

ELECTROCHEMICAL TREATMENT OF OILFIELD PRODUCED WATER

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Abstract

Oil production generates wastewater bearing oily hydrocarbons, referred to “produced water” (PW). PW from a heavy-oil field has been treated with stainless steel (SS) cathode and dimensionally stable anodes – passivated titanium and graphite. In the electrolytic cells with these electrodes, electrooxidation (EO) accompanied by electroflotation (EF) are the main processes leading to pollutants removal. An oxidation by in situ generated oxidizing agents is found as the most plausible mechanism for decomposition of oily hydrocarbons in the PW containing high concentration of chloride ions. Total oily hydrocarbons (TOH) content and chemical oxygen demand (COD) as integral parameters and gas chromatography / mass spectrometry as analytical method were used to evaluate the efficiency of the treatment. At the optimal conditions, 15 mA/cm² and 15 min, 92.5 % removal of TOH and 25 % removal of COD have been achieved through energy consumption 2.218 kWh per kg removed TOH by the EO. Additionally, the treatment of PW in a cell having SS cathode and iron as sacrificial anode has been performed, where electrocoagulation (EC) supplemented by electroflotation cause decrease of organic contaminants concentration. At the optimum conditions, current density 10 mA/cm² applied for 10 min (energy consumption 0.603 kWh/kg) or current density 8 mA/cm² applied for 15 min (energy consumption 0.629 kWh/kg) the TOH removal of 95.4 % and 96.4 % respectively have been determined. EC/EF has been found to be more effective than the EO/EF for treating the PW polluted by high-molecular alkanes. The EC/EF is an environmentally friendly and efficient method.

Key words: *electrocoagulation, electroflotation, electrooxidation, oily produced water treatment*

1. INTRODUCTION

Crude oil is one of the most important worldwide hydrocarbons' sources. The oil-well production fluid usually consists of oil and water, in different ratio, that is generally separated by physical techniques. The amount of PW generated during oil production varies: a new field produces 5–15 vol%, while at the end of its lifetime this amount reaches 75–90 vol% (Ramalho, Huitle & Silva2010). Produced water presents the largest waste stream obtained by the oil and gas industries (Hosny et al. 2016). The global amount of oily wastewater was estimated of 9–14 billion m³ in 2012 (Gitis and Rothenberg 2016). PW contains different organic and inorganic compounds. Its composition depends mainly on the oilfield geological conditions, the recovery method and the age of the production wells. The produced water characteristics and their ranges for different oilfields in the world are summarized in Table 1 (Tibbetts et al. 1992; Bessa, Sant’Anna & Dezotti 2001; Lu et al. 2006; Fakhru’l-Razi et al. 2009; Li, Guo & Li 2010; Sanyal and Butler 2010; Fox 2011; Nelson and Santos 2011; Cabral da Silva et al. 2013; Hosny et al. 2016; Jain et al. 2017).

Hydrocarbons can be dissolved in the water or dispersed, thus forming emulsion oil in water (O/W). Dispersed oil droplets usually have high surface charge, resulting in the stability of O/W system (An et al. 2017). That is why the oil removal from wastewater is regarded as the main challenge in the treatment practice. When PW is discharged into the environment, oily wastewater causes the formation of surface films and shoreline deposits, which affect ecological systems (Noh et al. 2015). The biodegradability of oil in natural ecosystem is low and oily components can hinder biological processes in the environment for a long time. Release of untreated oily wastewater poses significant threats to the surface and groundwater resources, soil, air, flora and fauna because of the hazardous nature of its contaminants.

Produced water is considered an oilfield waste which has to be managed before being discharged into natural water bodies or re-injected into the wells. Different methods have been proposed for PW

treatment – physical (such as gravity separation, use of sand filters and hydrocyclones, evaporation, freeze–thaw/evaporation); chemical (such as liquid phase oxidation with hydrogen peroxide, Fenton reagent, hypochlorite, ozone, supercritical water oxidation; chemically induced precipitation; physicochemical (such as adsorption on activated carbon, coagulation and flocculation, flotation, use of electrochemical and membrane processes), photocatalytic and biological degradation (Fakhru’l-Razi et al. 2009; Jamaly, Giwa & Hasan 2015; Dastgheib et al. 2016; Munirasu, Haija & Banat 2016; An et al. 2017; Yu, Han & He 2017). The above mentioned methods are used individually or in combination.

Table 1. Range of some parameters of produced water from different oilfields in the world

Parameter	Value	Parameter	Value	Parameter	Value
t, °C ¹	10 - 127	O&G, mg/L	31-275	Bicarbonates, mg/L	15-3990
pH	4.3 – 10.0 ²	TPH ⁴ , mg/L	49-64	Sulfides, mg/L	0.14 ⁵
Conductivity (χ), mS/cm	0.61-143.90	Total polar, mg/L	9.7-600	Sodium, mg/L	132-126755
Salinity, mg/L	79-143170	Volatile, BTEX, mg/L	0.39-49.67	Potassium, mg/L	24-4300
COD, mg/L	274-11541	Total oil (IR), mg/L	2-565	Calcium, mg/L	13-52920
BOD ₅ , mg/L	11-21 ³	Phenols, mg/L	0.009-23	Magnesium, mg/L	8-6000
TOC, mg/L	0-15005	Carboxylic acids, mg/L	2-4900	Barium, mg/L	0.25-650
TSS, mg/L	1.2-1000	Chlorides, mg/L	36-238584	Strontium, mg/L	0.02-1000
TDS, mg/L	675-141522	Sulfates, mg/L	2-13686	Heavy metals ⁶ , mg/L	0.068-48.38

¹Temperature depends on the well temperature and the ambient air temperature on the surface; ² Most often: 6.7 – 7.4; ³ Only Li et al., 2010; ⁴Total petroleum hydrocarbons; ⁵ Only Lu et al. 2006; ⁶ Considered elements in this case are: Sb, As, Be, Cd, Cr, Cu, Pb, Hg, Ni, Ag, V, and Zn

Although many advantages of these technologies have been reported, they exhibit some particular disadvantages. The gravity separation and use of natural evaporation have simple design and low energy consumption, but they require large space and are ineffective for the removal of very small oil droplets. The general disadvantages associated with the other physical methods include high initial capital costs, sensitivity to variable water input, and in addition, for filters and hydrocyclones low separation efficiency for fine oil droplets. The chemical treatment usually ensures good removal and rapid destruction of oily compounds, especially in the case of chemical oxidation. However, the hazardous sludge generated requires subsequent treatment and causes disposal problems, in addition to the high operating costs and sensitivity to initial concentrations of contaminants in the wastewater. Supercritical water oxidation provides fast and high conversion of oil but requires energy for operation at high pressure and elevated temperature. The biological treatment and photocatalysis under natural sunlight are clean technologies with low operating costs. They often require long reaction time and wide space, as well as show sensitivity to variations in water parameters (pH, temperature, concentrations of organic and inorganic pollutants). Flotation technology can be easily operated and high overflow rates can be attained. In order to improve the process, flotation reagents are added, which increases the retention time for separation, and generates large amounts of scums and sludge, that have to be handled. Sorption technology is characterized with simple operation and good oil removal, but these features are limited to water with relatively low oil content and small-sized oil droplets. Coagulation and flocculation is an adaptable technology that is suitable for removing emulsified oil, dissolved oil and some low-biodegradable organic polymers. Due to the complexity and wide-range composition of the oily wastewater, the selection of coagulants and technology parameters cannot be theoretically predicted correctly, thus a lot of preliminary experiments must be performed (Yu et al. 2017). Membrane technologies offer good oil removal efficiency and are relatively easily applied. Sludge is not formed during the membrane process, only a concentrate that has to be treated, which results in considerably less solid waste for disposal. Still, the technology

requires oily water pre-treatment to avoid membrane fouling. There are also some problems with the membrane's stability and installation's capacity to process large volumes of wastewater at reasonable cost. In addition, a single membrane separation technology cannot ensure achieving the concentrations of oily compounds in treated water, required by the environmental standards and it has to be combined with traditional methods (Yu et al. 2017). All above-described drawbacks of the mentioned technologies limit the suggestions for a general recommendation of produced waters treatment. Instead, many investigations have been carried out worldwide to discover the most effective technology for each particular oil or gas field PW at the specific place.

The electrochemical methods have been proposed as sustainable and efficient alternative for O/W emulsions treatment. In this process, electrodes are introduced in the treated water and current (in the most of cases direct current (DC)) is passed between the electrodes through an external source (a rectifier for DC). It is worth to mention that the chemical nature of the electrodes used determines the processes leading to the oil removal. When insoluble dimensionally stable electrodes (and especially anode) are used, the main processes occurring are electrochemical oxidation and electroflotation. The electrooxidation can be enhanced by use of electrodes with catalytic activity (Körbahti and Artut 2010). When soluble electrodes are applied, the main processes are electrocoagulation and electroflotation.

Electrocoagulation is a process based on *in situ* generation of coagulants by electrolytic oxidation of an appropriate sacrificial metal (such as aluminum, iron) used as anode upon application of a direct current:



In neutral aqueous medium, the cathodic reaction is described by eq. (2)



and by eq. (3) if dissolved O_2 is available in the water.



The generated metal ions react with hydroxyl ions to produce metal hydroxide species, which are able to act as coagulating reagent:



The generated coagulating agent promotes emulsion destabilization and its breaking down. The interaction between metal cations/hydroxides and pollutants can be described by several mechanisms, including charge neutralization, bonding oil droplets to generated flocs, precipitation and co-precipitation, and enmeshment (Vepsäläinen, Pulliainen, & Sillanpää 2012; An et al. 2017). During or in the end of the process, flocs are formed and "loaded" with the organic pollutants are removed either by sedimentation or by EF.

Since the electrochemical treatment is characterized by reduced sludge production, lack of additional chemicals, and easy operation, it has increased its popularity in wastewater management recently. Here, we have studied its application to the oilfield produced water separated after production of heavy crude oil from the wells. They have been exploited over 50 years and generated wastewater in amount more than 98% from the total fluid. All experiments were conducted by using a real wastewater from an oilfield.

2. METHODS AND MATERIALS

2.1. Experimental set up

In its simplest form, the reactor for electrochemical treatment represented an electrolytic cell with one anode and one cathode. The electrodes were two parallel plates with dimensions 10.0x3.0x0.3 cm made of different materials. The previous experience (Panayotov and Panayotova 2002), confirmed by Kongjao and co-authors (Kongjao, Damronglerd & Hunsom 2008), showed that the electrode

configuration with parallel monopolar connection was more effective than the other configurations. Electrodes were immersed in the polluted water. Different authors claim as optimal the distance between electrodes in the range of 1 – 3 cm. In our case in order to ensure good stirring the chosen distance was 5 cm, which could be considered as the most conservative case with respect to power consumption. A direct-current was supplied by a standard laboratory rectifier. The reactor was glass beaker of 1000 mL and the volume of oily water tested was 700 mL in all experiments. They were performed in batch mode of operation. Before each run, the electrodes were cleaned, rinsed and dried with filter paper. Magnetic stirrer (300 rev/min) was used during the entire electrolysis process. The foam formed was removed manually from the upper part of the reactor. The electrochemically treated water was kept in the reactor for 5 min. After that the treated clear water was separated by decantation from the sludge precipitated on the bottom and then it was analyzed. Filtration was not needed before the analysis.

2.2. Optimisation of experimental conditions

All electrochemical experiments were conducted at room temperature and pressure (25 °C and 0.1 MPa). Although it has been previously reported that the optimum removal of COD was at a current density 100 mA/cm² and a temperature of 50 °C (Santos et al. 2006), we estimated that in industrial scale treatment maintaining this temperature will be too expensive. Different current densities were reported in the literature as optimal – in the range of 1 – 100 mA/cm² (Dimoglo et al. 2004; Xu and Zhu 2004; Santos et al. 2006; An et al. 2017). We have chosen the most often studied relatively low range of 2 – 15 mA/cm², which is related also to less energy consumption.

Different authors have pointed out the insignificant impact of the initial pH value of the PW subjected to the electrochemical treatment when the water is practically neutral and iron anode is used (Xu and Zhu 2004; Zhao et al. 2014). Linares-Hernández and co-authors (2010) reported that the electrocoagulation - electrooxidation process is effective at the range of pH 3-10. Since the pH of our raw effluent was nearly neutral no pH adjustment was necessary, and pH was only measured.

El-Naas and co-authors (2009) reported better performance of aluminum electrode in batch electrocoagulation experiments on COD removal from petroleum refinery wastewater – in comparison with stainless steel and iron electrodes. Other studies (Yavuz, Koparal & Ögütveren 2010; Zhao et al. 2014; Pires da Silva et al. 2015) revealed better results when iron anode was used. Lee and coauthors found that when anode is made of iron and cathode of stainless steel, larger flocs with higher oil removal capacity were produced by the EC (Lee and Gagnon 2016). That is why we have chosen to use cathode made of stainless steel (SS) with the following composition, in %: Cr - 16 ÷ 18, Ni - 13 ÷ 15, Mo - 2.5 ÷ 3.1, Mn - 1 ÷ 2, C ≤ 0.03, Si ≤ 0.4, S ≤ 0.02, and P ≤ 0.035. SS containing Mo is known as resistant in chlorides containing solutions and alkaline media. Iron anode (made of mild steel, with the following composition, in %: Fe ~98, C - 0.05 ÷ 0.11, Si - 0.05 ÷ 0.17, Mn - 0.35 ÷ 0.65, Ni ≤ 0.25, S ≤ 0.04, P ≤ 0.035, Cr ≤ 0.1, Cu ≤ 0.25, and As ≤ 0.08) was the choice for the anode material in the EC experiments, which is much cheaper than the aluminium one.

In experiments where EO was attempted as one of the main electrochemical processes, the anode was made of preliminary passivated titanium (Ti/TiO₂). Possible contaminants on the Ti surface (for example, iron) were removed by electrode dipping for 10 min in 10 % HNO₃. To increase the anode corrosion stability it was electropolished under the following conditions: electrolyte, consisting of ethyl alcohol 700 mL/L, isopropyl alcohol 300 mL/L, aluminum chloride 60 g/L, and zinc chloride 250 g/L (Tajima et al. 2008); applied voltage 50 V; temperature 30 °C; time 15 min. The passive film formed improved the electrode stability in chloride medium and under anodic current. In another set of experiments the anode was made of carbon. In this case the electrode thickness was 0.5 cm.

Actually, it is worth to mention that in the real treatment process both EC and EO are supplemented by EF and the scum formed had to be removed.

For comparative purpose, experiments with calcium hypochlorite [Ca(ClO)₂] were carried out at the reagent initial concentration of 400 mg/L. This concentration was determined as the optimum one by

our previous experiments on the chemical oxidation of PW from the same oilfield plant. The volume of the water samples was 700 mL, the treatment time 15 min and the sample was stirred with a magnetic stirrer at speed 300 rev/min.

All presented data are average from two parallel trials.

2.3 Analytical methods

Temperature, pH value, Δ pH value (index of water saturation with respect to CaCO_3), Eh value, and conductivity were measured on site by using electrometric methods (with combined electrodes and WTW Multi 340i/SET device). Collected samples were preserved following the standard procedures and were transported in a cooling bag to the laboratories where other parameters were measured.

Dissolved oxygen was determined by the Winkler method. The concentration of calcium and magnesium ions was found by titration with EDTA. Concentration of chloride and bicarbonate ions were determined by titrimetric methods - titration against silver nitrate (Mohr's method) and hydrochloric acid solution (methyl orange method), correspondingly. Turbidimetry was applied to determine the concentration of sulfates. Concentration of sodium and potassium were determined by ICP-AES. The concentration of iron was determined spectrophotometrically, based on the iron reaction with a triazine derivative to form a violet complex. All above-described determinations followed the standard procedures (Bulgarian State Standards: Environment protection, 1989). Total oily hydrocarbons concentrations were determined by spectrophotometric method in the UV range. In the first step, extraction of hydrocarbons with CCl_4 was carried out, followed by measurement of the solution absorption (Petrova et al. 2004). Chemical oxygen demand (COD) was determined spectrophotometrically by using Spectroquant NOVA 60, a Merck COD cell test, after chloride depletion and sample digestion in a Spectroquant TR420 device. The method corresponds to DIN38409-41-2, DIN ISO 1575 and is analogous to EPA410.4, APHA 5220 D, and ASTM D 1252-06 B.

The gas-chromatography/mass spectrometry (GC/MS) analysis was conducted on Agilent Technologies 7890A device equipped with a mass detector 5975C. A capillary chromatographic column with length of 30 m, internal diameter of 0.25 mm and thickness of the immobile layer (polyethylene glycol) of 0.25 μm was used. The applied temperature regime was: injector – 280 °C; programmed column – from 100 (2 min) to 250 °C (10 min); transfer line - 230 °C, detector - 150 °C; electronic source - 230 °C. The duration of the analysis was 27 min. Helium was used as gas-carrier with velocity of 1.5 mL/min. The injected sample volume was 2 μL . Compounds were identified on the basis of their retention time and by using the mass-spectrometer library (NIST 05a). Additionally, the C13-C22 normal alkanes were identified by comparison with standards. Prior to chromatography measurements, the organic compounds were extracted with CCl_4 from the raw produced water and from the treated waters.

2.4. Data processing

Removal efficiency,

$$\% = \frac{C_0 - C_i}{C_0} \cdot 100 \quad (5)$$

where C_i is the concentration of the examined pollutant at time τ and C_0 is the initial concentration of the same pollutant.

The theoretical amount of electrode material dissolved at the anode during the EC process can be calculated by using the Faraday's law:

$$m = \frac{I \cdot \tau \cdot M_r}{z \cdot F} \quad (6)$$

where m is the mass of dissolved metal (g), M_r is the molecular weight of the anode material; I – the applied current (A), τ - the electrolysis time (s), z – the number of electrons involved in the reaction and F - the Faraday's constant (96,485.34 As/mol). The same equation governs also the theoretical production of hydrogen bubbles on the cathode, only M_r is the mass of hydrogen.

The electrical charge per volume of the treated water Q (Ah/L) passed in the electrochemical process was calculated by using the following equation:

$$Q = \frac{I \cdot \tau}{V} \quad (7)$$

where I - the applied current (A), τ - the electrolysis time (h), and V - the water volume (L).

The energy consumption E (kWh/kg) per mass removed oil from the wastewater was calculated with the following equation:

$$E = \frac{U \cdot I \cdot \tau}{V \cdot (C_o - C_i)} \quad (8)$$

where U is the average applied voltage (V), I - the applied current (A), τ - the electrolysis time (h), and V - the water volume (L), C_o and C_i – as described above.

3. RESULTS AND DISCUSSION

3.1. Water characterization

Data on integral parameters of the studied water are presented in Table 2. The concentrations of macro-components and iron are given in Table 3.

Table 2. Integral parameters of the studied water

t, °C	pH	Eh, mV	χ , mS/cm	Δ pH	rH	Diss.O ₂ , mg/L	COD, mg/L	TOH, mg/L
19.0	7.31	+65	6.13	+0.07	16.82	<0.08	38.0	297.6

Table 3. Concentration of macro-components and iron in the studied water samples

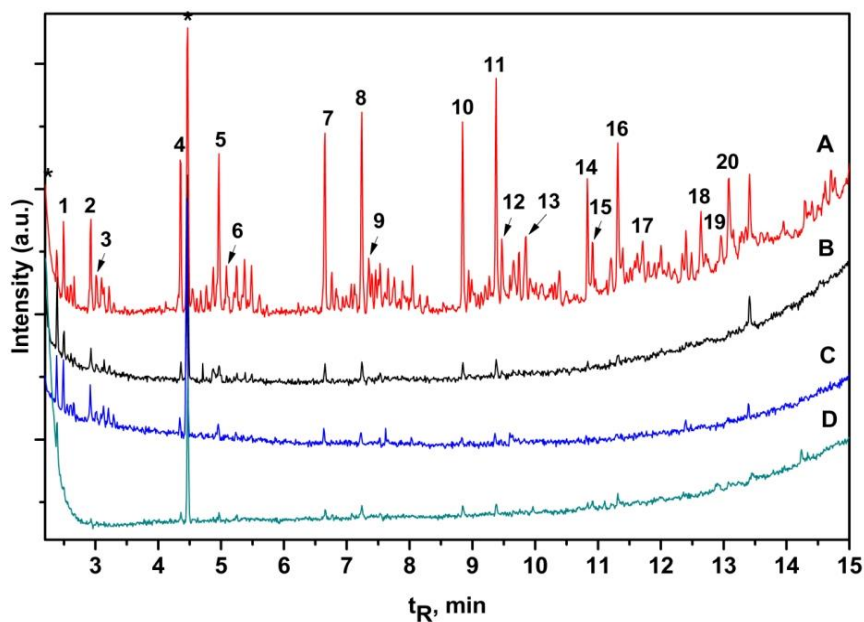
Component	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	Fe _(tot)
Concentration, mg/L	102	53.5	1260	21	1715	433	468	1.5

By comparing values presented in Tables 1, 2 and 3, it may be stated that the pH value of studied water is practically in the middle of the range of the typical values. The PW is in the lower edge of the worldwide reported temperatures, salt concentrations and conductivities. Measured Eh value is indicative for anaerobic conditions. This is in accord with the very low concentration of dissolved oxygen. Considering the calculated rH values, we can conclude that the water possess slightly reducing properties. The quick Δ pH test showed that water is practically in equilibrium with respect to calcium carbonate. The water is characterized with relatively high concentration of total oily hydrocarbons and low value of COD. Data for COD point at a low concentration of chemically oxidizable compounds by dichromate ions. Usually, this is the case when heavy organic compounds present in the wastewater as tiny droplets and they cannot be oxidized at the conditions of COD analysis. We have determined the density of the extracted crude oil as 0.952 g/cm³. The oil can be classified as heavy crude oil because its density falls in the range of 0.88 – 1.00 g/cm³ (Fingas 2015). The presence of high-molecular compounds in the PW was confirmed by GC/MS analysis.

3.2. GC/MS analysis

The chromatograms from the GC/MS analysis of the raw produced water (A), treated water by EO (graphite anode, 15 min, 15 mA/cm²) (B), treated water by EC at current density 10 mA/cm² and time duration 10 min (C) and treated water by EC at current density 15 mA/cm² and time duration 15 min (D) are presented in Figure 1. The identified compounds by GC/MS are given in Table 4.

Figure 1. GC/MS analysis of the PW: A- raw produced water before the treatment; B – EO treated PW (graphite anode, 15 min, 15 mA/cm²); C – EC treated PW (10 mA/cm², 10 min); D – EC treated PW (15 mA/cm², 15 min); the peaks denoted by * are due to the solvent's impurities



The aim of this study was to compare the initial and post-treatment PW content on a qualitative basis and to evaluate the efficiency of the electrochemical processes. The chromatogram (A) of the raw PW shows numerous peaks, indicating the complex composition of the PW. Most intensive of them were assigned to branched C₁₂-C₂₂ alkanes, while the weaker peaks are due to homologues C₁₃-C₂₂ alkanes with straight carbon chain (Table 4). The chromatograms (B) – (D), obtained for effluents from EO and EC treatment, display only very low-intensity peaks for identical organic compounds found in the initial produced water. There are no peaks for low-molecular compounds that might be obtained from oxidation of the bigger molecules. Thus, the GC/MS analysis reveals significant reduction in the concentration of organic pollutants by their mineralization into CO₂ and H₂O as a result of the treatment. It is consistent with the results for lower COD and TOH, which were determined by the corresponding analytical methods.

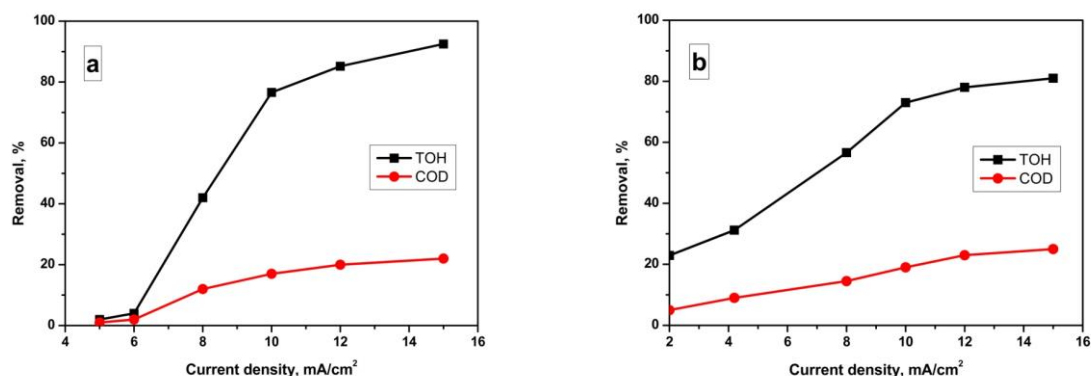
3.3. Electrooxidation

The PW treatment has been performed by using two sets of electrolytic cells containing a stainless steel (SS) electrode as a cathode and two types of dimensionally stable electrodes – preliminary passivated titanium (Ti/TiO₂) or graphite as an anode (denoted as SS/Ti-TiO₂ and SS/graphite). In both cases, the effect of the current density and reaction time on the TOH and COD removal has been studied. It was found in our preliminary experiments that the optimum reaction time is 15 min to reach high degradation degree per reasonable energy consumption. The results for TOH and COD removal as function of current density at 15 min treatment time in the both electrolytic cells are shown on Figure 2.

Table 4. Identification of compounds by GC/MS

Peak №	Name and empirical formula of identified compound	Peak №	Name and empirical formula of identified compound
1	2-methylundecane (C ₁₂ H ₂₆)	11	2,6,11,15-tetramethylheptadecane (C ₂₁ H ₄₄)
2	2,6-dimethyldecane (C ₁₂ H ₂₆)	12	n-Nonadecane (C ₁₉ H ₄₀)
3	n-Tridecane (C ₁₃ H ₂₈)	13	2,6,10,15-tetramethylheptadecane (C ₂₁ H ₄₄)
4	2-methyltetradecane (C ₁₅ H ₃₂)	14	2-methyleicosane (C ₂₁ H ₄₄)
5	2,6,11-trimethyldodecane (C ₁₅ H ₃₂)	15	n-Eicosane (C ₂₀ H ₄₂)
6	n-Pentadecane (C ₁₅ H ₃₂)	16	8-hexylpentadecane (C ₂₁ H ₄₄)
7	2-methyloctadecane (C ₁₉ H ₄₀)	17	n-Heneicosane (C ₂₁ H ₄₄)
8	2,6,10,14-tetramethylhexadecane (C ₂₀ H ₄₂)	18	2-methylheneicosane (C ₂₂ H ₄₆)
9	n-Heptadecane (C ₁₇ H ₃₆)	19	n-Docosane (C ₂₂ H ₄₆)
10	2-methylnonadecane (C ₂₀ H ₄₂)	20	8-heptylpentadecane (C ₂₂ H ₄₆)

Figure 2. Total oily hydrocarbons and COD removal by EO at overall treatment time 15 min: (a) for electrolytic cell SS/Ti-TiO₂; (b) for electrolytic cell SS/graphite



It can be seen that the oily hydrocarbons and COD removal increase with increasing of the current density. Two regions can be distinguished on the curves – the initial (up to current density 10 mA/cm²) where the removal efficiency raises fast with increasing the current density and the second one, where the removal is changed slowly. In the end of the treatment the COD removal was 22 and 25 % for Ti-TiO₂ and graphite anode, respectively. In the same time, the removal of oily hydrocarbons was greater and reached 92.5 and 81 % for Ti-TiO₂ and graphite anode, respectively. The energy consumption values were calculated to 2.218 and 2.529 kWh per kg removed TOH with Ti-TiO₂ and graphite anodes, correspondingly. Our results are similar to those obtained by other authors. Körbahti and Artut (2010) achieved 91.6–96.2 % removal of oil/grease for 240 min at 12.8 mA/cm² current density using Pt/Ir electrodes. Santos and co-authors (2006) achieved 40 % reduction of the COD after 20 hours with Ti/Ru_{0.34}Ti_{0.66}O₂ anode and current densities of 50 and 75 mA/cm².

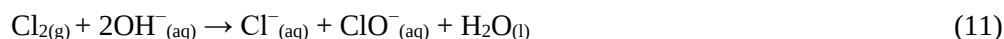
In both electrolytic cells, electrooxidation (EO) accompanied by electroflotation (EF) are the main processes leading to removal of the organic pollutants. It is known that in EO organic pollutants are removed from wastewater by direct and indirect oxidation. In direct EO, organic molecules are electro-oxidized at the anode and electro-reduced at the cathode forming smaller intermediate by-products (Körbahti and Artut 2010). The rate of direct oxidation of organic pollutants depends on

the electrocatalytic activity of the anode, the diffusion rate of organic compounds to the active sites of the anode, and the applied current density (Israilides et al. 1997). However, even with anodes possessing electrocatalytic activity the direct oxidation reactions of organics are very slow (Tarr 2003).

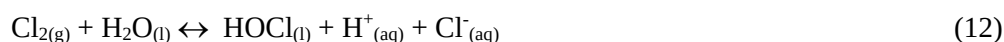
In our case, EO takes place at high concentration of chloride ions and neutral pH. Then the proposed reactions describing the anodic process can be presented by the following equations:



The cathodic reaction is described by equation (2). In the bulk of the solution chlorine, formed at the anode can react with hydroxide ions, produced at the cathode to give chloride and hypochlorite ions:



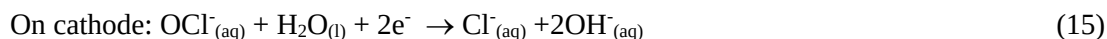
The chlorine can also hydrolyze via the reaction:



Hypochlorous acid is a weak acid ($\text{pK}_a=7.537$ at 25°C) and undergoes partially dissociation to hypochlorite ions (Morris, 1966):



On the other side, OCl^- ions are involved in secondary electrochemical reactions (14) and (15) that occur on the electrodes and recover chloride ions in solution:



Thus, in moderate alkaline and neutral brine solutions, a cycle of chloride–chlorine–hypochlorite–chloride arises, that begins with oxidation of Cl^- to Cl_2 , its hydrolysis to OCl^- which further regenerates the Cl^- ions in the solution (Israilides et al. 1997). This is the reason why the initial concentration of chloride ions remains practically stable. By using titration against AgNO_3 , we have estimated that the concentration of Cl^- ions decreased by 20-40 mg/L, which indicates consumption of chloride ions in the electrochemical reaction (10). At the same time, it is only negligible change as the total initial concentration of Cl^- in PW is 1715 mg/L.

Formation of free radicals such as $\text{OH}^\cdot$, $\text{Cl}^\cdot$, as well as H_2O_2 on the electrode surface is not excluded. During the EO process, the pH of the solution slightly increased. The acidity of the PW was monitored in all experiments. After the treatment the pH values were in the range of 7.55 – 7.65, showing increase of pH by ~ 0.3 , which most probably is due to formation of hydroxyl ions by reaction (2).

Hence, we assume that in the EO treatment, the organic compounds present in the oily PW were mineralized into CO_2 by wet oxidation in solution and close to the anode via the strong oxidants, such as O_2 , Cl_2 , OCl^- and/or free radicals that were generated during the electrochemical process.

For comparison purpose, we have carried out the chemical oxidation with calcium hypochlorite for 15 min treatment time, which resulted in TOH removal of 79.5 %. Obviously, the effectiveness of the EO (92.5%) is greater than that of the chemical oxidation, owing to electrochemical formation of active oxidizing species *in situ* which cause completely oxidation of the organic pollutants.

During the PW treatment, the EO process is accompanied by electroflotation. The evidence for EF was the presence of a layer of foam at the electrolyte surface in the reactor.

Electroflotation is based on the use of micrometer-sized bubbles (15–23 μm diameter), which are produced on the electrodes' surface (Sarkar, Evans & Donne 2010). In neutral aqueous medium, O_2 is produced on the dimensionally stable anode (reaction (9)) and H_2 on the cathode (reaction (2)). During the electroflotation process, finely suspended oil droplets in the PW can be separated by adhering to the surface of rising gas bubbles. According to Faraday's law (equation (6)) higher current will ensure

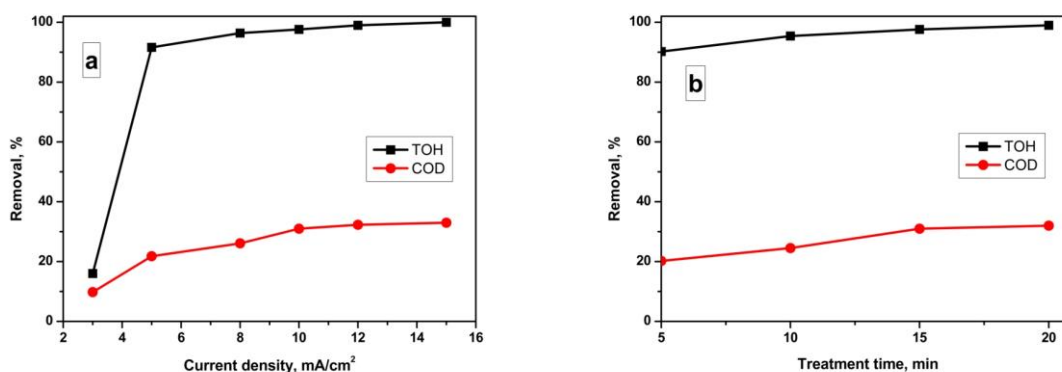
increased rate of production of gases on the electrodes (eq. (2) and (9)), if the energy is not wasted to produce heat.

The residual TOH values in the treated water were 22.3 and 56.5 mg/L, correspondingly for electrolytic cells SS/Ti-TiO₂ and SS/carbon. The both values are higher than the maximum allowable concentration (MAC), according to Bulgarian legislation (Bulgarian Council of Ministers 2000). The TOH concentrations achieved with the electrolytic cell SS/Ti-TiO₂ (22.3 mg/L) almost meet the legislation criterion (20 mg/L). In order to reduce further the level of TOH and to attain minimum impact of organic contaminants on the environment, we have designed electrocoagulation treatment of PW through using sacrificial anodes.

3.4. Electrocoagulation

The electrolytic cell for PW treatment was constructed by SS cathode and iron (mild steel) as sacrificial anode. The influence of current density and treatment time of the oil removal by EC is presented in Figure 3. As it can be seen in Figure 3a increasing the current density leads to increase in oil and COD removal until a plateau is reached, indicating that the effect of current density is approaching its critical point. In practice, 100 % oil removal was achieved by applying a current density 15 mA/cm² for 15 min. The GC/MS chromatogram (C) for the effluent (at current density 10 mA/cm² for 10 min) clearly shows minor peaks for organic compounds initially presented in the PW, which indicates that EC process effectively reduces the concentrations of high-molecular hydrocarbons. Increase of the current density or treatment time does not cause significant improvement of the result, as shows chromatogram (D) (Figure 1).

Figure 3. Oil hydrocarbons and COD removal as function of: (a) the current density at 15 min treatment duration; (b) treatment time at current density 10 mA/cm²



These data are comparable to previously reported by other authors for oil removal by EC with mild steel electrode. The removal of 81.53% was observed using current density of 0.57 A/dm², for 14.6 minutes, at pH 7.06 (Harinarayanan Nampoothiri, Manilal & Solomon 2016). Also, it was found that when the current density was increased above the optimum level, the results were worse (Mousa 2016). Moussavi and co-authors found that the increase in current density from 2 to 18 mA/cm² by using steel-iron as the anode-cathode electrode arrangement at neutral pH value increased TPH removal from 71.7 to 95.1% during the EC (Moussavi, Khosravi & Farzadkia 2011a).

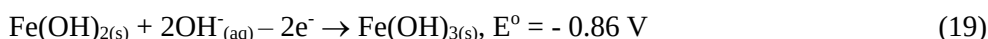
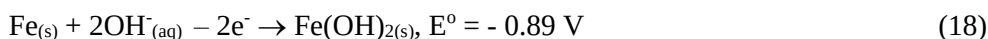
On the Figure 3b time dependence of TOH and COD removal at constant current density is shown. At current density 10 mA/cm² only 5 min were enough to achieve 90 % oil removal. Then, after 10 min treatment when the oil removal passed 95 % the process slowed down. Significant decrease in COD removal percentage after the tenth minute was reported also by An and coauthors (An et al. 2017) and after 15 min treatment – by Mousa (2016).

Our data on COD removal show the maximum removal of 32-33 % achieved by EC. This is about half of the result for the same parameter achieved by Zhao and coauthors (66 %). However, they carried out the treatment for twice longer time, 31 min (Zhao et al. 2014). One can assume that dissolved organics in low concentration that contribute to the initial low COD values, cannot be removed effectively by EC. Thus the final total COD removal is moderate in our case. Nevertheless, having in mind that the untreated produced water meets the requirements with respect to COD, placed to the companies in the oil/mining sector (Bulgarian Council of Ministers 2000), around 30 % decrease in the COD is a step ahead in the environment protection direction and it supports the conclusion for efficiency of the EC approach.

In the case of EC treatment of the studied water most probably the reaction (2) takes place at cathode and hydroxyl ions are produced. Bearing in mind the applied voltage during the experiments aimed to ensure the required current (respectively current density) and the fact that the water is stirred (i.e. OH⁻ ions can reach the anode), we could suggest the following reactions taking place at the anode:



Additional reactions:



In addition, in the bulk of the solution, iron ions generated on the anode react with the OH⁻ ions, which are formed on the cathode, to produce green Fe(OH)_{2(s)} and yellow Fe(OH)_{3(s)} flocs (Gheraout et al. 2008), which were observed with naked eye during the experiments. Since the reactor was open to the air and the water was stirred, oxygen molecules easily penetrated into the water and oxidized Fe²⁺_(aq) to Fe³⁺_(aq) to a some extent (Balla et al. 2010) and the Fe(OH)_{2(s)} to Fe(OH)_{3(s)}. The formed hydroxides are amorphous and according to Chou, Wang & Huang (2009) much larger and bulky than flocs formed by hydrolysis of iron salts. Moreover, Moussavi and co-authors (Moussavi, Majidi & Farzadkia 2011b) suggested that Fe(OH)₃ formed in the solution polymerizes to form Fe_n(OH)_{3n} which demonstrates better coagulating properties.

Lee and Gagnon (2016) proved that 70 –50% of the iron produced at the anode was ferrous. In our experiments, the X-ray analysis of the separated and dried sludge showed that around 95% amorphous hydrated iron oxide [FeO(OH)] is formed.

Ions generated from the sacrificial anode compress the diffuse double layer around the negatively charged oil droplets in O/W emulsions, thus destabilizing the emulsions and facilitating their coalescence (Volkov et al. 1996). Subsequently they are separated by settling through entrapping by the iron hydroxides flocs or by electroflotation.

The hydrophobic and nonpolar hydrocarbon compounds (HC), may be removed from the water through the formation of surface complexes with the Fe(OH)₃ precipitate. The HC molecules complex with the active sites present on the surfaces of growing ferric hydroxide flocs (co-precipitation) and undergo physical adsorption onto the amorphous Fe(OH)₃ flocs by Van der Waals forces (Martínez-Huitle and Brillas 2009).

Based on Faraday's law, the amount of dissolved sacrificial anode material and hence iron hydroxide flocs generation increases proportionally to the increase in current density (as indicated by equation (6)). The greater the amount of iron flocs generated the greater amount of O/W emulsion will be destabilized and the greater number of HCs would be immobilized by the flocs. Operating at higher currents also resulted in larger flocs until reaching the steady-state at the optimum current (Lee and Gagnon 2016). Larger flocs mean higher surface for sorption, entrapping and easier settling down.

The supplementing electroflotation is conducted with the aid of the hydrogen bubbles formed through reaction (2). The bubbles adhere to oil droplets or even to small flocs with entrapped oil and make them more buoyant. Oil or solids float to the surface of the tank where they are skimmed off as aerated

foam. Higher current density ensures higher amount of H_2 generated at the cathode. Chen reported that bubbles' size decreased with the increase of current density. This resulted in the bubble densities increasing and more intense upward flux. Smaller bubbles also provided larger surface area for particle attachment, ensuring high separation efficiency and higher flotation rate (Chen 2004). Besides providing more surface area for attachment of more neutralized oil droplets, the smaller bubbles also have slower velocity of rise which increases their collision probabilities as a result of increasing retention time in the bulk before floating to the surface (Mollah et al. 2004).

A region can be seen on the graphs (Figure 3) where further increasing in the current density or treatment time resulted in slight increase in removal efficiency, however this is related to higher energy consumption. The temperature of the treated water in our experiments was not increased which means that electricity was not wasted for the Joule heat.

Some authors point at declining in the oil removal percentage with increasing the current density over the optimal one (Liu et al. 2017). We have not reached such excessive current density, which does not mean that there is not a room for optimization.

Pires da Silva and coauthors (Pires da Silva et al. 2015) proposed the minimum time required for the treatment to be found by the intercept of the two lines ("reactive"- for which the removals increase regularly with time and "steady state" – line where further increases in time practically do not affect the removal efficiencies) clearly seen in their graph of oil removal, in %, as function of the time. For the applied current density 10 mA/cm^2 by using this approach we would conclude that the optimum time is 10 min in our case (Figure 3b).

However, we would apply other criteria – achieving the residual oil concentration in treated water which is lower than the maximum permitted by the standard with the minimum energy. Requirements toward the oil-drilling companies for discharging produced water are given by the Decree 6 (Bulgarian Council of Ministers 2000). The MAC which must not be exceeded for the oil hydrocarbons is 20 mg/L at water pH in the range of 6-9.

This MAC is in line with worldwide set standards. For example the United States Environmental Protection Agency regulations require the daily maximum limit for O&G of 42 mg/L and the monthly average limit of 29 mg/L (US EPA 2011). In Australia the permitted offshore discharge of oil and grease in produced water is 30 mg/L (Iggunnu and Chen 2014).

Table 5 shows the treatment conditions and the energy required for experiments where the residual oil concentration in treated water is less than 20 mg/L.

Table 5. Treatment conditions and the energy required to achieve residual oil concentration less than 20 mg/L

TOH final concentration, mg/L	Treatment conditions	Energy per mass removed oil, kWh/kg	Electrical charge Ah/L
13.6	10 mA/cm^2 , 10 min, Fe	0.603	0.071
10.7	8 mA/cm^2 , 15 min, Fe	0.629	0.086
7.0	10 mA/cm^2 , 15 min, Fe	0.886	0.107
3.0	10 mA/cm^2 , 20 min, Fe	1.164	0.143
3.0	12 mA/cm^2 , 15 min, Fe	1.267	0.129
0.08	15 mA/cm^2 , 15 min, Fe	2.110	0.161

Data presented in Table 5 show that the optimum conditions for the EC/EF are as follows: current density 10 mA/cm^2 applied for duration of 10 min and calculated energy consumption 0.603 kWh/kg, when the TOH removal of 95.4 % and COD removal of 24.5 % were achieved. Similar results, TOH

removal 96.4 % and COD removal 26.1 % were found for current density 8 mA/cm², treatment time 15 min and energy consumption 0.629 kWh/kg. If the aimed TOH concentration is less than 5 mg/L, then the energy consumption practically doubles.

Cânizares and coauthors (2007) investigated the influence of the electrical charge passed in the EC process with Al electrodes, and they reported that the demulsification was occurred for the values of the electrical charge higher than 0.1 Ah/dm³. As it can be seen in the Table 5, our values for the optimum conditions are near to that figure.

The lower energy needed per kg oil removed by EC/EF, higher TOH removal and ability to achieve residual oil concentrations less than MAC point at the superiority of EC/EF over the EO/EF at least for water polluted by heavy oil.

In addition, it has to be mentioned that the total iron concentration in the treated water at the end of all EC experiments was in the range of 1.0 -1.5 mg/L like in the raw water and less than the MAC requested by the Bulgarian legislation (Bulgarian Council of Ministers 2000).

The Bulgarian legislation (Bulgarian Council of Ministers 2000) requires the pH of the treated water to be in the range of 6 - 9. At the end of all experiments the pH value of water was slightly increased - the measured values were in the range of 7.75 – 8.05 and meet the standards.

4. CONCLUSION

The electrochemical treatment of produced water is an environmentally friendly process that demonstrates advantages over the other treatment methods, such as: (i) no addition of chemicals for the oil hydrocarbons removal and manipulation of water pH which in turn makes the treatment process both simple and cost effective, (ii) saving of energy, since the treatment is carried out at ambient temperature and the process can be optimized with the respect of energy consumption, and (iii) easy control because the processes are determined by the applied voltage or current density that can be readily adjusted as necessary.

A considerable decrease in the concentration of oil hydrocarbons and COD can be achieved by conducting electrooxidation accompanied by electroflotation, i.e. by carrying out the process with insoluble (dimensionally stable) anode. At the presence of chloride ions in high concentration in the PW, the most probable mechanism of pollutants removal is oxidation by *in situ* generated oxidizing agents.

Electrocoagulation (supplemented by electroflotation) carried out with iron sacrificial anode has been found to be more effective than the electrooxidation (accompanied by electroflotation) for treatment of the PW polluted by heavy hydrocarbons. MAC of TOH in the treated water requested by the legislation can be achieved with lower energy consumption, in comparison with the EO. Treated water meets standards with respect to residual iron concentration and pH value.

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