton method by iron and graphite electrodes. The experiments were performed in the same electrolytic batch cell with the same spacing between electrodes and electrode surface. The feasibility of treatment processes was monitored by the removal of total organic carbon (TOC) and chemical oxygen demand (COD).As a result of the study, the most efficient technology was the electrooxidation process where the removal efficiencies of TOC and COD were 93.5 % and 94 %, respectively. Additionally, electro-Fenton process led to higher removal efficiencies reaching 85 % and 87 % for TOC and COD, respectively. The electrocoagulation treatment of produced water by using iron and aluminum electrodes was moderately efficient for removal of TOC. However, it was inefficient for removal of COD. Furthermore, electrocoagulation remediation was proved to be an effective method for removal of inorganic species such as calcium, magnesium and sulfate. It can be concluded that electrochemical methods could be used for effective produced water treatment where it can be safely disposed of or effectively reused for injection and irrigation.

***Keywords**: Electrochemical technologies, Produced water, Electro-oxidation, Electro-Fenton, Removal.*

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1. INTRODUCTION

Produced water is any water present in the reservoirs which is produced along with the oil and gas. The reuse of produced water for hydraulic fracturing and water injection in oil and gas industry is becoming more attractive especially in locations that have scarcity in fresh water. Also, it can be used for other purposes such as irrigation and roads dust management. However, the impurities such as organic materials, metals, suspended solids, bacteria and hardness elements which exist in the produced water may cause its recycling ineffective. Therefore, the produced water must be treated to remove these contaminants to meet the operational goals.

There are many technologies used for conducting water treatment such as flocculation, coagulation, reverse osmosis, electrochemical technology (ET) and electrochemical advanced oxidation processes (EAOPs). ET and EAOPs represent the promising alternative technologies for degradation and mineralisation of organic and inorganic substances presented in the wastewater effluents. These technologies have the ability to treat and process challenging and toxic impurities which are difficult to treat with conventional chemical or biological processes. In addition, they have many advantages including high energy efficiency, safety, versatility and environmental compatibility.

Most studies have applied ET and EAOPs in the treatment of other industrial and municipal wastewaters but few focused on produced water from oil and gas industry. Ma and Wang [**17**] used an electrochemical method for treating the produced water to get the treated water for injection purposes. To achieve the treatment, iron as cathode and double anodes with graphite (C) and active metal (M) were used.

The results showed that both biochemical oxygen demand (BOD) and COD concentrations dropped by over 90 % in 6 min, calcium (Ca^{2+}) content by 22 %, total suspended solids (TSS) by 99 %, bacteria by 99 % and corrosion rate by 98 %. Ramalho et al. [**23**] addressed the anodic oxidation of organic contaminants in real produced water by changing the electrolyte flow rate. Dimensionally stable anode (DSA) (RuO_2–TiO_2–SnO_2) was used in their work. Under the galvanostatic condition where current density = 89 mA/cm^2, it was noted that the removal efficiencies were affected by the flow rates where they reached 98, 97, 95 and 84 % at flow rates of 0.25, 0.5, 0.8 and 1.3 dm^3/h, respectively. A complete degradation of organic contaminants was obtained between 0.5 to 2.5 h. Cardoso et al. [**6**] used a combination of oxidation, coagulation and flocculation technologies for treating the produced water from offshore. The results showed that total oil and grease (TOG) was removed completely and turbidity and color were reduced effectively. However, the removal of TSS was not affected by the treatment.

Rocha et al. [**24**] investigated the removal of organic pollutants from petrochemical produced water by using anodic oxidation process. Boron doped diamond (BDD) and Ti (Ti/Pt) were used as anodes. Under galvanostatic condition, 98 % COD removal was obtained by using BDD, and it was also found that the degradation efficiency increased as the current density rose from 15 to 60 mA/cm^2. The high degradation was attributed to the generated powerful radicals, OH*, and peroxodisulfates. However, COD was removed by 50 % at 15 and 30 mA/cm^2 when Pt electrode was used. This value reached 80 % at 60 mA/cm^2.

Da Silva et al. [**8**] studied the anodic oxidation of petrochemical produced water with different salinity using Ti/IrO_2-Ta_2O_5 and BDD electrodes. They observed that the removal efficiencies of COD and TOC using BDD were better than Ti/IrO_2-Ta_2O_5 under the same operating conditions. However, BDD showed higher values for both energy consumption and cost.

Gargouri et al. [**12**] compared the removal efficiencies of COD and total petroleum hydrocarbon (TPH) presented in real produced water using BDD and lead dioxide (PbO_2) by applying anodic oxidation. The final result of this study showed that BDD was more efficient than PbO_2 with 96 % and 85 % COD removal after 7 and 11 h, respectively.

Yan et al. [**29**] compared the impact of introducing iron particle (Fe^{2+}) and air simultaneously and separately into a real petroleum refinery wastewater by using electro-Fenton treatment. They found that simultaneous introduction was better at pH of 3, where the reduction in COD and NH_3-N were 89.91 % and 99.47 %, respectively.

Araújo et al. [**3**] treated a synthetic produced water by using DSA anode [Ti/ $(RuO_2)_{0.7}(IrO_2)_{0.1}(Sb_2O_3)_{0.2}$]. It was noted that 93.4 % and 99.8 % removal efficiencies for naphthalene and benzene were obtained at operating conditions of 2.4 V and 2 h, respectively.

Darvishmotevalli et al. [**7**] applied response surface methodology (RSM) to optimize the variables for the removal of TOC and COD from synthetic wastewater. The parameters considered in their work were voltage, salt concentration, pH and reaction time. They found that the optimal conditions were voltage of 7.41 V, salt content of 30. 94 g/L, pH of 7.69 and reaction time of 30.71 min. These conditions were applied on the experimental work and they found that there was agreement between the model and experimental results where COD and TOC removal efficiencies were 91.78 % and 68.49 %, respectively.

It is clear from the previous literature review that some of electrodes are relatively effective for destroying organic contaminants. However, they are very expensive and it is difficult to use them for large-scale application such as BDD. In addition, some of them have high risk of contamination such as PbO_2 electrodes which prevent their practical applications. Therefore, there is a need for trying different electrodes for the treatment to get electrodes that have low cost and better treatment efficiency. Furthermore, there is no obvious idea about the classes of contaminants that will be removed or reduced by using these treatment processes.

The main objective of this study is to apply the ET and EAOPs to come up with an innovative, cost-effective treatment process for the produced water to be reused or recycled or safely disposed. The electrocoagulation, anodic oxidation and electro-Fenton processes will be the main techniques that will be used for the produced water treatment in this research by using different types of electrodes.

Materials and methods

Produced water samples

Representative samples have been collected from an oil company. The produced water samples were stored at 4°C in a freezer to avoid the change of its properties. Many tests have been carried out for knowing the description and properties of the produced water such as salinity, conductivity, TOC, COD, total dissolved solid (TDS) and the metals content. The composition and properties of produced water are reported in **Table 1**. One can see from this table that produced water contains organic compounds (COD), heavy metals and solid ions. Therefore, it needs to be treated to remove these pollutants.

Table 1. The composition and properties of produced water under this study.

Parameter	Value	Heavy metals (ppm)	Value
pH	8.34	Aluminium (Al)	0.014
Turbidity, NTU	0.487	Cadmium (Cd)	0.0012
Conductivity, mS/cm	3.15	Chromium (Cr)	<0.0006
Salinity, ppm	1400	Copper (Cu)	<0.0158
TSS, mg/L	29	Cobalt (Co)	0.0004
TDS, mg/L	1894	Iron (Fe)	0.014
Total hardness, mg/L	332	Lead (Pb)	0.001
Alkalinity, mg/L	400	Manganese (Mn)	0.007
Resistivity, Ohm.cm	317.46	Nickel (Ni)	<0.0006
COD, mg/L	387.6	Zinc (Zn)	<0.0015
TOC, mg/L	129.2	Boron (Br)	-
Flouride, mg/L	1.11	Silicon (Si)	13.59
N.Amonia, mg/L	0.294	Barium (Ba)	0.245
Sulfate, mg/L	700	Phosphorus (P)	0.12
Nitrite, mg/L	0.02	Strontium (Sr)	4.732
K, mg/L	525	Titanium (Ti)	0.0001
Na, mg/L	577	Vanadium (V)	0.067
Ca, mg/L	60	Molybdenum (Mo)	0.0002
Mg, mg/L	43.68	Lithium (Li)	0.624

Chemicals

Na_2SO_4, NaCl and $FeSO_4.7H_2O$ of analytical grade (Merck) were used. 0.1 M solutions of NaOH and H_2SO_4 were used for pH adjustment. NaCl and Na_2SO_4 were utilized as supporting electrolyte to increase the conductivity of solution and thus decrease the resistance and the consumption of electrical energy. $FeSO_4.7H_2O$ as catalyst was used to generate ferrous ions which are required for electro-Fenton process. 1 M solution of H_2O_2 was used for electrocoagulation and electro-Fenton processes.

Electrolytic systems

The studies were conducted in a lab-scale reactor where all electrochemical treatments including electrocoagulation, electrooxidation and electro-Fenton processes were performed in reactor consisting of a 500 ml glass beaker equipped with electrodes as illustrated in **Figure 1**. A laboratory model direct current (DC) power supply system (EL302R) was used to supply DC power at the desired constant voltage (in the range of 0 to 32 V) or constant amperage (in the range of 0 to 2 Amp.). The solution was rigorously stirred with a magnetic bar at 500 rpm to enhance the mass transport towards the electrodes. The gap distance between the anode and cathode was 1.5 cm. Electrolyses were carried out at room temperature and different current densities were applied to achieve the treatment where the voltage was adjusted manually to get constant current density. After each run, the electrode plates were cleaned with HCl or acetone followed by distilled water to remove impurities from the electrode surface.

For electrocoagulation, two parallel plate electrodes (obtained commercially) as anode and cathode, namely, Fe-Fe and Al-Al, were used and housed vertically inside the reactor. Each of them has 6 cm length, 6 cm width and 1 mm thickness with apparent area of 36 cm^2. The pH solution of 8.34 was not adjusted. The supporting electrolyte was 3 g/0.5 L of NaCl. The applied current density was 10 mA/cm^2. The treatment was left for 80 min.

For electrooxidation, two parallel plate electrodes (obtained commercially) as anode and cathode, namely, graphite-graphite, were utilized and positioned vertically inside the electrochemical cell. Each of them has 6 cm length, 6 cm width and 5 mm thickness with apparent area of 36 cm^2. The supporting electrolyte was 3 g/0.5 L of NaCl. Lower value of current density was applied (5 mA/cm^2). The value of pH was changed to get the optimum one for the treatment. The treatment was left for 80 min.

For electro-Fenton, two parallel plate electrodes (obtained commercially) as anode and cathode, namely, Fe-Fe, graphite-graphite were used and placed vertically inside the electrolytic cell. Each of them has 6 cm length, 6 cm width and 1 mm thickness for Fe and 5 mm thickness for graphite with apparent area of 36 cm^2. The pH solution was adjusted to 3 by using 0.1 M solutions of NaOH, and H_2SO_4. The supporting electrolyte was 3 g/0.5 L of Na_2SO_4. The applied current density was 5 mA/cm^2. During the electroprocessing, 6 ml of H_2O_2 1 M solution was added. $FeSO_4.7H_2O$ was used as catalyst for generating Fe^{2+} ions. The treatment was left for 80 min.

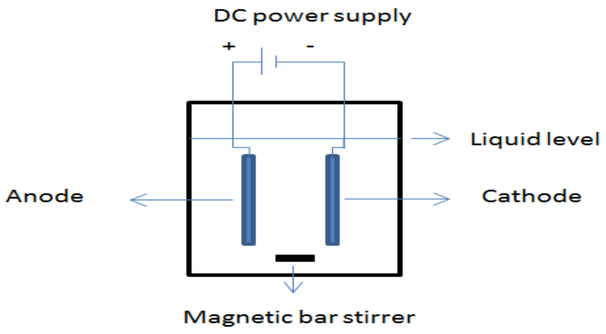

Fig.1. Schematic for the electrochemical treatment reactor

Investigated parameters

The removal efficiency of the pollutants and the electrical energy consumption are estimated as follows:

Removal efficiency

The removal efficiency of the pollutants presented in the produced water was estimated from the following formula:

$$RE = \left[\frac{X_i - X_o}{X_i}\right] * 100\ \% \tag{1}$$

Where:

RE = Removal efficiency

Xi = Initial pollutant concentration presented in the produced water before the treatment in mg/L

Xo = Final pollutant concentration presented in the produced water after the treatment in mg/L

Electrical energy consumption

The energy consumption was calculated from the following formula [**1**]:

$$EC = \left[\frac{(T * V * \frac{A}{S_v})(1 * 10^{-3})}{(\Delta COD * 1 * 10^{-6})}\right] \tag{2}$$

Where:

EC = The consumption of energy in KWh/kg of COD

T = Electrolysis time in h

V = Potential of cell in V

A = Current of electrolysis in A

Sv = Sample volume in L

ΔCOD = The difference in COD in mg/L

Treatment mechanism

(1) Electrocoagulation (EC)

In electrocoagulation process, metallic hydroxide is generated from metal dissolution (anode). Moreover, hydroxyl ions (OH^-) and hydrogen gas (H_2) are produced at the cathode [**9**, **10**, **27**]. In this study, the electrocoagulation by using iron and aluminum electrodes were applied.

Electrocoagulation by using iron electrodes

In this process, ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions are formed from sacrificial anode oxidation and H_2 and OH^- ions are generated from the reduction of water at cathode as explained in following equations [**27**]:

At anode:

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

$$Fe \rightarrow Fe^{3+} + 3e^- \tag{4}$$

At cathode:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{5}$$

The produced OH^-, Fe^{2+} and Fe^{3+} ions from the oxidation and reduction reactions react to generate different polymeric and monomeric compounds which finally result in situ formation of hydroxide flocs $Fe(OH)_2$ and $Fe(OH)_3$ as shown in following equations:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \tag{6}$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \tag{7}$$

These hydroxide flocs act as adsorbents for pollutants such as organic materials, ions and heavy metals leading them to the coagulation and coprecipitation. Also, H_2 leads to the flotation of pollutants from the wastewaters by adsorption [**13**].

Electrocoagulation by using aluminum electrodes

Electrocoagulation process by using aluminum electrodes leads to produce aluminum ions at anode and OH^- ions as well H_2 at the cathode [**10**]:

At anode:

$$Al \rightarrow Al^{3+} + 3e^- \tag{8}$$

At cathode:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{9}$$

The produced Al^{3+} and OH^- ions react to form numerous monomeric and polymeric compounds such as $Al(OH)^{4-}$, $Al_7(OH)_{17}^{4+}$ and $Al_{13}O_4(OH)_{24}^{7+}$ which finally result in situ formation of gelatinous $Al(OH)_3$ effecting the coagulation and coprecipitation. In addition, H_2 leads to flotation of particulates such as free oil and heavy metals from the solution by adsorption [**10**,**15**].

(2) Electrooxidation (EO)

This process can be divided into direct and indirect electrooxidation. In direct electrooxidation, the OH^* radicals are generated at the anode surface (**Eq.10**) and pollutants are directly oxidized on the anode.

$$H_2O \rightarrow OH^* + H^+ + e^- \quad (10)$$

In indirect electrooxidation, strong oxidants such as hydrogen peroxide, ozone and hypochlorite are produced in the bulk solution [**16**]. The following reactions show the formation of these oxidants [**4**]:

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (11)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (12)$$

$$HOCl \rightarrow H^+ + OCl^- \quad (13)$$

$$Cl^- \rightarrow Cl^* + e^- \quad (14)$$

$$Cl^- + OH^* \rightarrow Cl^* + OH^- \quad (15)$$

$$OH^- \rightarrow OH^* + e^- \quad (16)$$

$$H_2O \rightarrow OH^* + H^+ + e^- \quad (17)$$

$$2OH^* \rightarrow H_2O_2 \quad (18)$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \quad (19)$$

$$O_2 + O^* \rightarrow O_3 \quad (20)$$

These oxidants destroy and convert the organics and organometallic materials into stable compounds such as CO_2, water and inorganic ions as shown in the following equations:

$$\text{Organic pollutants} + \text{oxidants} \rightarrow \text{oxidation intermediates} \quad (21)$$

$$\text{Intermediates} + \text{oxidants} \rightarrow CO_2 + H_2O + \text{inorganic ions} \quad (22)$$

(3) Electro-Fenton (EF)

In the electro-Fenton process, OH^* radicals are formed from the reaction between Fe^{2+} and H_2O_2 in acidic solution as follows [**18**, **20**, **26**]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^* + OH^- \quad (23)$$

Fe^{2+} and H_2O_2 are produced and found in electro-Fenton experiments in two ways [**9**, **10**, **27**]:

- Fe^{2+} is added while H_2O_2 is electro-generated on a cathodic surface (**Eq. 24**) or Fe^{3+} is added and both H_2O_2 (**Eq. 24**) and Fe^{2+} (**Eq. 25**) are electro-generated on a cathodic surface:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (24)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (25)$$

- Fe^{2+} is generated from a sacrificial anode (**Eq. 26**) while H_2O_2 is added:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (26)$$

In this technology, the organic contaminants can be eliminated by oxidation with OH^*radicals as in (**Eqs.27** and **28**) and at the same time by electrocoagulation with $Fe(OH)_3$ precipitate [**5**, **30**].

$$\text{Organic pollutants} + OH^* \rightarrow \text{oxidation intermediates} \quad (27)$$

$$\text{Intermediates} + OH^* \rightarrow CO_2 + H_2O + \text{inorganic ions} \quad (28)$$

Results and discussion

(1) Electrocoagulation (EC)

In electrocoagulation experiments, the most common electrodes (iron and aluminum) were used for the treatment.

(i) Electrocoagulation by using iron electrodes

During the experiment, it was observed that there was significant change in current over time, indicating a change in the resistivity of the solution. In addition, it was noted that there were precipitation and flotation of the impurities. The initial COD of 387.6 mg/L decreased slightly to 334.7 mg/L in 80 min of electrolysis time, showing a reduction of about 13.64 % and the initial TOC of 129.2 mg/L reduced to 63.15 mg/L in 80 min of electrolysis time, showing a decrease of about 51.12 %. Based on the experimental results, it can be concluded that the electrocoagulation treatment of produced water by using iron electrodes was moderately efficient for removal of TOC. However, it was inefficient for removal of COD. This is because of COD removal is more difficult since the produced water generally has a variety of organic and inorganic contaminants.

(ii) Electrocoagulation by using aluminum electrodes

When the aluminum was used as electrode, it was noted that there was substantial variation in current over time, indicating a change in the resistivity of the solution. Furthermore, it was noted that there were precipitation and flotation of contaminates. The initial COD of 387.6 mg/L dropped slightly to 284.8 mg/L in 80 min of reaction time, showing a decline of about 26.52 % and the initial TOC of 129.2 mg/L decreased to 56.95 mg/L in 80 min of reaction time, showing a reduction of about 56 %. Based on the experimental results, it was noted that the aluminum plate has higher removal efficiency compared to iron plate in the same experimental conditions. This is likely because $Al(OH)_3$ effecting the coagulation and coprecipitation was higher than that for $Fe(OH)_2$ and $Fe(OH)_3$. Also, it can be seen that the electrocoagulation remediation of produced water by using aluminum electrodes was still moderately effective for elimination of TOC. On the other hand, it was ineffective for elimination of COD. This is because COD removal is more complicated since the produced water normally has a diversity of organic and inorganic pollutants.

Moreover, the results showed that there was significant removal for inorganic species such as heavy metals and solid ions as reported in **Tables 2** and **3**. Inorganic species cause many problems. For example, calcium ions lead to the formation of scales when they combine with carbonate, bicarbonate or sulfate ions. Similarly, magnesium ions cause scaling by co-precipitating with the calcium ions. The presence of iron is usually indicative of corrosion. Also, sulfate is the main source for different types of scale such as calcium sulfate, barium sulfate and strontium sulfate. These results indicated that electrocoagulation treatment could be also used for removing inorganic species from produced water.

In addition to the previous experiments, electrocoagulation by using Fe-Fe, Al-Al, electrodes and supplied H_2O_2 was carried out. **Table 4** outlines the results obtained from the previous and current work. Generally, it can be seen from this table that adding the H_2O_2 to the solution led to a slight increase in the removal efficiency. As for Fe-Fe electrodes, TOC and COD removal efficiencies were increased by 7% and 19 %, respectively. TOC and COD removal efficiencies were rose by 2 % and 3 %, respectively, when Al-Al electrodes were used. The increase in the removal efficiencies was due to H_2O_2 oxidant which destroyed the organic pollutants. On the other hand, the slight increase was because H_2O_2 is a weak oxidant. It is only effective for destroying cyanides, compounds of reduced sulfur and organics such as formic acid, aldehydes and some nitroorganic and sulfoorganic compounds [**21**]. Moreover, one can see that the removal efficiencies of TOC and COD obtained using Fe-Fe electrodes were higher than those obtained using Al-Al electrodes. This is because in addition to the electrocoagulation, some of pollutants can be removed by electro-Fenton at the same time.

Table 2. Removal efficiencies of inorganic species by using iron electrodes.

Parameter	Before treatment	After treatment	Removal efficiency, %
Ca, mg/L	60	52	13.3
Ma, mg/L	43.68	18.96	56.59
F, mg/L	1.11	0.49	55.85
Fe, mg/L	0.02	0.01	50
Sulfate, mg/L	295	198	32.88

Table 3. Removal efficiencies of inorganic species by using aluminium electrodes.

Parameter	Before treatment	After treatment	Removal efficiency, %
Ca, mg/L	60	46	23.3
Ma, mg/L	43.68	30.72	29.67
F, mg/L	1.11	0.22	80
Sulfate, mg/L	295	207	29.8

Table 4. The comparison between the results obtained from electrocoagulation and electrocoagulation with adding hydrogen peroxide.

Parameter	EC by iron	EC by iron + H_2O_2	EC by aluminum	EC by aluminum + H_2O_2
TOC removal efficiency %	51.12	58.7	56	57.63
TOC removal increase %		7		2
COD removal efficiency%	13.64	32.58	26.52	29.38
COD removal increase, %		19		3

(2) Electrooxidation (EO)

For electrooxidation, lower value of current density was applied (5 mA/cm^2). This is because graphite material has a smaller over-potential for oxygen evolution. Therefore, the effective degradation and elimination of pollutants on graphite anodes occurs only at lower values for current density. At higher values of current density, current efficiency tends to be less due to the generation of oxygen.

The first experiment was done by using the produced water without adjusting the pH which was then changed to 7, 6 and 3 in the second, third and fourth experiments, respectively. It can be seen from **Figure 2** that at pH of 8.34, the removal efficiencies of TOC and COD were very low which reached 31.3% and 38.2 %, respectively. These values increased to 79% and 81% at pH of 7. The higher values for removal efficiencies were obtained at pH of 6 where the removal efficiencies of TOC and COD jumped to 93.5% and 94%, respectively. In acidic media, when the pH was changed to 3, TOC and COD removal efficiencies were reduced to 73.5% and 64 %, respectively. The higher elimination of organic compounds indicated that moderate acidic is the optimum solution for the treatment, resulting in formation of sufficient quantities of a powerful oxidant (OH*) and other strong oxidants, such as ozone, hypochlorite ion and chlorine, which can attack and destroy organic compounds. At optimum conditions, the loss in graphite material was 0.0031 g and the produced sludge from the treatment was 0.23 g. These results and higher removal efficiencies indicated that graphite metal is electrochemically stable, chemically inert and effective for the treatment.

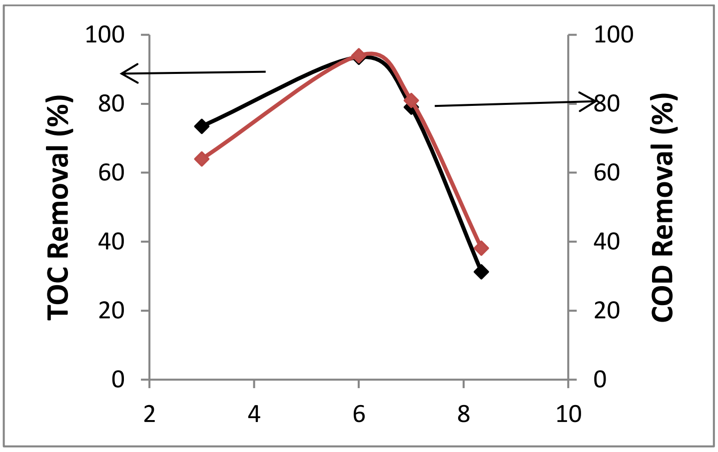

Fig. 2. Removal efficiency of TOC and COD as a function of pH.

(3) Electro-Fenton (EF)

During the electro-Fenton process, the initial COD of 387.6 mg/L decreased significantly to 49.4 and 93 mg/L in 80 min of electrolysis time, showing a reduction of about 87 and 76 % by using iron and graphite electrodes, respectively. The initial TOC of 129.2 mg/L reduced considerably to 19.73 and 20.2 mg/L in 80 min of electrolysis time, showing a drop of about 85 and 84 %. One can see from the results that the electro-Fenton process by using iron plates gave a little bit higher removal efficiencies compared to graphite plates. This was due to the generation of higher powerful oxidants from this process which attacked the organic pollutants and destroyed them to water, CO_2 and inorganic ions. In addition to electro-Fenton, in the same process, some pollutants can be absorbed with the produced $Fe(OH)_3$ and as a result they were eliminated by electrocoagulation.

The removal efficiencies of TOC and COD attained from all electrochemical methods were compared in **Table 5**. It is clear from this table that electrooxidation process with graphite electrodes was more efficient method compared to other methods for the remediation of produced water.

In order to know the benefits and outcomes of this research, the results obtained from this work were compared with the reuse and discharge standards as displayed in **Table 6**. It can be seen from this table that treated produced water can be safely disposed of or effectively reused for injection and irrigation in terms of COD.

The comparison between the results of this work and those obtained from other studies are presented in **Table 7**. Generally, the comparison showed that the electrochemical treatment for real produced water gave higher removal efficiencies for COD and TOC with lower energy consumption using cheaper electrodes compared to other expensive electrodes which were used in other studies.

Table 5. Comparison between electrochemical technologies in terms of TOC and COD removal efficiencies.

Parameter	**EC by iron**	**EC by iron + H_2O_2**	**EC by aluminum**	**EC by aluminum + H_2O_2**	**EO by graphite**	**EF by iron**	**EF by graphite**
TOC removal efficiency, %	51.12	58.7	56	57.63	93.5	85	84
COD removal efficiency, %	13.64	32.58	26.52	29.38	94	87	76

Table 6. Comparison of produced water characteristics in terms of COD with reuse and discharge standards.

Description	**COD, mg/L**
Electrooxidation by using graphite	22.65
Electro-Fenton by using iron	49.4
Chinese discharge standard [**32**]	100
Iranian discharge standard [**11**]	60
Kenyan discharge standard [**19**]	50
Heglig produced water for injection (Sudan)	50
French irrigation standard [**14**]	< 60
Italian irrigation standard [**14**]	< 100

Table 7. Comparison between the results of this work and those obtained from other studies.

Wastewater	**Type of process**	**Anode and cathode**	**Current density (mA/cm^2)**	**Electrolysis time (h)**	**T (°C)**	**Energy consumption**	**COD R.E (%)**	**TOC R.E (%)**	**References**
Oil refinery	EO-Batch	$Ti/TiO_2–RuO_2–IrO$ Graphite	54	20	30	235.3 kWh/kg	75	48	[**22**]
Oil extraction industry	EO-Batch	$Ti/Ru_{0.34}Ti_{0.66}O$ Pt	100	70	50	-	57	-	[**25**]
Synthetic creosote-oily solution	EO-Batch	Ti/RuO_2 Stainless steel	9.23	1.5	20-25	41 kWh/m^3	62	27	[**28**]
Petroleum refinery wastewater	EO-Batch	Ru-MMO Ru-MMO	20	3.5	20-25	2.5 kWh/g	70	-	[**31**]
Petroleum refinery wastewater	EF-Batch	Iron Iron	1	0.15	20-25	0.15 kWh/g	76	-	[**31**]
Petroleum refinery wastewater	EO-Batch	BDD BDD	3	1.5	20-25	4 kWh/g	95	-	[**31**]
Real produced water	EO-Batch	Ti/Pt Ti	30	10	25	-	46.5	-	[**24**]
Real produced water	EO-Batch	BDD Ti	30	10	25	-	57.5	-	[**24**]
Real produced water	EO-Batch	Ti/Pt Ti	60	10	60	140 kWh/dm^3	80	-	[**24**]
Real produced water	EO-Batch	BDD Ti	60	10	60	109 kWh/dm^3	98	-	[**24**]
Produced water in natural gas processing	EO-Cont.	Graphite Graphite	1.41	1	-	2.12 kWh/kgCOD	66.52	-	[**1**]
Real produced water	EF-Cont.	$Ti-RuO_2/IrO_2$ ACFF	156.6 mA	1.35	Room T.	0.9 kWh/kg	73	-	[**2**]
Real produced water	EO-Batch	Graphite Graphite	5	1.3	Room T.	1.53 KWh/m^3 (4.19 KWh/KgCOD)	94	93.5	**This work**
Real produced water	EF-Batch	Graphite Graphite	5	1.3	Room T.	1.3 KWh/m^3 (4.4 KWh/KgCOD)	76	84	**This work**
Real produced water	EF-Batch	Iron Iron	5	1.3	Room T.	0.74 KWh/m^3 (2.18 KWh/KgCOD)	87	85	**This work**

Conclusions

In summary, it is clear from the results obtained from this work that:

- The electrooxidation process with graphite electrodes was more efficient compared to other methods for the remediation of produced water. This is due to higher surface area of graphite for electrooxidation reactions allowing the higher generation of (OH^*) radicals from this process which attacked the organic pollutants and converted them into water, CO_2 and inorganic ions. In addition to that, it is likely that other powerful oxidants, such as ozone, hypochlorite ion and chlorine, can decompose and destroy organic compounds resulting in the TOC and COD reduction. Moreover, graphite is electrochemically stable which led to this result.
- The electro-Fenton process with Fe electrodes and supplied H_2O_2 in acidic solution was more efficient compared to electro-Fenton process with graphite electrodes for the remediation of produced water. This is due to the generation of higher powerful oxidants from this process which attacked the organic pollutants and converted them into water, CO_2 and inorganic ions. In addition to electro-Fenton, in the same process, some pollutants can be absorbed with the produced $Fe(OH)_3$ and as a result they were removed by electrocoagulation.
- The electrocoagulation treatment of produced water by using iron electrodes was moderately efficient for removal of TOC. However, it was inefficient for removal of COD. This is because COD removal is more difficult since the produced water generally has a diversity of organic and inorganic contaminants.
- It was noted that the aluminum plate has higher removal efficiency compared to iron plate at the same experimental conditions. This is likely because $Al(OH)_3$ effect on the coagulation and coprecipitation was higher than that for $Fe(OH)_2$ and $Fe(OH)_3$. Also, it can be concluded that the electrocoagulation treatment of produced water by using aluminum electrodes was still moderately effective for removal of TOC. On the other hand, it was ineffective for removal of COD. This was because COD removal is more complicated since the produced water normally has a variety of organic and inorganic impurities.
- Electrocoagulation gave significant removal for inorganic species such as heavy metals and solid ions. Therefore, it can be combined with electrooxidation and electro-Fenton processes to remove the organic and inorganic species.
- Electrochemical methods could be used for effective produced water treatment where it can be safely disposed off or effectively reused for injection and irrigation.

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