LIQUID PHASE OXIDATION AS A POSSIBILITY FOR THE REMOVAL OF OIL COMPOUNDS FROM PRODUCED WATER

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ABSTRACT. The extraction of oil is accompanied by the generation of a large amount of wastewater polluted with various organic compounds. In order to be discharged into natural water bodies or re-injected into the wells, the wastewater must be treated to meet the requirements laid down in the relevant legislation. This work presents: (a) the results of the analysis of real water samples produced in the course of oil production – discharged or re-injected; (b) the results of laboratory experiments carried out with real water samples that explore the potential of two liquid phase oxidation methods (using hydrogen peroxide and hypochlorite solution) to remove organic pollutants. Data from the hydrogen peroxide oxidation study at different concentrations of the added reagents are provided. Information on the effect of the added hypochlorite concentration and treatment time on the oil compounds and COD removal efficiency is presented. The kinetics of the process of decreasing the concentration of pollutants from both types of water (discharged and re-injected) has been monitored at the optimum concentration of the added hypochlorite.

Keywords: oilfield produced water treatment, oily wastewater purification, liquid phase oxidation

ОКИСЛЕНИЕ В ТЕЧНА ФАЗА КАТО ВЪЗМОЖНОСТ ЗА ОТСТРАНЯВАНЕ НА НЕФТОПРОДУКТИ ОТ ПРОДУКЦИОННА ВОДА

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РЕЗЮМЕ. Добивът на нефт е съпроводен с генериране на огромно количество отпадъчна вода, замърсена с различни органични съединения. За да бъдат заустени в естествени водосборни басейни или реинжектирани, отпадъчните води трябва да бъдат третирани, за да отговарят на изискванията, предвидени в съответното законодателство. Настоящата работа представя: (а) резултатите от анализа на зауствани или използвани за реинжекция реални водни проби от добив на нефт; (б) резултатите от лабораторни експерименти, проведени с реалните водни проби и изследващи възможностите на два метода за окисление в течна фаза (с водороден пероксид и с разтвор на хипохлорит) с цел отстраняване на органичните замърсители. Предоставят се данни от изследване на окислението с водороден пероксид, при различни концентрации на добавения реагент. Дава се информация за влиянието на концентрацията на добавения хипохлорит и времето за третиране върху ефективността на отстраняване на нефтопродукти и ХПК. Проследена е кинетиката на процеса на намаляване на концентрацията на замърсителите в двата вида води (зауствани и използвани за реинжекция) при оптимална концентрация на добавения реагент.

Ключови думи: третиране на отпадъчна вода от добив на суров нефт; пречистване на отпадъчна вода, замърсена с нефтопродукти; окисление в течна фаза

Introduction

Oil well production fluid usually consists of oil and water that is generally separated by physical techniques. The water stream is referred to as "produced water" or in broader sense – "oily wastewater". The composition of the produced water depends mainly on the oilfield geological conditions, the recovery method, and the age of the production wells. Although concentrations of different pollutants can vary by order of magnitude, the contaminants in the produced water can be divided into the following groups: dissolved and dispersed oils, dissolved formation minerals, production chemicals, production solids, and dissolved gases (Ahmadun et al., 2009). Oil is a natural mixture of hydrocarbons, such as benzene, toluene, ethylbenzene and xylenes (BTEX), naphthalene, phenantherene, dibenzothiophene (NPD), polyaromatic hydrocarbons (PAHs), and phenols. The polar constituents distributed between the low and medium carbon ranges are water-soluble. BTEX and phenols are the most soluble compounds in produced water. Organic acids (formic and propionic) are typically found in produced water. Aliphatic hydrocarbons, phenols, carboxylic acid, and low molecular weight aromatic compounds are most often included as soluble oil compounds in produced water. Usually, PAHs and some of the heavier alkyl phenols (C6–C9 alkylated phenols) are less soluble in produced water and less present as dispersed oil. The dissolution of the formation minerals leads to the availability of inorganic anions and cations, and radioactive materials in produced water. Salt concentration can vary in very wide ranges. Production chemicals are added to treat or prevent operational problems. However, their concentration in produced water is usually as low as 0.1 mg/L (Veil et al., 2004). Production solids are a wide range of materials (formation solids, corrosion and scale products, bacteria, waxes, and asphaltenes). In anoxic produced water, sulfides (polysulfides and hydrogen sulfide) are generated by sulfate reducing bacteria (Neff, 2002).

Produced water is the largest waste stream generated in oil industry (Hosny et al., 2015). Table 1 summarizes the range of produced water characteristics in different oilfields in the world (Tibbetts et al., 1992; Bessa et al, 2001; Li et al, 2006; Lu et al., 2006; Ahmadun et al., 2009; Li et al, 2010; Hosny et al., 2015).

Table 1.
Range of produced water characteristics in different oilfields in the world

Parameter	Value	Parameter	Value
pH	4.3 – 10.0[1]	Phenols, mg/L	0.009-23
COD, mg/L	274-2,517	Chlorides, mg/L	274-2,517
BOD_5, mg/L	11-21[2]	Sulfates, mg/L	2-1,650
TOC, mg/L	0-1,500	Bicarbonates, mg/L	77-3,990
TSS, mg/L	1.2-1,000	Sulfides, mg/L	0.14[4]
TDS, mg/L	675-141,522	Sodium, mg/L	132-97,300
O&G, mg/L	31-275	Potassium, mg/L	24-4,300
TPH[3], mg/L	49-64	Calcium, mg/L	13-25,800
Total polar, mg/L	9.7-600	Magnesium, mg/L	8-6,000
Higher acids, mg/L	<1-63	Barium, mg/L	0.25-650
Volatile, BTEX, mg/L	0.39-35	Strontium, mg/L	0.02-1,000
Total oil (IR), mg/L	2-565	Heavy metals[5], mg/L	0.068-48.38

[1] Most often: 6.7 – 7.4
[2] Only Li et al., 2010
[3] Total petroleum hydrocarbons
[4] Only Lu et al., 2006
[5] Considered elements in this case are: Sb, As, Be, Cd, Cr, Cu, Pb, Hg, Ni, Ag, V, and Zn

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 produced water treatment: physical (such as the use of sand filters and cyclones, evaporation, freeze–thaw / evaporation), chemical (such as liquid phase oxidation with hydrogen peroxide - H_2O_2, Fenton reagent, hypochlorite, ozonation, supercritical water oxidation), physicochemical (such as adsorption on activated carbon, coagulation and flocculation, flotation, the use of electrochemical processes, the use of membrane processes), photocatalytic, and biological. The methods mentioned are used alone or in combination (Ahmadun et al., 2009; Yu et al., 2013; Jamaly et al., 2015; Seyed et al., 2016).

Chemical oxidation relies on the oxidation half-reaction, whereby a substance loses electrons, and a reduction half-reaction, whereby a substance accepts electrons. Both half-reactions always occur together since free electrons cannot exist in a solution and electrons must be conserved (RPSEA, 2012). Oxidants commonly studied in produced water treatment applications include hydrogen peroxide, ozone and calcium hypochlorite. The appropriate oxidant for a given application depends on many factors such as raw water composition, specific contaminants present in the water, and local chemical and power costs. Chemical oxidation is a well-established technology for treating wastewater. Generally, it requires minimum equipment. Oxidation can be employed to remove organics and some inorganic compounds, like iron and manganese, from produced water. The degree of removal or oxidation rate may be controlled by applied chemical dose and contact time between oxidants and water. No pre-treatment is required for oxidation.

Within 30 min, Wenhu and co-authors (2013) achieved up to 70 % COD removal from oily wastewater in batch experiments using wet hydrogen peroxide oxidation. Chemical oxidation of produced water separated from the gas stream of a gas refinery in Iran has been attempted by using hydrogen peroxide, ozone, and calcium hypochlorite (Shokrollahzadeh et al., 2012). The stoichiometric amount of hydrogen peroxide for the complete COD removal from produced water achieved 15% degradation of organic materials. Ozonation of produced water for 1 hour ended at 12% COD removal. Increasing the pH of the water to 10 improved treated water quality which indicated higher ozonation efficiency of the produced water at higher pH values. Maximum COD removal was achieved by using calcium hypochlorite as an oxidant - in the range of 36-70% depending on the hypochlorite concentration. The reaction was completed within 30 minutes.

Some authors find H_2O_2 as a proper oxidizing reagent, while others claim it is inefficient and report high oxidation efficiency when calcium hypochlorite is used; therefore, we have decided to test both reagents for the treatment of wastewater from a Bulgarian oilfield plant.

Methods and materials

Two water samples (noted as No 1 and No 2) were collected from two points where the produced water is discharged into a surface water body. Another two samples (noted as No 3 and No 4) were picked up from produced water re-injected into wells. Temperature, pH value, ∆pH value (index of water saturation with respect to $CaCO_3$), Eh value, and specific conductance 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. Hardness, respectively 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. The turbidimetric method was applied to determine the concentration of sulfates. The concentration of sodium and of potassium was determined by ICP-AES. Oil hydrocarbons concentrations were determined by the spectrophotometric method in the UV range, after their separation by extraction with CCl_4 (ASTM, 1979; BDS, 1989;

APHA, 1992; Krawczyk, 1996; UNEP/WHO, 1996). Sulfide concentration was determined spectrophotometrically. The method is based on the fact that sulfide ions and hydrogen sulfide form a sulfur-containing compound with dimethyl para-phenylenediamine in an acidic medium, which, upon oxidation with iron (III) chloride passes into methylene blue (BDS, 1989). Phenol concentration was determined spectrophotometrically by using Spectroquant NOVA 60 and Spectroquant phenol test. The method is analogous to EPA 420.1, APHA 5530 C+D, and ASTM D 1783-01. 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 concentration of residual active chlorine was determined by using Chlorine Test (free chlorine) in freshwater and seawater of Merck (1.14670.0001). The determination of chlorine is based on the reaction between tetramethylbenzidine (TMB) and free chlorine.

Water treatment with H_2O_2 was conducted at initial reagent concentrations of 25 mg/L and 200 mg/L of H_2O_2 for 30 min reaction time. Experiments with calcium hypochlorite [$Ca(ClO)_2$] were carried out at different initial concentrations (50, 200 and 400 mg/L) for 30 min of treatment time. In each experiment, 700 mL of the corresponding wastewater sample was used. All samples were stirred with a magnetic stirrer at a speed of 400 rpm. The presented data are average from two parallel trials.

Results and discussion

Data on integral physicochemical parameters of the studied samples are presented in Table 2. The values of concentration of macro-components are summarized in Table 3.

Table 2.
Integral physicochemical parameters of the studied water samples

No	t °C	pH	Eh mV	rH	χ mS/cm	ΔpH	Diss.O_2 mg/L
1	20.2	7.46	-14	14.45	5.76	+0.07	<0.08
2	19.0	7.42	-16	14.30	3.45	-0.01	<0.08
3	25.2	7.23	-86	11.55	4.43	-0.01	<0.08
4	30.3	7.67	-141	10.57	5.74	-0.07	<0.08

Table 3.
*Concentration of macro- and meso-components of the studied water samples, mg/L**

No	1	2	3	4
Ca^{2+}	101	73	83	100
Mg^{2+}	54	40	47	56
Na^+	1052	624	900	1050
K^+	17	16	15	16
Cl^-	1782	980	1312	1780
HCO_3^-	433	500	567	580
SO_4^{2-}	18	18	22	28
S^{2-}	2.40	1.96	3.42	9.76
Hardness	4.74	3.47	4.0	4.8

*Hardness – in mmol/L

Table 4 shows some integral chemical parameters of the analyzed water samples.

Table 4.
Some integral parameters of the studied water samples

No	COD, mg/L	Oil compounds, mg/L	Phenols, mg/L
1	46	52	0.11
2	39	262	0.18
3	39	47	0.07
4	58	184	0.21

By comparing the values presented in Tables 1 and 2, it may be stated that the pH value of the studied water is in the range of the typical values. Having in mind the existing relation between salt concentration and specific conductance, it is clear that the produced water under consideration is practically in the lower edge of the worldwide reported salt concentrations of produced water. The measured Eh values are indicative for anaerobic conditions. This is in accordance with the very low concentrations of dissolved oxygen and concentrations of sulfides determined in most samples (Table 3). Considering the calculated rH values, we can conclude that all tested waters possess slightly reducing properties and those are more pronounced for re-injected waters. The quick ΔpH test showed that waters are practically in equilibrium with respect to calcium carbonate.

As expected for the produced oilfield water, Na^+ is the major cation and Cl^- is the major anion found in studied waters (Table 3). Concentrations of all other macro-components are in the lower edge of the worldwide reported concentrations in produced water (Tables 1 and 3).

Requirements toward the oil-drilling companies for discharging produced water are given by Decree 6 (Bulgarian Council of Ministers, 2000). The limits which must not be exceeded are given in Table 5.

Table 5.
Maximum permissible concentrations / levels of some water pollutants subjected to observation in oilfield production water intended for discharge (Bulgarian Council of Ministers, 2000)

Parameter	Threshold value
pH	6 - 9
Oil hydrocarbons	20 (40^1) mg/L
Phenols	1.0 mg/L
Sulfides	1.0 mg/L

^{1} - at production capacity of less than 10, 000 t/day

The comparison between the limits given in Table 5 and the values found and presented in Tables 2, 3 and 4 shows that the water samples meet the legislation criteria with respect to pH values and concentration of phenols, while higher concentrations of sulfides and oil compounds were observed. The measured COD values are below those reported for non-treated produced water by other authors (compare with Table 1). The data for COD point out that all studied samples show low concentration of chemically oxidizable compounds by dichromate ions. Usually, this is the case when heavy organic compounds are present in the wastewater as tiny droplets. We have determined the density of the extracted crude oil of 0.952 g/cm^3. The oil can be classified as heavy crude oil - with density in the range of 0.88 – 1.00 g/cm^3 (Fingas, 2015). This finding is supported also by the gas chromatography that shows availability in the produced water not only of typical low molecular weight hydrocarbons but also of compounds having a molar mass that is higher than 300 g/mol and corresponds to polycyclic aromatic hydrocarbons (Marvin, 1999). According to Fingas (2015), heavy crude oil is rich in tri- to pentacyclic terpenes and aromatic steranes.

Treatment of all samples with 25 mg/L of H_2O_2 led to the removal of oil compounds by less than 3 %. Increasing the H_2O_2 concentration up to 200 mg/L did not cause significant chemical oxidation of organics and the determined removal was no more than 5 %. Therefore, the wet oxidation with H_2O_2 is not suitable for the studied type of produced water and further experiments with this oxidizing reagent were aborted.

Results on oil compounds removal by oxidation with calcium hypochlorite are presented in Table 6.

Table 6.
Oil compounds removal (%) by hypochlorite treatment at different concentrations for 30 min

No	Oil Removal, %		
	50 mg/L	200 mg/L	400 mg/L
1	18	77	78
2	77	84	86
3	3	42	81
4	3	11	55

The results presented in Table 6 show: (a) Increasing the reagent concentration from 200 to 400 mg/l does not improve the results significantly for samples 1 and 2; (b) For samples 3 and 4 only the highest concentration of the oxidant results in good oil removal. Such behavior corresponds to the two types of studied waters – discharged (1 and 2) and re-injected (3 and 4).

The only significant difference between these two types of water samples can be found in the concentrations of sulfides, the Eh and rH values, which reveals different reductive properties of the media. The oxidizability of the oil compounds present in the water depends not only on the oxidizing agent but also on the solution properties and results in a different degree of decomposition of organics.

A reported drawback of using calcium hypochlorite is the high concentration of residual active chlorine in the treated water (Shokrollahzadeh et al., 2012). In our case, such disadvantage was not observed and the measured residual chlorine concentration was less than 0.3 mg/L, which is within the limits for drinking water (Bulgarian Council of Ministers, 2001).

It is worth mentioning that a lower removal for samples 1 and 4 was determined and it may have been due to a short reaction time. In order to study the kinetics of the reaction, we chose these two samples (1 and 4) for further experiment. Our preliminary experiments showed that a concentration 200 mg/L of $Ca(ClO)_2$ causes good oil removal for sample 1 and would allow us to study the kinetics of the oxidation process for 60 min. Sample 4 requires higher oxidant concentration to achieve a moderate removal, and the kinetic study was performed with 400 mg/L of $Ca(ClO)_2$ for 60 min.

The kinetic curves for samples 1 and 4 are presented in Figure 1.

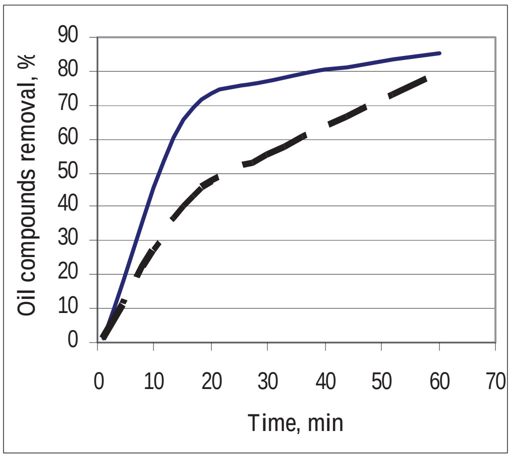

Fig. 1. Kinetic curves of oil compounds removal by oxidation with $Ca(ClO)_2$: sample 1 ―, sample 4 - - -

As can be seen in Figure 1, increasing the treatment time leads to higher oil removal for both samples. We can relate that to the more complete oxidation for a longer time. Kinetic curves reveal that the reaction consists of two stages – 1st “fast” and 2nd “slow”. Generally, it shows that different processes take place and limit the oxidation reaction rate during the fast and slow step. Despite of lower oxidant concentration for sample 1, its initial reaction rate for the first 20 minutes is higher than that for sample 4. Most probably, the oil contaminants in water 4 are compounds that are more stable to oxidation. After this period, the reaction rate for both samples decreases, but the rate for sample 1 drastically lowers due to the consumption of oxidant. The rate for sample 4 seems to become higher than that of sample 1, which may relate to the oxidation of organic compounds with lower molecular weighs produced during the first stage of the reaction. In the end of the reaction time, the removal for sample 1 is 85% and for sample 4 is 79%. We cannot assume that complete oxidation will be achieved, unless a large excess of the oxidant is used, because the whole amount of oxidant added in wastewater may not be available for the oxidation of organic matter only. Some amount of oxidant is expected to react and oxidize inorganic pollutants present in the wastewater (for example, heavy metals and sulfides).

Chemical oxygen demand is another parameter that was controlled during the treatment of produced water. Taking into consideration the kinetic study results, we applied $Ca(ClO)_2$ in concentration 200 mg/L for sample 1 and treated it for 30 and 60 min, while for sample 4 we have used higher concentration of $Ca(ClO)_2$, 400 mg/L. Results on COD removal for samples 1 and 4 by oxidation with hypochlorite are presented in Table 7.

It seems that (Table 7) the increase in treatment duration leads to an increase in the COD removal. The impact of the reaction time on COD removal was more pronounced for sample 4, which contained more organics that were stable to oxidation and was treated with higher concentration of the oxidizing reagent.

Table 7.
COD removal for samples 1 and 4 by hypochlorite treatment for 30 and 60 min reaction time

No	Treatment conditions	COD removal, %
1	30 min, 200 mg/L $Ca(ClO)_2$	14.6
1	60 min, 200 mg/L $Ca(ClO)_2$	18.2
4	30 min, 400 mg/L $Ca(ClO)_2$	17.5
4	60 min, 400 mg/L $Ca(ClO)_2$	36.6

Such finding is in accordance with the data observed for the oil removal parameter (Table 6 and Fig. 1). Similar percentage of the COD removal, at similar concentrations of the $Ca(ClO)_2$ used, were reported by other authors as well (Shokrollahzadeh et al., 2012). It is worth to mention that in many cases, the COD removal is considerably lower in comparison with the oil removal. It can be considered as an indirect evidence for the transformation of oil compounds with big molecular weight to smaller molecules upon treatment with oxidant, and then low-carbon-chain organics are easily oxidized by dichromate, which cause a higher analytical result for COD. Further studies are needed to clarify the mechanism of chemical oxidation of various oily compounds.

Conclusions

In this study, we explored the possibility for chemical oxidation treatment of oilfield produced water, generated after gravitational separation of heavy crude oil from the extraction fluid. We found that the wet oxidation with H_2O_2 is not suitable a method for the produced water polluted with high molecular and polycyclic oil compounds.

Oxidation with calcium hypochlorite is a promising technology for removing heavy oil compounds and decreasing the water COD. Chemical properties of the oil compounds, treatment time and oxidant dose are important factors that influence the oil removal efficiency. Generally, the increase of oxidant concentration and treatment time increase the oil compounds and COD removal efficiency.

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