

# A Review on overboard CEOR discharged produced water treatment and remediation

H Rawindran<sup>1,2</sup>, S Krishnan<sup>1,2</sup>, C M Sinnathambi\*<sup>1,2</sup>

1. Centre of Research Enhanced Oil Recovery (COREOR), Universiti Teknologi Petronas (UTP), Seri Iskandar, 32610 Tronoh, Perak, Malaysia

2. Department of Fundamental and Applied Sciences, Universiti Teknologi Petronas (UTP), Seri Iskandar, 32610 Tronoh, Perak, Malaysia

E-mail: chandro@utp.edu.my

**Abstract.** Produced water is a waste by-product generated during oil and gas recovery operations. It contains the mixture of organic and inorganic compounds. Produced water management is a challenge faced by the petroleum practitioners worldwide. Build-up of chemical wastes from produced water causes huge footprint, which results in high CapEx and OpEx. Different technologies are practiced by various practitioners to treat the produced waste water. However, the constituents removed by each technology and the degree of organic compound removal has to be considered to identify the potential and effective treatment technologies for offshore industrial applications. Current produced water technologies and their successful applications have advantages and disadvantages and can be ranked on the basis of several factors, such as their discharge limit into water bodies, reinjection in producing well, or for any miscellaneous beneficial use. This paper attempts to provide a review of existing physical and chemical treatment technologies used for management of produced water. Based on our analysis, suitable methods will be recommended for offshore waste water treatment technologies.

## 1. Introduction

Oil production is separated into three phases; primary process, which involves the usage of artificial lift for oil recovery. Secondary process utilizes water alternating gas injection (WAG) method. These two recovery methods leave up to 70% oil in the well. Tertiary oil recovery method plays its role to recover the conventional primary and secondary oil recovery phase could not produce. There are several EOR techniques available in the industry; which includes, Chemical ( $C_{EOR}$ ), Thermal ( $T_{EOR}$ ), and miscible displacement process [1].

Oil recovery method has become highly effective and technological, therefore there are always renewed interest in enhanced oil recovery (EOR), specifically chemical enhanced oil recovery (C-EOR). C-EOR has the potential to unlock million barrels of unrecoverable oil from offshore reservoirs. Nevertheless, several technical and regulatory limitations has to be met before these techniques are implemented by the industry.

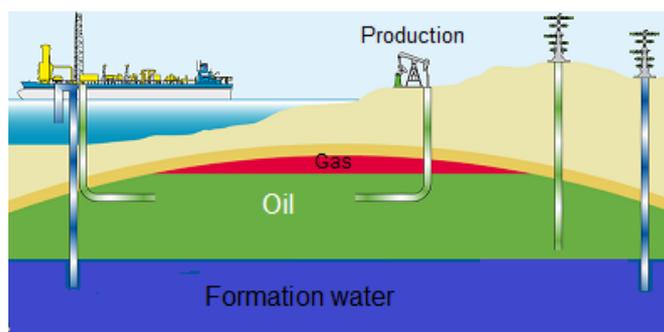
During the oil production, produced water that comes along with the recovered oil has to go through a series of treatment before it is discharged to the water bodies. Produced water is one of the largest by-product stream associated with oil and gas production. Therefore, driven by the urgent need to develop cost-effective produced-water management for the best interest of society, a lot of conventional as well as new treatment options has been introduced. This is particularly applicable to the treatment of produced water in offshore EOR applications, such as CEOR [2]. Treatment of produced water can lead to value through incremental oil recovery from water flood projects and by incurring a lower cost for disposal via injection of clean water [3].



### 1.1 Produced Water

Oil is the primary energy sources worldwide. In offshore platform, there is naturally trapped water underground called formation water. During oil recovery, this water along with the injected chemicals will flow through the well. The water that comes up to the surface along with the oil and gas is called the produced water.

Produced water originated from the formation water that was in contact with hydrocarbon-bearing formations. At the surface, hydrocarbons are separated from the produced fluid or produced water [4]. Therefore, it contains some of the chemical characteristics of the formations as well as the hydrocarbons. It may also include water from the reservoir, water previously injected into the formation, and residuals of those chemicals added during the production process [6].



**Figure 1.** Illustration on the overview of oil and gas platform [5]

### 1.2 Characteristics of Produced Water

Produced water can be characterized as saline water [7]. Generally, the constituents and characteristics of chemical substances in the produced water are interrelated to the geological characteristics of their respective reservoirs. The quality of produced water varies among the wells and fields. Major constituents of produced water are; salt content (Degree of salt present is expressed as salinity, in terms of total dissolved solids (TDS) or electrical conductivity), oil and grease (this is measured by an analytical test that measures the group that organic compounds belong to), natural inorganic and organic compounds (Ca, Mg, Ba and S are some of the chemicals that causes hardness and scaling) [8]. Other than these, components such as dispersed oil, aromatic hydrocarbons, alkylphenols (AP), heavy metals, and naturally occurring radioactive material (NORM) are some of the chemical additives that are used during drilling, fracturing and well operation which may hold toxic properties that exist in the produced water and serve as environmental threat [9].

## 2. Literature Review

### 2.1 Treatment Technologies of Produced Water

The offshore oil and gas industry generates hundreds or thousands litres of produced water from offshore oil production facilities in daily basis. Most of them are discharged into the ocean [10]. Operational discharges of produced water from offshore oil and gas platforms are a continuous source of contaminants to the ecosystems. Often disposal is chosen as an option to manage the produced water, as that is the cost effective method. But, prior to the disposal, many researches as well as technologies has been developed. This is to ensure that the environmental regulations are met.

Regulators usually specify the standards of pollutant discharges to offshore operators based on the best available technology (BAT). This BAT for the treatment of produced water has to be efficient in removing most free oil before discharged into the water bodies. Therefore, the oil that remains in the produced water is discharged into the ocean in dispersed and dissolved forms [10].

## 2.2 *Physical Treatment of Produced Water*

To meet up with these objectives, the regulators have developed treatment options for produced water management by physical or chemical means [11]. Treatment of produced water has the potential to be a harmless and valuable product rather than a waste. Some of these options are reviewed in the next section.

The treatment goals are essentially the same, i.e.; for reuse, reinjection or disposal, although the level of organic pollutant removal required for reuse can be significantly higher, depending on the quality of the produced water. Therefore, some of the treatment technologies employed are:

### 2.2.1 *Physical Adsorption*

Adsorption process is the physical adhesion of the contaminant chemicals onto a solid surface [12]. Adsorption process can be carried out by utilizing zeolites, organoclays, activated alumina and activated carbon. These adsorbents are potential of removing chemicals such as iron, manganese, total organic carbon, BTEX compounds, heavy metals, as well as oil from produced water. Organic compounds of produced water therefore adhere to porous media of carbon surfaces. After several experiments, the wet air oxidation process can regenerate activated carbon. This activated carbon can remove soluble BTEX which differs from organoclay that can remove insoluble free hydrocarbons. Organoclay is a mixture of sodium montmorillonite clay with a cationic quaternary amine salt. When organoclay is used in conjunction with activated carbon, hydrocarbon concentration falls below water quality standards. Copolymer beads are prepared based on methylmethacrylate (MMA) and divinylbenzene (DVB) by suspension polymerization. These copolymers can reduce oil content of produced water to around 85 % [14].

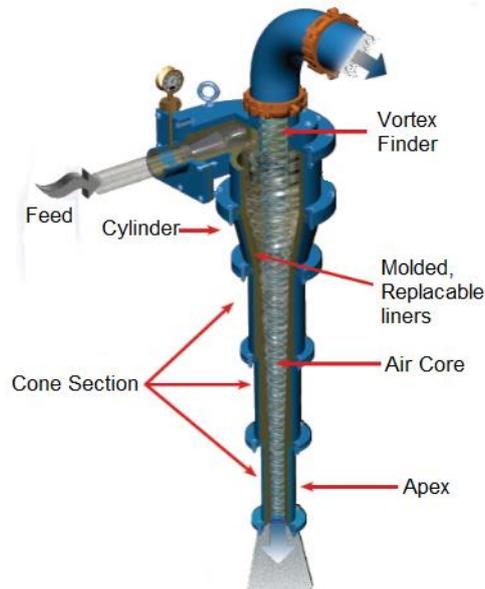
Zeolites are commonly used as ion-exchange resins. This hydrophobic zeolite pellets are usually in a fixed bed to adsorb dissolved organic compounds in produced water. At the same time, another study conducted by Mitchell et al, showed that a resin-filled column can be used to eliminate soluble organic compounds. The similarity of these two processes is, acid backwash and solvents can regenerate the adsorbers [4].

Adsorbents are capable of being exerted with large concentrations of organics, which makes this process to serve best as a polishing step rather than as a primary treatment process. This process works on the aid of gravity and does not require any energy, except for the backwash process [13].

Media usage rate is known as one of the main operational costs for adsorptive processes. When all active site of the adsorptive material have been consumed, the material must either be regenerated or disposed. Regenerating the materials will result in a liquid waste for disposal. Solid waste disposal is necessary when the material needs to be replaced entirely.

### 2.2.2 *Hydrocyclone*

The function of hydrocyclones is to separate solids from liquids according to the density of the material. Hydrocyclones usually has a conical base and cylindrical section at the top portion, where the liquid is fed tangentially (Figure 2).



**Figure 2.** Overview of hydrocyclone structure [10].

The utilization of hydrocyclones do not require any pre- or post-treatment nor any chemicals or energy. There will be no energy consumption with this equipment usage, as long as the plant setup needs to deliver water to the hydrocyclone through forwarding pump. Depending on the size and configuration of the hydrocyclone, a large pressure drop can occur across the hydrocyclone. Hydrocyclone generates waste in the slurry form of concentrated solids. This is the product from this equipment that requires disposal [13].

Compared to the conventional produced water treatment system, hydrocyclones offers offshore operators many advantages. This includes its benefits of being light weight, compact size, easy and reliable operation, and low maintenance, complete insensitivity to platform motions, low utility requirements and highly predictable capacity. When water production increases, hydrocyclones can be added without extensive piping modifications or additional costly construction. All these features are present at lower costs for a non-revenue producing function, and provides a cost effective alternative for meeting stringent environmental standards [5]. However, the disadvantage of using a hydrocyclone is that, this equipment has low efficiency and it is unable to remove dissolved components [16].

### 2.2.3 Evaporation method

Evaporation does not require any kind of chemical treatment that prevents the risk of secondary sludge handling. This process also does not require highly skilled labour. On the contrary, the requirement of energy for evaporation process is very high especially in the offshore platform, which could lead to increase in operating cost. The energy consumption could be brought down by reusing hot vapor to heat the fresh feed [15].

There are several types of evaporation method present for produced water treatment; such as, vertical tube, falling film, and vapour compression evaporation. These methods are effective because they eliminate physical and chemical treatments. Hence, no chemical sludge is produced, causing costs of waste and life cycle to be lowered [4].

A study conducted by Heins et.al, states that evaporation process by generating steam can be carried out at any heavy oil production to recover up to 98% of the produced water as high quality distillate (<10 ppm [mg/L] non-volatile inorganic TDS) for reuse or reinjection [15]. By using this

approach, the overall life cycle costs were found to be lesser for an evaporative produced water treatment system compared to the conventional approach [16].

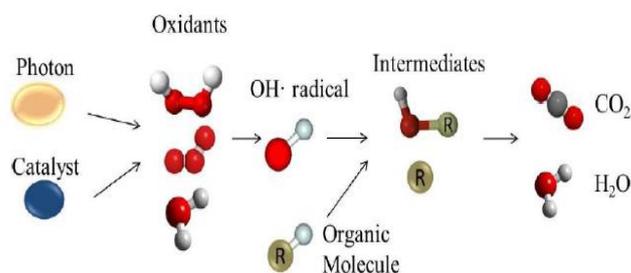
### 2.3 Chemical Treatment of Produced Water

#### 2.3.1 Demulsifiers

Demulsifiers functions to improve the oil and produced water separation. Depending on the respective demulsifier properties, the chemicals will partition between the oil and the water in the process. The reaction products and residual chemicals from those that partition to the water phase will be released to the water bodies with the produced water discharge. They reduce the oil-water interfacial tension. Demulsifiers are surface active agents that would disrupt the effects of surfactants. But a number of solids like silts, iron sulphide and paraffin, etc., present in the crude oil complicate the process [15].

#### 2.3.2 Advanced Oxidation Process

Advanced oxidation process (AOP) involves the generation of highly reactive hydroxyl radicle ( $\text{HO}\bullet$ ) and this have emerged as one of the important and promising technology to reduce chemical contaminants and toxicity. The degraded effluent can be reintroduced to receiving streams and/or to conventional sewage streams. One class of AOP utilizes photo-activated reactions for degradation of surfactant. These reactions are characterized by the free radical mechanism initiated by the photon interaction with a specific amount of energy with a catalyst (photocatalytic oxidation). *Madjene et al.*, stated that photocatalytic oxidation reactions tend to completely mineralize organic compound to carbon dioxide, water vapor and inorganic substance by UV light (Figure 3) [18].



**Figure 3.** Degradation process using AOP process [17]

Therefore, attack by ( $\text{HO}\bullet$ ) leads to mineralization of the organic compounds and AOP results in reducing the contaminants concentration from several hundred ppm to less than 5ppb. The strength of the free radical depends on its relative oxidation power (ROP). Various oxidizing species are available for this application. Table 1 listed the various relative ROP.

**Table 1.** Relative oxidation power of oxidation species [18]

Oxidizing Species	Relative Oxidation Power
Chlorine	1.00
Hypochlorous Acid	1.10
Permanganate	1.24
Hydrogen Peroxide	1.31
Ozone	1.52
Atomic Oxygen	1.78
Hydroxyl Radical	2.05
Titania <sup>+</sup>	2.35

AOP's offer many ways for hydroxyl generation using non-photochemical or photochemical (with UV radiation) methods. The UV radiation acts as a source of energy to activate and enhance the production of hydroxyl radicals from various sources like water. Unfortunately HO● is non-selective but powerful. Targeting the surfactant using activated HO● makes AOP technique a better and favourable option.

Figure 4, summaries the different AOP technologies, and the reactive species produced for the degradation of organic pollutants.

AOP	Reactive species
Ozone treatment: O <sub>3</sub>	•OH, HO <sub>2</sub> •, HO <sub>3</sub> •, O <sub>2</sub> <sup>-•</sup> , O <sub>3</sub> <sup>-•</sup>
O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	•OH, O <sub>2</sub> <sup>-•</sup> , O <sub>3</sub> <sup>-•</sup>
Fenton processes: H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup>	•OH, HO <sub>2</sub> •
Photo-Fenton processes	•OH
UV/O <sub>3</sub> , UV/H <sub>2</sub> O <sub>2</sub> and UV/O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	•OH, HO <sub>2</sub> •/O <sub>2</sub> <sup>-•</sup> , O <sub>3</sub> <sup>-•</sup>
V-UV (λ < 190 nm)	•OH, H <sup>+</sup> , e <sup>-</sup> <sub>aq</sub>
Photocatalytic treatment: UV/Vis light using TiO <sub>2</sub> , ZnO, etc. as catalysts	•OH, h <sup>+</sup> , O <sub>2</sub> <sup>-•</sup> , e <sup>-</sup> , <sup>1</sup> O <sub>2</sub> , HO <sub>2</sub> •, HOO•
Ultrasonic treatment	•OH, •H
γ-Radiolysis	•OH, •H, e <sup>-</sup> <sub>aq</sub>

**Figure 4.** Reactive Species for Different AOP's [18]

### 2.3.3 Chemical precipitation

Suspended solids and colloidal particles can be removed by the means of coagulation and flocculation. There are few coagulants, such as modified hot lime and FMA (a mixed metal polymer), calcite and ferric ions used as coagulant to treat produced water. In a study conducted by Fakhrul et. al, modified hot lime process produced water containing 2000 ppm hardness, 500 ppm sulfides, 10,000 ppm TDS, and 200 ppm oil could be successfully converted to steam generator-quality feed-water[15].

In another study on treatment of offshore produced water, an oxidant, ferric ions, and few flocculants were used to remove hydrocarbons, arsenic, and mercury. The oxidation–reduction potential of the wastewater was controlled by oxidant addition to allow the required arsenic oxidation to occur while maintaining the mercury in elemental form. Results showed that effluent streams had

less than about 10 parts per billion (ppb) of mercury (calculated as Hg), less than about 250 ppb, and preferably less than 100 ppb of arsenic (calculated as As), and less than about 40 ppm of TPH. The major drawback of this process is its ineffectiveness in treating for dissolved components and increased concentration of metals in the sludge formed.

### 2.5 Comparative studies of physical and chemical treatment options.

Conventionally, physical treatment has been used as produced water treatment option. However, the physical technique does not degrade the pollutants, but only isolate or traps them [19]. Commonly, physical processes of treatment are considered to be less environmentally friendly, costly and capable of generating large volumes of chemical sludge. These technique usually come with many limitations, especially in offshore operation. The major problem is that, the treatment of high volume effluent requires high residence time for separation. Another problem is the build-up of chemical waste or sludge, which is environmental hazard. This is unfavourable for offshore operation as it incurs large storage, huge footprint resulting in high operating and capital costs together with its environmental unfriendly by-products. As a consequence, chemical techniques are found to be suitable for destruction of organic pollutant (mineralization) and disposed as safe by-product as a result protecting the environment.

### 3. Conclusion

In the treatment of produced water, it is necessary to ensure that the level of contaminants/ organic compounds present in the water are within the acceptable range set by the regulators. Achieving the various treatment goals requires the use of multiple treatment technologies, including physical and chemical treatment processes. Current produced water technologies and their successful applications have advantages and disadvantages and can be ranked on the basis of their efficiency in eliminating the organic pollutant in produced water. Therefore, from the literature reviews done, the suitable technology for produced water treatment will be the combination of both physical and chemical process. This will aid in the trapping as well as the degradation of contaminants in produced water.

### Acknowledgement

The authors would like to thank Universiti Teknologi PETRONAS (UTP) and the Enhanced Oil Recovery, mission oriented research division for their financial support. We would also like to express our sincere and honest gratitude to colleagues from UTP and PETRONAS Research Sdn Bhd (PRSB), and friends who have guided and assisted us during the study.

### References

- [1] Pwaga S, Iluore C, Hundseth O, Perales F J and Idrees M U 2010 Comparative Study of Different EOR Methods *Department of Petroleum Engineering Norwegian University of Science & Technology, Trondheim, Norway*
- [2] Boysen B, Henthorne L, Johnson H and Turner B 2013 *Project System Technologies Oil Gas Facilitie*
- [3] Duhon H 2012 *Oil Gas Fac.* **1** (1) 29-30
- [4] Fakhru'l-Razi A, Pendashteh A, Abdullah L C, Biak D R A, Madaeni S S, and Abidin Z Z 2009 *J. Hazard. Mater.* **170** (2) 530-551
- [5] Westgarth V W S 2014 Produced Water, <http://www.vvswestgarth.com/en/markets/offshoreoilandgas/producedwater/>
- [6] Veil J 2015 U.S. Produced Water Volumes and Management Practices in 2012, Ground Water Protection Council United States.
- [7] James P R and Engelhardt F R 1992 Produced Water: Technological/Environmental Issues and Solutions, Pittsburgh, Pennsylvania.
- [8] NPC North American Resource Development Study 2011 Management of Produced Water from Oil and Gas Wells.

- [9] Neff J, Lee K and De Blois E M, 2011 Produced water: overview of composition, fates, and Produced Water, *Springer*, New York
- [10] Fraser G S, Russell J and Von Zharen W M 2006 *J. Marine Ornithology* **34** 147–156
- [11] Ebenezer T I and George Z C 2012 *Int. J. Low Carbon Technol.* **0** 1-21.
- [12] Okiel K, Mona El-Sayedb and El-Kadyc M Y 2011 *Egyptian J. Petrol.* **20** 9–15
- [13] Drewes J E, Cath T Y, Xu P, Graydon J, Veil J and Snyder S 2009 An integrated framework for treatment and management of produced water RPSEA Project, 07122-12.
- [14] Choi M. S 1990 Hydrocyclone produced water treatment for offshore developments *SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers.*
- [15] Duraisamy R T, Beni A H and Henni A 2013 *State of the art treatment of produced water* INTECH Open Access Publisher.
- [16] Heins W and Peterson D 2005, *J. Canadian Petrol. Technol.* 44 01.
- [17] Madjene F, Lamine J, Sadek I, Hafida L and Belkacem B 2013 *J. Sci. Technol.* **3** 10
- [18] Bokare A. D and Choi W 2014, *J. Hazard. Mater.* **275** 121-135
- [19] Ikehata K and El-Din M G 2004 *Ozone: Sci. Eng.* **26** (4) pp 327-343