Research Article

Oil field produced water recovery and boosting the quality for using in membrane less fuel cell

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Abstract
With recent surge of strict regulations to treat the produced water, many companies start preparing efficient treatment methods to create the end permeate that can be disposed. This produced water is produced in massive amount during the crude oil and gas production either onshore or offshore. Furthermore, this wastewater has distinctive characteristics as it has many different contaminants packed inside which are mostly due to variation of organic and inorganic compounds. However, this water with proper treatment can preserve microbes which are very prominent in it. The key is to maintain the feed for the microbes and remove unnecessary contaminants that hinder microbes activities which creates conducive environment. Thus, the methods for this study was chosen to remove the dissolved oil droplets using coagulation/flocculation, microfiltration membrane and forward osmosis. These methods will be able to remove grease and oil while maintaining the chemical oxygen demand and other organic compounds that act as the feed for the microbes that are already in the produced water. At the end of the experiment, the conductive environment for the microbes achieved. This enables the end permeate to be further treated with microbial fuel cell that not only treat the organic compounds in the water, it can also produce electricity that can be commercialized.

Keywords Component · Microbes · Microbial fuel cell · COD · Water treatment

1 Introduction

The definition of produced water is it is the trapped water that was found in underground formations that is brought to the surface along with the oil and gas [1]. The volume of this waste water amounts to around 70% of the total waste water produced during the oil production [2]. The properties of PW and characteristics can vary based on the field geographic location which the geographic formation the PW was in contact with for thousands of years. Its properties and volume can change throughout the lifetime of the reservoir. Furthermore, PW is filled up with many inorganic and organic compounds that can cause toxicity. The compounds can be from naturally occurring in PW and some may from related to chemicals that have been added for well control purposes such as Enhanced Oil Recovery (EOR) [1]. Due to increasing stringency of environmental regulations require extensive treatment, hence the treatment and disposal of such volumes costs the industry annually more than USD 40 billion (Fig. 1). The figure below shows the increasing trend of produced water as the years increases [3].

The produced water varies greatly with quality and quantity which might become useful or even salable commodity. In the beginning it is considered as the waste but now with current technology, it can be a potential profit generator [4]. The generated wastewater needs to be treated and or regenerated in the most economical and environmental ways to save both energy and environment [5]. The treatment for these waters ranges from removal of larger oil molecules to completely treating it to be clean disposable water.

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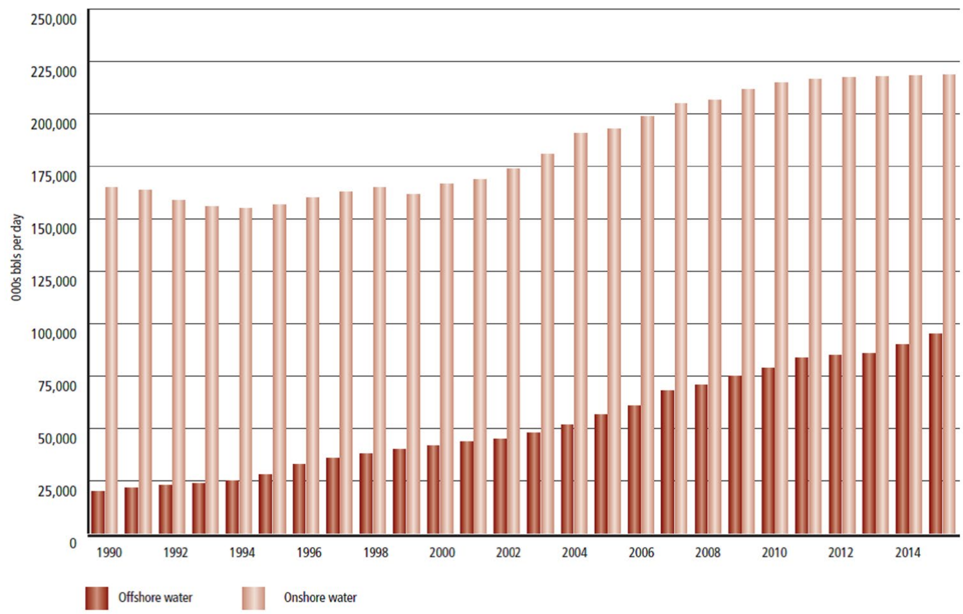


Fig. 1 Global onshore and offshore water production [3]

However, recent papers and reports, with many physical and chemical separation processes such as coagulation, acidification and membranes processes had been performed, these processes alone did not provide the petroleum waste discharge standards [2]. The proper method that gives best permeate requires a series of pre-, and post-treatment operations to remove various contaminants [6]. Pre-treatment involves separation techniques such as removal of oil, grease, suspended solids, microfiltration, ultrafiltration, forward osmosis etc. The post-treatment focuses on removal of organic compounds such as electroflocculation, adsorption, bioreactors and microbial fuel cell [6].

By combining a separation method and an organic compound degradation method this project aims to produce a conducive environment for the bacteria that are already in the produced water to undergo biodegradation for fuel cell in post-treatment by pre-treating the produced water. The pre-treatment that was selected for this project is by using the coagulation/flocculation treatment method, microfiltration membrane and forward osmosis method to produce an optimal environment for the bacteria to undergo biodegradation.

Coagulation and flocculation process takes place when the dispersed fine oil particles being converted into large agglomerated flocks. This method is often used for the primary purification process due to its ability of having high efficiency of grease and oil removal, cost effective ease of operation and uses almost no external energy input to conduct the treatment than other treatment method [7]. Based on previous researches, the efficiency of removal was more than 90% of grease and oil for samples using alum at pH 6–7 at 1 g/L. If pH 5 was chosen, the concentration of coagulant had to be increased to 2 g/L to get the same result. Similar results were also obtained with grease and oil removal efficiency of 90% [8].

The pre-treatment of PW using microfiltration (MF) considered as removal of macro constituents. In one of the reports that discusses the combination of different membrane filtration for PW treatment proved microfiltration as a good pre-treatment method. The COD removal efficiency that can be achieved by this method was found about 92% [9]. For the oil removal, the finding [6] reported that 0.2 µm MF membrane alone able to reduce the oil content as much as 93%. While this in full agreement by the report from [10], the same report also suggest using MF membrane after removing the bulk of the oil components. The main reasoning behind this is due to the membrane fouling as the MF can only handle oil droplets from 0.1 to 10 µm. However, it can also remove dispersed oil down to the size of 100 nm which is very efficient in removal of dissolved oil [10].

Forward osmosis is a membrane technology similar to the microfiltration. The FO has permeate side that contains very high osmotic solution that act as draw solution and due to osmotic pressure difference between feed and draw solution the separation occurs spontaneously. Previous study shows that the FO could give permeate to almost complete rejection of oil and NaCl [11]. While this seems very good environment for the microbes for optimum biodegradation, the availability of the microbes itself after the treatment in the PW is questionable. This investigation will be conducted in this experiment to determine whether the current can be produced using MFC when using this type of treatment.

According to Produced Water Society, produced water salinity can range from 100 to 400,000 mg^{-1}. In 1999, it was estimated, the total volume of produced water being produced amounted to be more than 210 million bpd approximately 3 times the world oil production [12]. The soluble compounds found in this water mostly consists of phenolics and other oxygenated aromatics and aromatic hydrocarbons. It also contains other traces of metals and H_2S. Combined all of these, produced water can be a significant potential source of toxic aromatic contaminated hypersaline [12]. Thus, the treatment of produced water is very essential to safely remove the contaminants before disposing it properly.

With current technologies, produced water can be treated by various methods either by physical, chemical or biological method. Numerous studies conducted that identify, verify, and compile existing and newly developed techniques demonstrate the economical benefits of produced water treatment [4]. One of the methods that received exceeded attention recently is the biological treatment. However, biological treatment such as activated sludge system does not function at hypersaline environment [12].

Recent studies more focused on isolating the bacteria from different environments to be introduced into the produced water [13]. This creates an unfavorable environment for the bacteria. Furthermore, the hypersaline environment requires the bacteria such as the pseudomonas sp. to be isolated from hypersaline environment [14]. Although this bacterium holds tremendous ability to degrade organic matter such as aromatics and COD, they can be harder to obtain and maintained.

The objectives of this study are to treat produced water by removing large oil particles and inorganic matter using coagulation/flocculation; to produce a conducive environment for the microbes to undergo biodegradation by removing dissolved oil droplets using microfiltration membrane and forward osmosis method and to study the parameters such as COD, pH, grease and oil and the current produced from the treatment sample using microbial fuel cell.

2 Materials and methods

2.1 Materials

- 1 mol H_2SO_4 acid was used for acidification.
- 1 g/L aluminum sulphate for coagulation/flocculation.
- 2 mol NaOH was used to adjust pH to 7.
- 47 mm Whatman 0.45 µm cellulose membrane was used for microfiltration.
- CTA FO sized 80 mm long, 60 mm wide and 2 mm thick membrane was used for FO treatment.
- 0.25% sodium hypochlorite solution (NaOCl) was used to clean the membrane prior to each testing.

2.2 Apparatus and procedure

2.2.1 Cogulation/flocculation procedure

First step for the experiment, initial COD, grease and oil and pH was measured. Then, H_2SO_4 was used for acidification of 1 L of produced water until pH 3. The experiment was to be conducted using Phipps and Bird standard Jar test unit for three samples. The samples were allowed to stir at 30 rpm for 20 min [8] followed by retention period of three days.

Then, the treated effluent was to be introduced with coagulant (alum). The experiment was further conducted using the Phipps and birds standard jar test unit. The samples used were coagulated under conditions of rapid and slow stirring at 100 rpm for 2 min and 30 rpm for 20 min [8]. The final COD, grease and oil and pH was measured for all three samples and averaged (Fig. 2).

2.2.2 Microfiltration membrane procedure

The produced water was conditioned initially at constant temperature of 25 ± 1 °C and 1 L was pumped at 20 bar pressure to the 0.45 µm cellulose microfiltration membrane unit. The surface area of the membrane used is 4.91 cm^2. Filtration was initiated, and pH, grease and oil and COD were measured in raw and treated water [9]. This was repeated for three similar cellulose membranes and the results were averaged. The pre-treated water are then supplied to the microbial fuel cell to check for the resulting electricity produced and the amount of COD reduced (Fig. 3).

2.2.3 Forward osmosis procedure

The flat-sheet CTA FO membrane from HTI was installed on the test cells. The FO membrane system is operated in

Fig. 2 Phipps and bird standard jar test unit

FO mode where the active layer is facing the feed channel and the pressure is maintained at atmospheric pressure (14.7 psia). The size of FO membrane is 80 mm long, 60 mm wide and 2 mm thick.

The draw and feed solutions flowed co-currently at flow rates of 500 ml/min in each channel on both sides of the membrane, using peristaltic pumps and flowmeters. After filtration, properties of the feed and draw solutions were measured. A new FO membrane coupon was used for each produced water solution. The system was cleaned thoroughly using 0.25% sodium hypochlorite solution (NaOCl) for 30 min, followed by de-ionized water for 1 h prior to each experiment. The experiment was repeated three times and values were averaged. The setup was done as per Fig. 4 below.

2.2.4 Analysis of fourier-transform infrared spectrocopy (FTIR)

The used microfiltration and FO membranes were then tested using FTIR from wavelengths of 500–4000 cm^{-1} for the presence of biofouling and filtration residue identification.

3 Results and discussion

3.1 Results obtained

After all the pre-treatment done, the main parameters such as pH value, grease and oil and COD has been measured for each filtration method. The Table 1 below shows values for parameters mentioned above.

The efficiency of removal was calculated using the below equation:

$$\textit{Removal efficiency}\ (\%) = \frac{\textit{Pure PW value} - \textit{After pretreatment value}}{\textit{Pure PW value}} \times 100\%$$

Using the equation above, the efficiency of each filtration method is tabulated in Table 2.

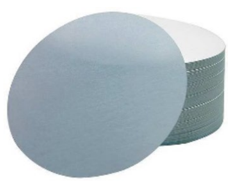


Fig. 3 0.45 µm cellulose microfiltration membrane

Fig. 4 FO membrane setup

3.2 COD removal efficiency

For the coagulation/flocculation, the COD removal efficiency is much smaller than the microfiltration method which is only 6.4% compared to 35.1% from the latter method. The main reason behind this is microfiltration allows for anything bigger than its pore size (0.45 µm) to be filtered out from the PW. Despite being more efficient than coagulation/flocculation method, the filtration

Table 2 Efficiency for each filtration method

Parameters	Coagulation/flocculation	Micro-filtration	Forward osmosis
COD (%)	6.4	35.1	88.4
Grease and oil (%)	43.2	50.8	90.4

Table 1 Results for various treatment method

Parameters	Pure PW	Coagulation/flocculation	Micro-filtration	Forward osmosis
COD (ppm)	5629	5267	3651	650.67
pH	2.35	7.1	2.35	7.64
Grease and oil (ppm)	6.6	3.75	3.25	0.63

had caused the membrane to foul and needed a second replacement to continue running the experiment. On the other hand, as the main intention of this experiment, the COD should be retained high as the feed for the microbes. The FO membrane gives to almost 88% COD removal efficiency which is the highest among the treatment methods. However, the treatment took the longest time up until 4–5 days just to run 80 ml of sample despite being much less prone to membrane fouling than the microfiltration membrane.

3.3 Grease and oil removal efficiency

Analyzing the result for grease and oil, the similar trend can be seen for the microfiltration method which yields 50.8% efficiency of removal with a margin of 7.6% difference from the coagulation/flocculation method. However, the membrane fouling again plays an important role as the filtration happens much slower as the pores of the membrane gets blocked by the grease and oil which prevents from filtrate to flow easily. The effect of membrane fouling can be seen from the figure below. On the other hand, FO membrane removed highest grease and oil up to 90.4% of removal efficiency. Despite being less prone to membrane fouling than microfiltration membrane, the total time taken to complete the treatment was significantly longer (Figs. 5, 6).

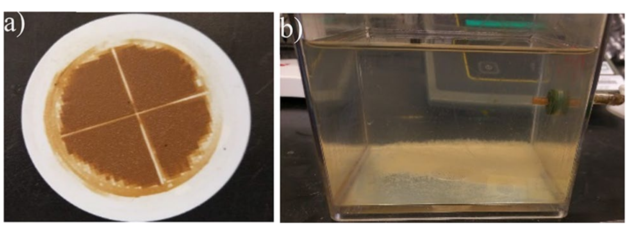


Fig. 5 **a** Microfiltration membrane grease and oil accumulation **b** flocculated grease and oil for coagulation/flocculation treatment

3.4 FTIR test

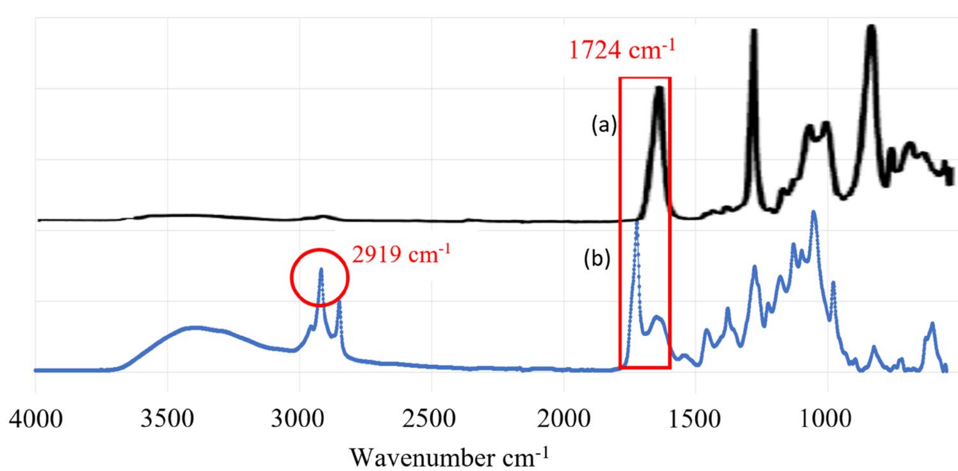
FTIR gives plot of transmittance percentage against wave number which was used for analysis and interpretation. The aim of FTIR for this study was to investigate the biofouling effect of the treatment membranes used which were cellulose microfiltration membrane and FO membrane and the consequence of possible microbes filtered out on current generation at MFC. From the plot at around 1705–1725 cm^{-1} C=O stretching can be found that attributes the nitrocellulose property of the membrane. The properties are: (1) there is hydrophobic interaction between the carbon containing nitrocellulose and hydrophobic part of biomolecule and/or (2) the existence of an electrostatic interaction between the dipoles of nitrocellulose nitrate groups and the dipoles of the biomolecules. This gives the ability of the membrane to reject organic compounds that can be found in the produced water [15, 16].

Further evidence can be found at peak around 2900 cm^{-1} which indicates the existence of C-H stretching from alkane functional group. Note that the peak present on plot (b) is absent in plot (a). This peak represents the presence of C–H stretching of alkane functional group which are prominent in produced water mainly occur after biodegradation of microbes took place. The presence of

Table 3 IR absorption table

Absorption	Functional group	Compound class
3000–2840	C–H stretching	Alkane
1725–1705	C=O stretching	Aliphatic ketone

Fig. 6 FTIR for microfiltration before (a) and after water treatment (b)



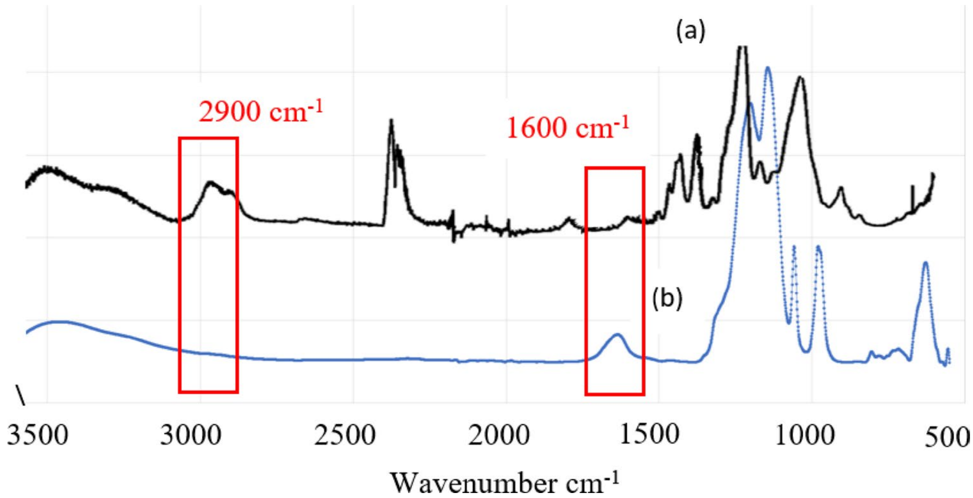


Fig. 7 FTIR of FO membrane before (a) and after water treatment (b)

this functional group indicates the fouling that took place on the membrane (Table 3; Fig. 7).

From the plot above several untreated FO membrane peaks disappeared or weakened when biofouling took place on the membrane during treatment. This is evident in the peaks of around 2900 cm^{-1} represented aliphatic methylene group found in fats or lipids and around 1600 cm^{-1} indicating amide I. Amide I corresponds to the peptidoglycans found in bacterial cell walls [16]. From this, it can be concluded that bacteria had been filtered out together with dissolved oil due to biofouling during the treatment of the produced water. This can result in lesser current density generation during the MFC treatment.

3.5 pH value

The pH value for the pure PW and microfiltration method is 2.35. Microfiltration method did not decrease the pH value due to the membrane only act as to remove the physical pollutants of the PW and do not alter the chemical properties of the water. The acidic property of the PW influences the biodegradation activity which will be discussed later. However, coagulation/flocculation method yielded pH value of 7.1 which is in the range of neutral value. The main reason is the treatment involves the adding sodium hydroxide to increase the pH to continue using the alum as the coagulant for maximum efficiency of removal.

3.6 Microbial fuel cell (MFC) results of filtration sample

After all the filtrations was done, the resulting pre-treated waters were tested using the MFC to investigate the amount of current produced due to biodegradation of the microbes using the organic matter found in the water and result is shown in Table 4.

The above result shows that coagulation/flocculation treated PW has more impact on the microbial fuel cell than microfiltration. The efficiency of COD removal for coagulation/flocculation treated sample is almost double the microfiltration one. This is because the amount of COD retained after treatment is used by the microbes to generate current. Thus, more COD is used by the microbes to generate more current. However, the FO membrane treated water yielded the smallest current density mainly due to absence of microbes to undergo biodegradation.

Table 4 MFC result

Filtration sample	Actual pre-treated COD (ppm)	After MFC COD (ppm)	Removal efficiency (%)	Current density (mA/m^2)
Coagulation/flocculation	5267	2822	46.42	1.99
Micro-filtration	3651	2800	23.31	0.32
Forward osmosis	650.67	639	1.69	0

4 Conclusion

1. The outcome of this study validates pre-treated PW should have neutral pH value and very low amount of grease and oil which creates a conducive environment for the microbes.
2. The permeate that was passed to the microbial fuel cell to generate current for coagulation/flocculation sample has double the COD removal efficiency and much higher current density than the microfiltration and FO sample. This concludes that although coagulation/flocculation treatment yields lesser efficiency of COD removal and grease and oil, the result for coagulation/flocculation sample for microbial fuel cell proven superior than the microfiltration and FO sample.
3. From this study, it can be concluded that, the best treatment method to create conducive environment for the microbes to undergo the most productive biodegradation is coagulation/flocculation method.
4. This is because this treatment method was able to produce an environment which has neutral pH, low amount of grease and oil and high COD compared to other treatment methods.
5. The FTIR proved both membranes able to filter dissolved oil and microbes. Reduction of microbes caused the lesser biodegradation took place and resulted in lesser current density production at MFC.
6. The recommendations mainly come with the availability of testing using dissolved air flotation. This method is very practical and efficient on removing large oil droplets and serves as the pre-treatment before introducing the filtrate to a finer filtration method such as the microfiltration method.
7. Another method that is more conventional is to use the water collected from the gravity-separation separator from the production facility. The water collected here is much easier to treat as the crude oil is separated into three phases: oil, water and gas.
8. The MFC used can be improved by modifying to better electrode material properties for better current reading [17].
9. It also recommended the experiment conducted using the actual produced water obtained directly from the offshore without gravity separation via separator to get the best representative result. This is also important for the COD content as higher amount of its content will give better result for the microbial fuel cell.

Compliance with ethical standards

Conflict of interest The author(s) declare that they have no competing interests

References

1. Veil JA, Puder MG, Elcock D, Redweik RJ Jr (2004) A white paper describing produced water from production of crude oil, natural gas, and coal bed methane. Argonne National Laboratory, USA
2. Sirivedhin T, Dallbauman L (2004) Organic matrix in produced water from the Osage-Skiatook Petroleum Environmental Research Site. Chemosphere 57:463–469
3. Dal Ferro B, Smith M (2007) Global onshore and offshore water production. Oil & Gas Review OTC Edition
4. Arthur JD, Langhus BG, Patel C (2005) Technical summary of oil & gas produced water treatment technologies. All Consulting, LLC, South Cheyenne Ave
5. Jafary T, Wan Daud WR, Aljlil SA, Ismail AF, Al-Mamun A, Baawain MS, Ghasemi M (2018) Simultaneous organics, sulphate and salt removal in a microbial desalination cell with an insight into microbial communities. Desalination 445:204–212. https://doi.org/10.1016/j.desal.2018.08.010
6. Ebrahimi M, Willershausen D, Kikavous AS, Engel L, Placido L, Mund P, Balduan P, Czermak P (2010) Investigations on the use of different ceramic membranes for efficient oil-field. Desalination 250:991–996
7. Mousa KM, Al-Hasan AA (2017) Oilfield produced water treatment by coagulation/flocculation processes. In: The second conference of post graduate researches (CPGR'2017), Baghdad, Iraq
8. Rattanapan C, Sawain A, Suksaroj T, Suksaroj C (2011) Enhanced efficiency of dissolved air flotation for biodiesel wastewater treatment by acidification and coagulation processes. Desalination 280:370–377
9. Çakmakce M, Kayaalp N, Koyuncu I (2008) Desalination of produced water from oil production fields by membrane processes. Desalination 222:176–186
10. Munirasu S, Abu Haija M, Banat F (2016) Use of membrane technology for oil field and refinery produced water treatment—a review. Process Saf Environ Prot 100:183–202
11. Zhang S, Wang P, Fu X, Chung T-S (2014) Sustainable water recovery from oily wastewater via forward osmosis-membrane distillation (FO-MD). Water Res 52:112–121
12. Piubali F, Grossman MJ, Fantinatti-Garbogini F, Durrant LR (2012) Enhanced reduction of COD and aromatics in petroleum-produced water using. Int Biodeterior Biodegrad 68:78–84
13. Yengejeh RJ, Sekhavatjou M, Maktabi P, Soleimani A, Khadivi S, Pourjafarian V (2013) The biodegradation of crude oil by bacillus subtilis isolated from contaminated soil in hot weather areas. Int J Environ Res 8(2):509–514
14. Ausama WA, Fawzi SA, Subhi JH (2014) Biodegradation of crude oil in contaminated water by local isolates of enterobacter cloacae. Iraqi J Sci 55(3A):1025–1033
15. Fridley GE, Holstein CA, Oza SB, Yager P (2013) The evolution of nitrocellulose as a material for bioassays. Mater Res Soc 38(4):326–330
16. Bell EA Long-term fouling and performance of forward osmosis membranes. In: Colorado School of Mines, Golden, Colorado

17. Ghasemi M, Jafary T, Alam J, Saad AA, Yusup Suzana (2017) Carbon-based polymer nanocomposites as electrodes for microbial fuel cells. https://doi.org/10.1016/b978-0-12-813574-7.00015-0