Oilfield-produced water characteristics and treatment technologies: a mini review

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Abstract. The produced water considers as the largest waste stream in the oilfields and refineries, which has a high concentration of hydrocarbons, heavy metals besides other pollutants. As per the increase in the activity of industries, the generated produced water has increased all over the world and treating it for reusing becomes now important from the environmental point of view. Treatment of produced water can be achieved within different processes or methods including physical (filtration, adsorption, etc.), chemical (precipitation, oxidation), and biological (activated sludge, biological aerated filters and others) methods. The aim of this paper is to highlighting and discussing the characteristics of produced water in detail besides the physical, chemical, and biological techniques used for the treatment of the produced water.

1. Introduction
The techniques of recycling water within the oil refineries have gained great attention due to the big quantities of wastewater produced from industries and the excessive depending on water sources besides the continuous shortage of those resources [1]. On the other hand, oil refining and gas desalination processes produce a big amount of aquatic wastes, commonly named as "process water". The large consumption of water produces big quantities of wastewater, it is declared that the oil refinery aquatic wastes reach about one and a half times of produced crude oil [2,3]. The industrial wastewater is the most important wastes within various types of wastewater, because of the high variety of pollutants that form it such as nitrogen oxides, volatile organic compounds carbon dioxide, sulfur dioxide, and heavy metals which they are not easy to degrade and can harm groundwater reservoir and other water resources if they are discharged in a not appropriate way into the environment. so, these pollutants have to be removed first from wastewater then discharged to the environment [4].

The main purposes of this review are:

- To show produced water and oil refinery wastewater origin and characteristics.
- To brief the current technologies that available to treat produced water.
- For developing the produced water treatment in and minimizing the depending among the limited freshwater resources.
2. Oilfield and refineries wastewater

Within the oilfields and refineries, oil-related to water is named as the produced water during crude oil extraction operations. This water is considered as the largest aquatic wastes that produced in industries and [5]. Produced water conducts through:

- During the extraction process of crude oil that conduct a combination of both oil and water as its naturally within the cavities of subsurface formations.
- Injecting water into the oil field to far up the oil to the ground level but this step will make a future problem by increasing the water quantities within the aquifers eventually.

With regard to formations of subsurface, rocks are penetrated with a combination of oil, water and gas. "It is believed that rocks are completely saturated with water in most oil-bearing formations due to the invasion and trapping of oil". This water can flow from below, above, or inside the hydrocarbons area or can flow due to the additives that were injected during extraction and production. Before starting the production process and bringing the fluids upward, the produced fluid is named formation water. As a result, any water within the hydrocarbon zone that is produced with crude oil or natural gas and brought up by well pumps is named as the produced water. The figure below shows the typical oil field production [5].

![Figure 1. Production profile for a typical oilfield.](image)

During extraction and production, the ratio of water produced to oil is about 3:1. However, due to the progress in the aging of the aquifer or reservoir, the raw material production decreases in and consequently increases the produced water quantities. Thus, the volume of water produced can reach about 98% in exhausted oil fields [6].

3. Why produced water must be removed?

It is important to treat the wastewater associated with the crude oil operations, where this untreated water may affect the quality of the oil, its price, and its properties. In addition, it affects this produced water on human health, the environment, soil and groundwater, therefore there's a need to deal with for the purpose of free crude oil, water, suspended solids and other materials [7]. Many studies showed that the oil-field produced wastewater may cause problems in the environment in several ways [8]:

- clay deflection which caused by over sodicity.
- Plant harming by dehydrating and dying due to the increase of soluble salts.
- Aquatic environment damage as per to the reduction of oxygen level.
• Deep formation plugging by suspended solids which leads to increase in injection pressure and decrease the flow rate of injected produce water.

• The impact of chemical additives such as corrosion inhibitor and H2S scavenger.

4. Produced water volume and management
There is no fixed volume for the produced water, it depends on the reservoir location and the extraction technology that was operated [9]. Produced water volume in a certain reservoir varies from while to while. At the beginning of the extraction process, the produced water quantity is very little but when the aging of the reservoir increases, the amount becomes more [10]. Table 1 shows the highest volumes that are produced all over the world. The management of wastewater in oil fields has a big inspiration to people interested in the aquatic environment for the latest years due to restrictions and regulations of keeping a safe environment for all human beings and this have motivated many institutes to develop novel strategies for the treating of effluents and reuse the water [1].

Table 1. The highest produced water volumes within various countries [9].

| Country     | USA       | Oman      | Australia | Iraq       | Colorado | China       |
|-------------|-----------|-----------|-----------|------------|----------|-------------|
| Volume (bbl/year) | 21,000,000,000 | 1,840,000,000 | 207,570,000 | 105,853,190 | 92,274,300 | 45,917,000 |

The management for the purpose of treating is very costly and should be considered in any production plan which has an effective role in making the economic recovery determination of the reservoir that may lead to having a substantial number of recoverable hydrocarbons in the reservoir. The most important options of produced water managing can be summarized in [11,12]. The alternatives ways can be briefly listed as [10]:

• The produced water can be injected again into the same formation of a reservoir or another suitable formation in order to reduce cost and also compensating pressure in the reservoir.

• The discharging of produced water to the aquatic environment after a specific treatment to meet required discharge regulations of the environment.

• Reusing the produced water in the drilling and maintenance operations of the well sites in accordance with treating it to meet the desired quality.

• The produced water can be used for commercial purposes after proceeding a significant treatment to meet the minimum limits for the reuse in irrigation, rangeland restoration and live organism consumption.

5. Produced water characteristics
Its composition varies from simple to complex i.e. it's not a single component, "it is a combination of dissolved and particulate organic and inorganic chemicals". The wastewater properties differ depending on many parameters like the geographical site of the field, the depth and age of geological formation, the method of extraction, hydrocarbon-bearing formation geochemistry, type of conducted hydrocarbon, in addition to the chemical components of the reservoir. The effluent composition of oily wastewater of refineries highly depending on the quality of crude oil, the origin of wastewater pollutants and the operating conditions. Therefore, the big variance was shown in the wastewater characteristics within the researches of investigations and a wide domain of contaminants at varying quantities. Oil and grease are the most mixtures in the oil refinery wastewater and oilfield-produced water which are a mixture of hydrocarbons like BTEX (benzene, toluene, ethylbenzene, xylene) besides phenols (which have highly solubility features in water). As well as, calcium and magnesium are hardness causing natural chemicals. 4000 mg/L was the average COD
concentration however, the COD concentration in the oilfield-produced water and oil refinery wastewater was 21000 mg/L according to [13]. Thus, it is very challenging to be removed by conventional treatment methods.

Table 2 shows the components of the oilfield-produced water and oil refinery wastewater [5].

### Table 2. Most important pollutants of produced water and their concentration.

| Parameter | Conc. (mg/l) | Parameter | Conc. (mg/l) | Parameter | Conc. (mg/l) |
|-----------|--------------|-----------|--------------|-----------|--------------|
| Major parameters | | | | | |
| COD | 1220–2600 | Xylene | 0.01–1.29 | Ti | 0.01–0.7 |
| TSS | 1.2–1000 | Total BTEX | 0.73–24.1 | Cr | 0.002–1.1 |
| TOC | 0–150 | Saturated hydrocarbons | 17–30 | Mn | 0.004–175 |
| TDS | 100–400,000 | Oil and grease | 2–565 | K | 24–4300 |
| Organic acids | 0.001–10000 | Phenol | 0.001–10,000 | Pd | 0.008–0.88 |
| Production treatment chemicals | | | | | |
| Glycol | 7.7–2000 | Na | 0–150,000 | Cl<sup>-</sup> | 0–270,000 |
| Corrosion inhibitor | 0.3–10 | Sr | 0–6250 | B | 5–95 |
| Scale inhibitor | 0.2–30 | Zn | 0.01–35 | Ca<sup>2+</sup> | 0–74,000 |
| BTEX | | | | | |
| Benzene | 0.032–778.51 | Al | 0.4–410 | Mg<sup>2+</sup> | 0.9–6000 |
| Ethylbenzene | 0.026–399.84 | As | 0.002–11 | HCO<sub>3</sub> | 0.15,000 |
| Toluene | 0.058–5.86 | Ba | 0–850 | |
| Other ions | | | | | |
| Glycol | 7.7–2000 | Na | 0–150,000 | Cl<sup>-</sup> | 0–270,000 |
| Corrosion inhibitor | 0.3–10 | Sr | 0–6250 | B | 5–95 |
| Scale inhibitor | 0.2–30 | Zn | 0.01–35 | Ca<sup>2+</sup> | 0–74,000 |
| BTEX | | | | | |
| Benzene | 0.032–778.51 | Al | 0.4–410 | Mg<sup>2+</sup> | 0.9–6000 |
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### 6. Methods of produced water treatment

Overall, the most favorable method is the cheapest one and the cost of treating mostly related to the influent type, plant's capacity, besides the desired effluent quality.

Generally, there are three steps of the produced water treatment process which are "the pre-treatment step, the main treatment step and the final polishing step".

- **Pre-treatment**
  It aims to absorb the large size of oil droplets, gas bubbles and rough solid particles to eliminate pollutants.

- **Main treatment**
  There are two treating procedures primary and secondary within the main treatment step. The primary treatment intends to remove small oil droplets and solid particles and this will be conducted by utilizing skimming tanks, plate pack interceptors and API separators. The secondary includes the abstracting of very small oil droplets and solid particles through the use of gas flotation, hydrocyclones and centrifuges.

- **Final polishing treatment**
  It’s commonly utilized to eliminate ultra-small oil droplets besides solid particles and dispersed hydrocarbons which are less than 10 mg/l using some processes like the membranes.

Tertiary treatment is considered as an optional step that is used for the removal of dissolved matter, gases and dispersed hydrocarbons which are less than 5 mg/l. So there’s a need for further treatment [11]. In the following sub-sections biological, chemical, physical treatment techniques are discussed individually.
6.1. Biological treating methods

It’s an effective and excellent method as well as one of the cheapest processes for the treating of oily wastewater, where aerobic or anaerobic situations are carried [14]. Two-liquid phase partitioning bioreactor “TLPPB” was developed then used to eliminate the hydrocarbons concentration which was nearly 6000 mg/L, the removing efficiency for the hydrocarbons pollutant was raised to 100% was in the two-liquid phase partitioning bioreactor while the “TLPPB” treated efficiency of crude oil in the one-phase traditional biological reactor was 69-78% as in [15].

Pseudomonas aeruginosa and Klebsiella pneumoniae shows a fair growth in replicate within culture in the heavy crude oil. P. aeruginosa has more ability to biodegrade the heavy crude oil (74 wt.%) comparing with K. pneumoniae (66.22 wt.%) [16]. Moreover, 0.2–10 μm size of bacteria, algae and fungi are present in produced water as they can grow up by depending on the nutrient sources [17].

There are many disadvantages of biological treatment such as a large amount of biological sludge that's require more treatment more contact time which gives lower efficiency. Other disadvantage is the stationary infrastructure

6.1.1. Activated sludge

It's a commonly method used aerobic treatment processes of wastewaters by adsorbing and occluding soluble and insoluble materials. Total petroleum hydrocarbons removal efficiency that can be conduct through the activated sludge is 98.5% [18] and 40% COD concentration removal. The advantages of this method can be summarized as being a simple, cheap and clean technology but its disadvantages are that a large amount of oxygen is needed and big dimensions of filter also sludge appear eventually besides It required further treatment for separating precipitated solids, biomass, and dissolved gases [19]. This type of treatment is effective in removing COD, Total petroleum hydrocarbons, Suspended solids and Heavy Metals.

6.1.2. Biological aerated filters (BAF)

This process does not require post-treatment or use of any chemicals and can applied for a large quantities of water to reduce the concentrations of COD, BOD, SS, Nitrogen, Oil and Ammonium and quality with expecting a long-life cycle with little maintenance. It was declared that this process can remove efficiently different pollutants such as COD, BOD, nitrogen, oil, and SS in excellent removal percentage [20]. But the major drawbacks are the need to get rid of sludge and solids that generated and created sediments in the basins where the removal is costing nearly half of the entire cost of the process.

6.1.3. Microalgae based process

It can be used as an alternate source of energy and power generation beside, its remediation of contaminated effluents and that can be achieved through utilizing microalgae according to the ability through getting a benefit of some pollutants as a feed such as Water-soluble fraction (WSF) gasoline, BTEX, Nitrogen and Phosphorus. Parachlorella Kessler which is a specific microalgal species can utilize BTEX as a sole source of carbon also BTEX can affect the growth of microalgae. On the other hand, sometimes pollutants concentration increases with time if the microalgae cultures inhibited [21, 22].

6.2. Chemical treating methods

The chemical treatment methods include coagulation or flocculation combined with flotation and filtration, precipitation-flocculation, electroflootation, electrokinetic coagulation, conventional oxidation methods using many oxidants which can break multiple pollutants. Furthermore, various parameters affect the oxidation rate including chemical dosage, type of oxidant, wastewater components, and contact time [4].
Although of efficient removal for pollutants from produced water, these chemical methods are often costly, unattractive from the commercial view and accumulate sludge which leads to a disposal problem. There is also there’s a chance to appearing another pollution problem because of the use of chemicals besides the demand for electrical energy demand and other reasons. Within the chemical treatment methods, the result of using Ion exchange technology (IE) declared that the pollutant removal was about 90% for dissolved organic within the ion exchanger unit (continuous system) with three columns (cation, anion, and mixed bed) [23]. In water treatment, a new type of low-cost eco-friendly coagulants, Strychnos potatorum seeds, was used for eliminating the turbidity, which the water was prepared synthetically by kaolinite and the results showed that it’s appropriate and the removal was nearly 93% of kaolinite turbidity [24].

6.2.1. Precipitation
It’s a conventional chemical process for the treating of produced water, where more than 97% of Suspended Solids (SS) and colloidal particles, removed effectively by this process besides the inorganic metals (iron, magnesium and aluminum polymers), phosphorous, carbonaceous compounds and oil. Although of this removing efficiency, but it’s less efficient for the removal of hydrophilic compounds and nitrogen [25].

6.2.2. Chemical oxidation
This process used for removing BOD, COD, Color, Odor, Organic, and some inorganic matter with a minimum requirement of equipment and it can achieve an almost 100% water recovery rate [5]. This process depends on both of the oxidation and the reduction reactions in order to conduct free electrons in the solution. But the oxidants can be affected by various parameters like the chemical dosage, type of oxidant, contacting time, and the sources of the wastewater and it's quality. Although the process not require pre-treatment due to not generating any wastes or sludges, but the cost of chemicals are high beside its need maintaining and calibrating for the equipments between whiles [26].

6.2.3. Electrochemical technologies
It’s widely used in treating different types of wastewater and it’s efficiently for organics, hydrocarbons, COD, BOD, Sulphate, Suspended solids (SS) and Ca^{2+} removal However, It was suggested as a future technology for treating [27]. Also electro-photo coagulation was used as an untraditional oil removal operation, where sets of experiments were carried out to find the efficiency of the process to remove the concentrate soluble oil from water. Multivariable were studied such as applied potential, space between the two electrodes, settling time and initial soluble oil concentration and it was found that these variables have an effect on the soluble oil [28]. Ultrasonic-assisted electrocoagulation (U-ELE), was utilized for the removal of nitrates from water under a particular situation. It was found that the nitrate eliminating using only ELE method was about 77% but the results showed that employing ultrasonic for about 10 min. (the U-ELE method) has increased the removal rate to 87.8% [29].

6.3. Physical treating methods
Different physical methods are widely used for wastewater treatment especially the produced water, such as “membrane – filtration processes (nanofiltration, reverse osmosis, electrodialysis (ED) and electrodialysis reversal (EDR) and adsorption processes” [30].

According to numerous literature data, the adsorption in liquid-status is the most common for pollutants removal also the appropriate design of the unit of adsorption carries out an obvious efficiency for the treatment purpose, mostly when the adsorbent is a low-cost material and not require pretreatment before its implementation [31].
6.3.1. Filtration
In general, the filtration process is effective for removing COD and Nitrogen, Ammonia, Phosphorus, Oil and grease, TOC, TSS, Chloride, Sulphate, TDS, salts and Turbidity. There are two methods for the microfiltration process that has been examined, the first one is the dead-end and the second is the crossflow. These methods were applied to oil-emulsion which is prepared from vegetable oil and motor oil (classic oil 20W-50). In the dead ends method, the rejection percentage reached 97.8%, while in crossflow it reached 98% with a recovery ratio of 44.8% [32, 33]. "The nanoporous hydrophobic hollow fibers membranes" have the ability to eject nearly all the TDS pollutant from the wastewater when though after 100 hours of continuous operation and the effluent was suitable for industrial reuse [6].

Also, natural filtration was done by utilizing agricultural wastes (1:1 ratio of Reed and Straw) for the removal of iron ions from synthetic wastewater and it was found that about 33% of iron was removed by the natural wastes [34].

The membrane processes have been extensively used for produced water treatment. Membrane bioreactors (MBRs) were noted that its application for a pretreatment helps to decrease about 85% of COD concentration. therefore a combination of Membrane bioreactors (MBRs) with RO considers a perfect treatment method for COD removal and the reduction of conductivity. while the other membranes ability was below 25% of COD [35].

6.3.2. Flotation
In brief, it’s depends on the gas bubble generation which can separate the suspended particles that can not be extracted through the sedimentation process. It’s achieved by injecting gas bubbles into the influent wastewater, then pollutants "suspended particulates and oil droplets" will be attached with bubbles and will be risen up and this leads the produced formation to be removed by skimming process. There are two different gas flotation technologies which differ in the way of generating fine bubbles and controlling the bubble size these techniques are induced gas flotation (IGF) and Dissolved gas flotation (DGF) [11], [36].

Reference [37] declared that within coagulation-flotation; the oil, COD and turbidity are affected by the initial concentration of oil, dosage of coagulants and SDS (Sodium dodecylsulphat surfactants) concentration and It was noticed that during the use of coagulants, the flotation rate increases. The rapid removal rate was conducted within optimum pH 4 and the removal was (87%) for flotation and (95.7%) for sawdust+bentonite and (97%) for alum.

6.3.3. Adsorption
It is one of the most favorable treatment techniques for reaching the best water quality because it can minimize the contaminant concentration to the least levels. Its effectively used to remove heavy metals, organic and inorganic compounds, manganese, iron, TOC, COD, Oil, BTEX compounds and synthetic organic chemicals. On the other hand, the waste disposal requirement for the produced waste and employing a media to the regeneration process of media besides the necessity to regenerate the absorbent material frequently gives an elevated cost for system installation or maintenance [38].

Activated carbon utilizing like an adsorbent is further favorable for the water treatment over other processes due to its simplicity, economy, and efficiency. cheap and good adsorbent like activated carbon is conducted through a sequence modifying which developed it to achieve more pores through increasing the surface area [39]. Also, A fluidized–bed technique achieved a good efficiency of oil and total dissolved solids (TDS) removal from oily wastewater. Stem date was used in the fluidization bed system as an adsorbent and the removal efficiency reaches was about (71%) with modifying some parameters such as increasing bed height, volumetric flow rate, decreasing particle size and initial oil concentration of the wastewater [40].

Adsorption and electrochemical techniques (AD-EL) were used for the effluents of industries treatment such as COD and turbidity where the results showed that COD and turbidity were decreased by 72% and 85%, respectively through the AD-EL method and the optimum conditions [41].
7. The reuse of oilfield-produced water

The freshwater shortage is increasing within time, the growth of population and living requirements. So nowadays, the produced water reuse is the focus of attention if appropriate treatment applied. The attention on demand, recycling and reusing of water could meet the needs of the communities but the standards for drinking water are more strict so, the treatment of produced water not simple and needs many stages. There are alternative uses of produced water like irrigation, livestock watering, firefighting, and many industrial purposes. According to the produced water criteria, the treatment stage that is desired depends on the implementing that the reused water will be utilized in. For instance, the least treatment efficiency is needed in oil and gas and industries while a high treatment efficiency is needed for drinking water. Eventually, the cost is the most important parameter for the treatment and the reuse of produced water [42].

8. Conclusion

Due to the shortage of freshwater resources and ecological problems made by Oilfields and other industries, the treatment is getting high attention. The deep details of this review appeared that the features of produced water excessively vary from a site to another. subsequently, the methods of treatment should be assessed for an individual origin of produced water. otherwise, the treating cost of produced water also has an impact on choosing a treatment technology. In this review, many techniques and a set of various methods were used in Treatment. To reduce the environmental hazards of industries and to meet the water demands, it is necessary now to enhance the treatment of produced water to eliminate the environmental impacts of the industry. This is in particular important for the countries that suffer from water scarcity, where population and economic growth are increasing stresses on the limited water resources of the region.

9. References

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