REVIEW ARTICLE

# Produced water from oil - A review of the main treatment technologies

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With the increasing demand for oil and its derivatives, the increasing production of oily water and its treatment has been a challenge due to the complexity and amount of waste generated, because this undesirable effluent requires treatment before its final disposal in order to meet the legal requirements for disposal in the environment or technical requirements for injection into oil wells. Thus, research for the best technology or set of technologies for the treatment of oil produced water are highlighted with a view not only for more efficient removal and recovery of oils and other toxic agents, but also financial viability along these technologies. In this sense, the purpose of this article is to present some of the main technologies used for the treatment of produced water from oil.

**Key Words:** *Oil; Produced water; Wastewater treatment*

Oil production is usually accompanied by significant water use. The water production is basically formation of water naturally present in the reservoir and the water previously injected into the reservoir. These water productions generally contain high salinity, suspended solids, potentially toxic elements, insoluble and soluble organic matter, suspended oil, chemicals and in turn some radioactivity, making them a pollutant difficult to discard worsening by the significant volume involved.

According to Sthephenson (1), the volume of water produced in a mature field, one that is naturally found in declining productivity towards the exhaustion of its recoverable reserves, may exceed 10 times the volume of oil produced. In view of this magnitude, the final disposition of this water becomes important, either for operational or environmental reasons.

Produced water will have to undergo effective treatments in order to fit into the current legislation with a view of its final destination. If re-injected or if there are other re-uses, it will need to be treated to meet the standards necessary for the process to be used.

Some technologies have been developed to try to solve the problem of disposal of produced water. However, because of its complexity, it is suggested that treatment proposals should be studied, including the combination of physical and/or chemical and biological treatments. Such combined processes can reduce energy consumption and increase the purification efficiency, proving to be an interesting alternative, with regard to compliance with environmental requirements.

In this context, this paper was carried out in order to present some of the main technologies used for the treatment of produced water from oil.

## LITERATURE REVIEW

### Oil industry

Etymologically the word "petroleum" is derived from the Latin word, petra (rock) and oleum (oil), oil that comes from rock. The first oil wells were drilled in the United States of America (USA) and recorded in 1859, the first successful oil exploration by Mendonça et al. (2).

In Brazil, the first concession to extract bituminous material was signed by Olinda de Pombal in 1858, by Decree No. 2266 and granted to José Barros Pimentel. This first operation took place on the Marau River, in the Province of Bahia. Subsequently, the oil discovery in the Bahian Recôncavo enabled the exploration of other onshore sedimentary basins. In 1961, in the Sergipe Riachuelo field, the activities of Petrobras began. The year 1963 was marked by the discovery of Carmópolis field, which according to Pontes (3), is the largest onshore oil field in the country.

Attempts at securing CMV-specific T-cell adoptive immunotherapy were unsuccessful. Notably, the patient demonstrated full marrow engraftment with initial lymphocyte recovery at the 8 months mark post-transplant; this may explain the continued relative stability of CMV viremia and CMV disease despite the discontinuation of CMV specific therapy.

At present, it is known that oil is a product formed over thousands of years, resulting in physical and chemical processes undergone by the organic matter that is deposited along with fragments at the bottom of lakes and seas that are slowly covered by sediments. Due to the effect of high temperature and pressure on this organic matter, complex chemical reactions occur forming oil (3,4).

According to Gomes et al. (5), the accumulation of this oil depends on the existence of source rocks (sedimentary) containing the raw material and the presence of reservoir rocks (porous), which have empty spaces (pores) to store oil.

The main components of oil are hydrocarbons, including organic acids, polycyclic aromatic hydrocarbons and volatile phenols (6).

## LIMITATIONS OF THE OIL PRODUCTION INDUSTRY AND THE WASTEWATER TREATMENT

There are substances in the oil that must be removed for the oil to reach the refinery at its best and that will not damage the equipment in the process of obtaining the final products. The leading causes of these problems are found in contaminants such as sulfur compounds, nitrogen, oxygenates, among others (7).

Another relevant aspect in the industry oil is the presence of dissolved salts in the wastewater which creates various problems such as corrosion in pipes and loss of quality of the produced oil. In the oil production process, the coproduction of unwanted contaminants is common, which includes the production of water generally in the emulsified form and with high salinity (8-10).

### Oil produced water

Produced water is the largest source of pollution related to oil activities, as they contain contaminants, including hydrocarbons, heavy metals potentially toxic elements and chemical additives (6,10). Among the more soluble and toxic species present in the produced water, aromatic compounds, such as benzene, toluene, ethylbenzene, xylene isomers and phenols standout. The removal of these compounds is extremely difficult and, due to their toxicity, the direct use of a biological treatment cannot be recommended (11,12).

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At the start of production, the amount of produced water along with oil is usually low, but as the oil well ages, the produced water may exceed several times the volume of oil produced, because the decay of the oil production and gas (13,14). Water is one of the main effluents linked to extraction and production of oil (15). This water is treated, even with the purpose of recovering some of this present oil. A fraction of the treated produced water is mainly applied in its own oil extraction, since it is re-injected into wells to maintain pressure and assist the flow of oil to the surface increasing production and the remaining fraction is discarded into the sea, with or without treatment (15-17).

The direct provision, that is, without any treatment, the produced water in the sea, in many cases affects the marine ecosystem, due to the high amounts of oil and suspended solids to be discharged continuously. The oil and grease content (OG) is considered one of the major parameters for disposal of produced water (18).

In the Campos Basin located in the state of Rio de Janeiro, the main oil producer in Brazil, about 150 $m^3$/h of produced water is generated in oil exploration (19). With advances in oil exploration technology in deep water and the increasing stringency of environmental standards, there is a growing necessity to have a treatment that is a solution to the challenge of falling within the effluent discharge standards, with appropriate economic viability.

It is estimated that in the North Sea will generate 90 million $m^3$ of produced water in the coming years. In the United States, on the onshore (land) producing fields of oil and gas, a volume of 33 million barrels of produced water is generated annually (20).

Thus, a careful study to determine the best treatment technology and set the disposal method is required.

## OIL AND GREASE CONTENT (OG)

The oil and grease content is the quantity of hydrocarbons present in the produced water. According to Rodrigues (21), even in small quantities, they are difficult to remove because they are stable in light and heat and biologically non-degradable; decrease the contact area between the surface of the water and atmospheric air thus preventing the transfer of oxygen from the atmosphere into the water.

The process of separating oil and produced water is complex. When the separated water has dispersed oil droplets in the water, treatment for their disposal or reuse is required to be in accordance with the standards established by environmental agencies. Thus, all the produced water obtained is generally managed as a high-risk material for the oil industry (15).

OG is the only parameter to be regulated by legislative bodies. The amount of OG varies with each country; usually the monthly average is 40 mg/L and at most 100 mg/L. In Brazil, the body that operates overseeing this parameter is the National Environmental Council (CONAMA), which in Article 5 of Resolution No. 393 on August 8, 2007 states that for disposal of produced water, the monthly average concentration of OG should be 29 mg/L and the maximum value of daily disposable is 42 mg/L. For reinjection in oil wells, the water should not exceed 5 mg/L of oil and grease.

## SOME OF THE MAJOR TREATMENTS OF OIL PRODUCED WATER

Various types of treatments are employed in the oil industry, aiming to remove the maximum amount of oil and grease associated with water and conditions it for reinjection or sea disposal.

The conventional system of oil produced water treatment used on offshore platforms is basically composed of hydro cyclones and floaters. The water coming from the separator vessel undergoes removal stages of oily residue in hydro cyclones batteries and is forwarded to floaters by induced or dissolved gas (22). The use of walnut shell filters, centrifuges and mixed-bed filter is also performed.

Other technologies have been developed seeking a better management of oil produced water. Amongst these technologies, adsorption, the electrochemical process, filtration and flotation may be mentioned.

The viability of the treatment technologies has low operating cost and high efficiency. In the case of offshore installations (off-shore field), these technologies should also be compact, due to space and weight constraints (23).

However, the performance of each of these technologies will depend on process variables for each facility, such as the type of reservoir and oil, temperature, pressure, viscosity, emulsion stability, size of the oil drops, salinity and speed flow among others (24).

### Adsorption

Adsorption is based on the principle that a solid surface in contact with a fluid, tends to accumulate a surface layer of solute molecules due to the imbalance of existing surface forces (25).

According to Braga et al. (25), the adsorption phenomenon is closely connected to the surface tension of solutions and its intensity depends on the temperature, nature and concentration of the adsorbed substance, nature and the physical state of the adsorbent and the fluid in contact with the adsorbent.

The use of adsorption techniques is associated not only purifying plants, but also in the separation of high value-added products, such as oil from water (26).

The activated carbon (AC), activated alumina, silica gel and molecular sieve adsorbents are the most widely used by the industry (27).

AC is referred to as broad spectrum adsorbent because it can remove a variety of organic compounds (28). Although AC has been shown to be an effective adsorbent for some organic compounds, among these, fatty acids and phenols, the connection adsorption between the functional surface groups and some organic species is usually so strong that the desorption process is difficult and incomplete. This undesirable effect limits the AC used as an adsorbent for the treatment of certain industrial wastewaters (28,29).

Macro cross-linked polymeric resins have been used as an alternative for the use of the AC adsorbent in removing specific organic compounds from contaminated water (29,30).

These resins can reversibly adsorb organic compounds from solutions or suspensions and may also reduce the desorption problem because the bond formed between the organic compounds and the surface of the resin (31,32). This change in functionality, surface area and porosity for the polymer resins shows the ability of the resins to be conditioned for selective removal of specific organic compounds (33).

Vermiculite is also widely used in the treatment of water contaminated by apolar organic compounds, especially oil and its derivatives (34-36). In this process, the clay mineral is used in a hydrophobized form; such a step is subsequent for expansion. Martins and Fernandes (35), who developed (and patented) the hydrophobization process of expanded vermiculite, however, is known to search for hydrophobization which renders the produced water treatment process more efficiently and economically feasible.

Due to the high price of some adsorbents, alternative methods have been studied (37,38). A method which has been used commercially to remove the free oils and suspended solids from water in refineries is the walnut shell filter. In this method, water is introduced into a down flow where the oil is adsorbed and suspended solids are filtered.

Queiros et al. (39) conducted research using columns packed with polymeric resins such as alternative materials for treatment of oily water. The water after the treatment, showed the OG as less than 1.0 mg/L. The authors observed that the maximum performance was achieved at a rate of 7 mL/min; however, the flow range from 5.0-50.0 mL/min, the column efficiency was not less than 98% of oil reduction (40-45).

Silva (46) conducted studies on the potential of clay and vermiculite expanded organoclay hydrophobized as an adsorbent in the treatment of oil-water emulsions. The tests were conducted using 0.0005 kg of vermiculite to 50 mL emulsion treated for 1 and 3 h of stirring. Under these conditions, organic vermiculite showed 90.80% reduction for 1 h of treatment and 89.72% reduction for 3 h of treatment and hydrophobized vermiculite showed 84.21% reduction for 1 h of treatment and 86.90% reduction for 3 h of treatment for emulsions with a concentration of 100 mg/L.

## ELECTROCHEMICAL PROCESS

At present, the electrochemical process has been extensively studied, wherein, by electron action of toxic substances and harmful to the environment are removed or processed through oxidation-reduction reactions into less toxic substances. This may be a promising alternative to the conventional methods of treatment of petrochemical wastewater. As for noting the advantages of this process, the relative availability of electricity, reduced reactive power conditions, highly reproducible and easily controllable allowing the automation and ease of assembly of relatively compact plant systems (40-43).

This method of treatment allows one to expand treatment capacity of the traditional physical-chemical systems, because it uses the same basic concepts of coagulation-flocculation and further provides elements that enhance the method for generating oxygen and hydrogen in the electrolysis reactions, forming up flow micro bubbles that interact with all of the effluent into the electrolytic reactor, this being subjected heavily to the oxidation and reduction reactions, facilitating the flocculation and flotation of the existing pollution load, increasing the efficiency of the treatment process (44).

The electrochemical process occurs when a difference of electric potential is applied by an external source of an electric current, causing a non-spontaneous chemical reaction in the aqueous medium by means of sacrificial metal electrodes, promoting metal dissolution with generation of ions and gases, which results in appropriate pH coagulation-flocculation reactions suitable for the treatment of liquid waste (44,45). This process has been presented as the most promising method for treating wastewater polluted with colloids, dyes or oil in water emulsions; besides having a good removal of BTEX (43,46).

The electrochemical treatment can also be used in a wastewater refinery, with satisfactory results in the application of this technique (47).

Santos et al. (48) studied the feasibility of applying electrochemical technology for the treatment of oil produced water. We used a pair of DSA® electrodes as electrode material during 10 h of electrolysis. The influence of current density and concentration of the produced water was examined. In the first step, the concentration of the effluent was set (50% dilution water production) and varied the current densities (25, 50 and 100 mA cm-2). For all current densities, reduced carbon concentration was observed; however, there was only a slight increase in process efficiency due to the increase of current density: 41, 47 and 50% reduction of the carbon concentration for the densities of 25, 50 and 100 mA cm-2, respectively after 8 h of electrolysis. The increased process efficiency was not proportional to the increase in current density because the applied current was used in parallel reactions such as the reaction of oxygen or chlorine detachment occurring simultaneously with oxidation reaction. In the second step, the current density of 100 mA cm-2 was fixed and the concentration of the solution varied at 25, 50 and 100% of the produced water in solution. The treatment was effective for treatment of diluted solution (25% produced water) and a 100% carbon reduction after 8 hours of electrolysis was observed.

**Filtration**

According to Huisman (49), filtration is a purification action wherein the water/wastewater flows through a porous medium, where there is partial removal of suspended material and colloidal material, reducing bacteria concentration and changes in their chemical constituents, resulting in better water quality.

The filtration may be faster or slower, depending on the filtration rate, yield of contaminants and final quality of the product or effluent. In order to increase productivity, filtration is preceded by pre-treatment units. In petroleum plants, filtration is also used in wastewater contaminated with oil (50-52).

Successful treatment of oil produced water generally requires pre-treatment operations, in which different contaminants are removed (53). Among the most investigated separation techniques for removing oil, grease, and suspended solids are filtration in a granular bed amid hard and tangential microfiltration through a ceramic medium.

The filtration processes with membranes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis are used in the treatment of stable emulsions of oil/water, especially soluble oily waste water, rather than free-floating oil and unstable oil/water emulsions (54). The membranes are effective in the treatment of oily wastewater of micron size, usually less than 10 μm and when the oil concentration is very low (54). These cases cannot be solved by conventional techniques such as gravity separation, addition of chemical, thermal and biological methods of demulsification. The porous matrix of the membrane promotes the coalescence of droplets of oil of micrometer and submicrometer size into larger ones, which can easily be removed by gravity (55).

Rosa et al. (55) studied the crossflow microfiltration treatment in oil produced water. The filter system used was composed by a porous ceramic type of filter media wrapped in a PVC casing with outlets for the power suspension and the concentrated tangential removed to the surface of the filter medium. The operation was conducted under a vacuum; the filtrate was removed in the axial direction of the filter. The filter performance was measured in terms of turbidity of the filtrate and OG removal efficiency. The final achieved average turbidity was 1.6 NTU, having reached about 80% efficiency in removing oil and grease (33).

**Flotation**

According to Silva et al. (34), flotation is one of the processes most commonly used for oil recovery in oil produced water by means of gravitational separation. The present flotation efficiency ranges between 85% and 90% removal of oil (13). In addition to efficiency, this process has a lower cost compared to other separation methods.

The use of the processes, dissolved air flotation (DAF) and induced air flotation (IAF) have been used in the petroleum industry, in order to reduce the production OG suspended in water at appropriate levels. These techniques consist of four basic steps: generation of air bubbles in oily wastewater; contact between the air bubbles and the oil droplets suspended in water; joining the drops of oil to the gas bubbles; lifting the air/oil combination to the surface where the oil is removed (48).

Among the flotation methods, electroflotation stands out among others because it is a process that floats pollutants to the surface of the water by using tiny gas bubbles generated by water electrolysis at the base of an electrochemical reactor, thereby promoting clarification of the effluent. Upon reaching the surface of the reactor, the suspension may be removed by conventional methods, such as scraping and suction.

According to Pletcher and Walsh (53), the size of bubbles generated determines the separation efficiency in the process, being directly influenced by the current density applied, as well as the characteristics of the effluent and the electrode surface. Generally, bubbles with smaller sizes promote larger surface areas of contact, resulting in improved efficiency in the separation process.

Eletroflocculation is a process that uses electric current, involving electrochemical reactors, where coagulants are generated in situ by electrolytic oxidation of a suitable material on the anode. Generally, in the anodic region, iron or aluminum is employed because they are low cost materials, effective and readily available. The generation of metal ions occurs at the anode, while hydrogen gas occurs at the cathode.

In eletroflocculation, agglutination of the destabilized particles occurs through the iron hydroxides and/or aluminum, which are natural coagulants favoring the formation and growth of flocs. These flocs can be removed by decantation, filtration or flotation (7,33,34).

When compared to other flotation units, electroflotation has aroused considerable interest because their units are compact and require little maintenance and lower operating costs (21,41). In addition, electroflotation is distinguished by its simplicity of operation and application for the treatment of many types of effluent.

Cerqueira and Marques (18) evaluated the electrolytic process of alternating current for the treatment of emulsified synthetic effluent of produced water. This technology consists of altering the electromagnetic wave of alternating current of 60 Hz marketed by power utilities in a wave with variable voltage and a frequency greater than 1 to 120 Hz. The best results were observed when using a frequency of 60 Hz alternating current, pH 9, the distance between electrodes of 0.005 m, an electrolysis time of 180 s and applying a current intensity of 3 A. Removals of 97% OG, 99% color and 99% turbidity were achieved.

Hansen and Davies (22) studied technologies for treating produced water originated from oil and gas reservoirs: ion exchange to remove heavy metal, adsorption on synthetic zeolites, membrane filtration, drag gas or vapor, adsorption AC and biological treatment to remove dissolved organic matter. However, they observed that most of the treatments were not efficient enough to remove all the “undesirable” component groups present in the produced water.

The development of new technologies or the improvement of existing technologies is extremely important for the oil industry to continue to expand without impacting the environment.

## CONCLUSION

This review article aimed to present some of the main technologies used for the treatment of oil produced water, as the oil removal processes of oil produced water is of paramount importance, since they make it possible to obtain of water with a lower OG index, in this way, not only for the specifications of environmental agencies, but disposal could also be possible without further damage to the environment.

Therefore, considering the removal of OG, among the methods of oil produced water treatment studied, the most used are the treatments by adsorption, electrochemical, filtration and flotation.

The process of filtration membranes have a high value compared to others due to the filter media that is used, therefore it is worth mentioning the importance of investment in the area of searching for new treatments for oil-contaminated wastewater, offering greater treatment possibilities taking into consideration the operating cost of the process.

Among the cases cited, flotation is one of the most used for oil recovery in oil produced water and from flotation methods, it is notable that electro flotation has aroused considerable interest because of its easy operation and application for the treatment of various types of effluent.

Furthermore, the use of associated processes can lead to water features suitable for reuse, either for reinjection itself, or disposal, but the total cost of the process should be taken into account.

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