




# Oil field–produced water treatment: characterization, photochemical systems, and combined processes

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## Abstract

Produced water, a mixture of inorganic and organic components, comprises the largest effluent stream from oil and gas activities. The removal of contaminants from this wastewater is receiving special attention of the researchers since most of them are persistent and difficult to remove with simple techniques. Several technologies from conventional to advanced oxidation processes have been employed to treat produced water. However, the achievement of greater efficiency may be conditioned to a combination of different wastewater treatment techniques. Hereupon, the present paper discusses three important aspects regarding produced water treatment: analytical methods used for characterization, relevant aspects regarding photochemical systems used for advanced oxidation processes, and combined techniques for treating oil field wastewaters. Analytical methods employed for the quantification of the main species contained in produced water are presented for a proper characterization. Photochemical aspects of the reaction systems such as operating conditions, types of irradiation sources, and technical details of reactors are also addressed. Finally, research papers concerning combined treatment techniques are discussed focusing on the essential contributions. Thus, this manuscript aims to assist in the development of novel techniques and the improvement of produced water treatment to obtain a high-quality treated effluent and reduce environmental impacts.

**Keywords** Produced water · Combined techniques · Wastewater treatment · Analytical method · Advanced oxidation processes · Photochemical reactors

## Introduction

During oil and gas extraction, processing, and refining activities, large volumes of waste are generated. The aqueous effluent brought to the surface along with hydrocarbons is known as oil field–produced water and represents the largest byproduct stream generated by the oil and gas industry (Guerra et al. 2011). It consists of water naturally present in the reservoir and water injected to enhance oil recovery. Produced water has a complex composition, which includes

dissolved and dispersed organic and inorganic species, microorganisms, and chemical compounds added during drilling and production (Neff et al. 2011; Dudek et al. 2020).

The quality of produced water may vary strongly depending on the field location, geological formation, and the type of hydrocarbons produced (Veil et al. 2004). Additionally, the quantity of produced water also changes during the lifetime of the reservoir. The water-to-oil ratio is about 3:1, but the volume of wastewater brought to the surface might be as high as 95% for mature oil fields (Kaur et al. 2009).

Nowadays, the two main alternatives for the management of produced water are reinjection, either for enhanced oil recovery or for disposal purposes, and surface discharge (Echchelh et al. 2018). However, for both approaches, the effluent must be previously treated to meet environmental regulations. Besides, if properly treated, produced water can be applied to different beneficial uses outside the oil and gas industry, like irrigation and livestock (Iggunnu and Chen 2014). Hereupon, to meet environmental standards and reuse this waste, many researchers have been focusing their

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attention on finding cost-effective ways to treat produced water (Fakhru'l-Razi et al. 2009).

Several technologies are currently being applied for treating produced water, including hydrocyclones, settling, flotation, adsorption, and filtration (GWPC 2019). Due to the complex chemistry of this effluent, it is usually necessary to use a combination of methods in order to achieve the required quality levels. Therefore, knowing the constituents of produced water and its ultimate use are essential steps for choosing suitable treatment techniques (Veil 2020).

Advanced oxidation processes (AOPs) are among the alternative methods currently proposed for oil field-produced water treatment. They are based on the formation of highly reactive species capable of reacting with both organic and inorganic compounds, mineralizing, or at least converting, them into less harmful products (Bahri et al. 2018). AOPs were proven to be effective in the degradation of various petroleum wastewaters, in which the reactor configuration plays an important role in the process efficiency (Aljuboury et al. 2015; Mota et al. 2018; Jiménez et al. 2019). In the midst of various types of reactors intended for AOP methods, photoreactors are highlighted due to the use of an irradiation source as the driving force of the process, contributing to operating cost reduction. Several types of photoreactors have also been reported in the literature, not only for treating produced water but also for pharmaceutical (Lou et al. 2017; Jallouli et al. 2018; Li et al. 2019; Majhi et al. 2019; Sbardella et al. 2020; Zhang et al. 2020) and dye species (Genuino et al. 2012; Farzana and Meenakshi 2013; Petrella et al. 2014; Manjunath et al. 2020). This study provides an overview of the technical aspects of the photochemical systems aiming at produced water treatment. In addition, it was found worthwhile to point out different photochemical approaches, including homogeneous and heterogeneous reactors (Freitas et al. 2016; Petala et al. 2019; Audino et al. 2020).

Produced water treatment is usually a combination of two or more physical, chemical, photochemical, or biological techniques. A series of review articles have also been reported in the literature concerning petroleum wastewater characteristics and treatment procedures (Fakhru'l-Razi et al. 2009; Igunnu and Chen 2014; Nasiri et al. 2017; Jiménez et al. 2018; Al-Ghouti et al. 2019; Dudek et al. 2020; Li et al. 2021; Liu et al. 2021; Simões et al. 2021).

The present work aims to provide an updated review of literature contributions, focusing on three aspects: analytical methods used for produced water characterization, aspects of the photochemical systems, and combined techniques for treating oil field wastewaters. Issues of scale-up and intensification were also considered in the analysis of the literature reports. The approach of this manuscript was chosen in a way that might be useful for researchers to conceive produced water treatment units.

## Oil field-produced water characterization

A large volume of produced water needs to be treated and managed daily, which makes it an environmental concern issue. The average amount of produced water in Brazil is 1.2 Mm<sup>3</sup>/day, calculated with data obtained between July 2019 and June 2020 (ANP 2020), while world production is estimated at 39.5 Mm<sup>3</sup>/day (Jiménez et al. 2018).

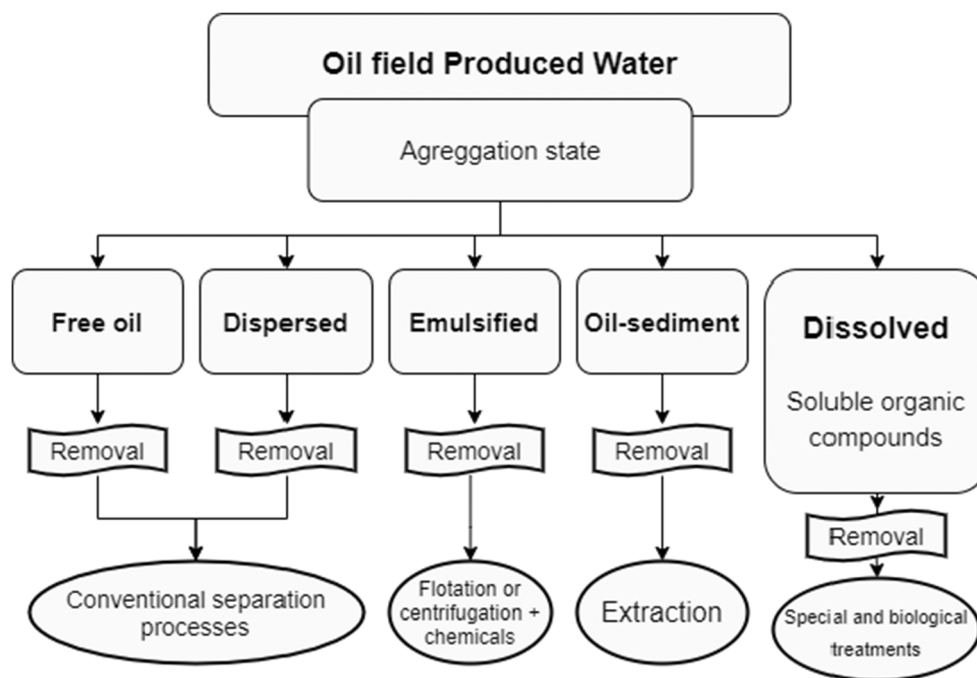
Produced water is a complex mixture of both organic and inorganic species. The properties of produced waters depend on the nature of the geological formation, the type of production and storage, the operating conditions, and the chemicals used during processing activities (Fakhru'l-Razi et al. 2009). In summary, it is a multi-component system, containing contaminants in diluted concentrations, often recalcitrant, highly toxic, and corrosive. Another issue regarding this effluent is that only part of the constituents is dissolved. In this sense, specific techniques of compositional and statistical analysis must be applied, for example, PCA (principal component analysis). Based on the review of the literature, several types of systems were found: real produced waters, refinery wastewaters, synthetic produced waters, and aqueous solutions containing model components, such as phenol, xylenes, benzene, and sodium chloride (Shim et al. 2009; Silva et al. 2012; Amin et al. 2013; Igunnu and Chen 2014; Hu et al. 2018; Jafarinejad and Jiang 2019).

The aggregation state characteristics of produced water, as well as its composition, vary according to the reservoir nature (light and crude oil), as well as to the geological and extraction characteristics. For the initial periods of oil extraction, 10% of what is extracted is usually water, while for the exploitation of mature wells it can reach an amount of water in oil of 70 to 90% (Yu et al. 2020). Due to the different proportions of the two-phase oil-water, the mixture becomes unstable and can be found in the form of oil-water, water emulsion, water in oil emulsion, oil-sediment aggregation, or dissolved organic compounds (Qi et al. 2021). Fig. 1 shows the likely aggregation states of the oil field-produced water and the applicable methods for the corresponding removal processes.

According to Fig. 1, oil field wastewater can be classified in five forms (Qi et al. 2021; Afenyo et al. 2020; Bennett and Shamma 2010): (1) free oil corresponds to oil floating at the surface; (2) dispersed small oil droplets (> 20 µm) in water; (3) emulsified oil droplets (5 and 20 µm) in water; (4) oil sediment in which aggregates can be found as oil-in-sediment or flake/solid aggregate; (5) dissolved species, such as phenol, BTEX, salts, and metals, which will require more specific treatments, such as biological and photochemical processes.

Table 1 presents the main inorganic components, while Table 2 shows the main organic substances present in real produced water samples. The concentrations observed for each compound are reported to give an order of magnitude

**Fig. 1** Oil field–produced water aggregation state



of produced water composition. The analytical methods applied to actual produced waters are also highlighted.

Figure 2 presents concentration ranges for the main inorganic components, based on Table 1, found in different oil fields. The same type of representation is shown in Fig. 3 for the main organic species, based on Table 2.

Inorganic ions, such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Cl}^-$  are the main causes of depassivation and oxidation of metal alloys, resulting in scaling and mechanical fractures of structures and machinery in the oil industry. In addition,  $\text{SO}_4^-$  and sulfur ions ( $\text{S}^{2-}$ ) in solution, even in small quantities, may indicate the presence of  $\text{H}_2\text{S}$  in the field where the produced water is located, representing a major risk to operators and metal structures (Alipour and Azari 2020). According to Table 1, produced water also contains a wide variety of heavy metals in its composition, such as lead, cadmium, copper, strontium, chromium, nickel, arsenic, manganese, and cobalt, with concentrations that can vary from  $<0.001 \text{ mg L}^{-1}$  (cadmium) up to  $256.8 \pm 19.7 \text{ mg L}^{-1}$  (strontium). These metals are the most recalcitrant components among the inorganics present in produced water, representing one of the greatest difficulties in the treatment of this effluent.

The oily organic compounds present in produced water can be found in dissolved or dispersed forms and consist of a mixture of different hydrocarbons, such as BTEX, PAHs (polycyclic aromatic hydrocarbons), and phenols (Iggunu and Chen 2014). Petroleum hydrocarbons present the greatest environmental concern due to their toxicity (Neff et al. 2011).

Several chemical additives may also be found in oil field–produced waters originated from enhanced oil recovery and stimulation operations. Examples of these compounds include

solvents, surfactants, polymers, cross linkers and breakers, clay stabilizers, and corrosion, scale, and biofouling inhibitors (Luek and Gonsior 2017; Li et al. 2021). For instance, Ferrer and Thurman (2015) identified different hydraulic fracturing additives in produced water samples located in Weld County (USA). Some of the chemicals reported by the authors are guar gum, glutaraldehyde, cocamidopropyl dimethylamine, and alkyl dimethyl benzyl ammonium chloride. Thurman et al. (2014) found polyethylene glycols and linear alkyl ethoxylates in flowback and produced water samples. Lester et al. (2015) identified small-chain carboxylic acids (acetic, n-butyric, and propionic acids) in flowback water from Colorado.

In addition to the analytical methods mentioned, there are several standard protocols, established by EPA (Environmental Protection Agency), USGS (United States Geological Survey), NEMI (National Environmental Methods Index), and ASTM (American Society for Testing and Materials), developed for drinking water, and domestic and industrial wastewaters (Jiang et al. 2021). Up to now, there are no approved protocols for oil field–produced water analyses. Therefore, researchers have been applying the standard protocols for such wastewater characterization (Santos et al. 2018). A list of these standard methods can be found in Table 3.

Produced water parameters, such as total organic carbon, chemical oxygen demand, and total suspended solids, present variations over time (Rosenblum et al. 2017; Oetjen et al. 2018). In this sense, intending to evaluate an effluent with less composition variability, several authors performed different treatment experiments using synthetic produced waters. In

**Table 1** Main inorganic components, analytical methods, and reported concentrations in various real produced water samples found in the literature.

Compound	Analytical method <sup>a</sup>	Concentration (mg L <sup>-1</sup> ) <sup>b</sup>
Ammonium nitrogen <sup>c,d,e</sup>	Ammonia selective electrode method, colorimetric method	18–91
Ammonium <sup>c</sup>	Ion chromatography (IC)	598.6 ± 10.2
Arsenic <sup>e,f</sup>	Inductively coupled plasma optical emission spectrophotometry (ICP-OES)	0.024–0.992
Barium <sup>c,d,f,g</sup>	ICP-OES	0.2–670
Bromide <sup>c,e,f,i</sup>	IC	12.2–591.1
Cadmium <sup>c,d,f,g</sup>	ICP-OES	<0.001–0.150
Calcium <sup>c,e,f,g</sup>	IC	60–6750
Chloride <sup>c-g</sup>	IC	395–109,089
Chromium <sup>c,d,g</sup>	ICP-OES	<0.005–0.024
Cobalt <sup>h</sup>	Flame atomic absorption spectrometry (FAAS)	0.003–0.004
Copper <sup>d,f,g,h</sup>	ICP-OES, FAAS	0.001–0.29
Cyanide <sup>c,d</sup>	Selective electrode method	<10
Fluoride <sup>c,d</sup>	IC	0.67–16
Iron <sup>c,d,f,i</sup>	ICP-OES	0.04–140
Lead <sup>c,f,g</sup>	ICP-OES	<0.01–0.91
Lithium <sup>e,f</sup>	ICP-OES	0.273–18.8
Magnesium <sup>e,f,g,i</sup>	IC	34.4–1820
Manganese <sup>d,e,f,h,i</sup>	ICP-OES, FAAS	0.04–7.5
Nickel <sup>c-h</sup>	ICP-OES, FAAS	<0.01–0.790
Nitrate <sup>c,d</sup>	IC	<0.1–1.28
Phosphate <sup>c</sup>	IC	2.63–4.21
Potassium <sup>c,e,g,h</sup>	IC	125–4000
Sodium <sup>c,e,f,g,i</sup>	IC	6–44,200
Strontium <sup>c,e,g</sup>	ICP-OES	4–256.8
Sulfate <sup>c,d,f,g</sup>	IC	1–2243
Sulfur <sup>c,i</sup>	Inductively coupled plasma-atomic emission spectroscopy (ICP-AES)	16.1–345
Total dissolved solids (TDS) <sup>c,e,f,g,j</sup>	Gravimetric volatilization	7–162,880
Total phosphorus <sup>c,d</sup>	Colorimetric analysis using orthophosphate	<0.1–3.0
Total suspended solids (TSS) <sup>c,d,f,g,j</sup>	Gravimetric volatilization	1.9–21,820
Zinc <sup>c,f,g,h</sup>	ICP-OES	<0.020–1.74

<sup>a</sup> Analytical methods utilized in the correspondent references

<sup>b</sup> Concentration observed in the oil field–produced water in the correspondent references

<sup>c</sup> Ozgun et al. (2013)

<sup>d</sup> Gabardo et al. (2011)

<sup>e</sup> Hu et al. (2020)

<sup>f</sup> EPA (2000)

<sup>g</sup> Kose et al. (2012)

<sup>h</sup> Dórea et al. (2007)

<sup>i</sup> Almaraz et al. (2020)

<sup>j</sup> Khan et al. (2016)

addition, different preparation procedures of synthetic water samples can be found in the literature, for example, the dissolution of crude oil in distilled or saline water, or the preparation of a solution containing compounds commonly found in

real produced waters. For instance, Younker and Walsh (2014) prepared synthetic water from the emulsification of crude oil in distilled water (2 g L<sup>-1</sup>) using Triton-X as an emulsifier. Besides, 32 g L<sup>-1</sup> of sea salt, 5 mg L<sup>-1</sup> of phenol,

**Table 2** Main organic components, analytical methods, and reported concentrations in various real produced water samples found in the literature

Component	Analysis method <sup>a</sup>	Concentration (mg L <sup>-1</sup> ) <sup>b</sup>
Acenaphthene <sup>c</sup>	Gas chromatography-mass spectrometry (GC-MS)	0.0016–0.0024
Alkyl benzene <sup>d</sup>	GC-MS	74.63–5,092.60
Alkyl propo-benzene <sup>d</sup>	GC-MS	9.34–209.15
Anthracene <sup>e</sup>	GC-MS	0.0008–0.0017
Benzene <sup>c,d,f</sup>	GC-MS, GC with with photoionization detector (GC-PID)	0.079–778.51
Benzo[a]anthracene <sup>e</sup>	GC-MS	0.0016–0.0019
Benzo[e]pyrene <sup>e</sup>	GC-MS	0.0024–0.0026
Benzo[g,h,i]perylene <sup>e</sup>	GC-MS	0.0009–0.0031
BTEX <sup>g</sup>	GC	6.31–38
C1-naphthalenes <sup>d</sup>	GC-MS	0.38–4.20
Chloro-benzene <sup>d</sup>	GC-MS	0.02–0.35
Chrysene <sup>e</sup>	GC-MS	0.0059–0.0099
Dissolved organic carbon (DOC) <sup>d,h</sup>	TOC analyzer	63.45–369
Ethylbenzene <sup>c,d,e,f</sup>	GC-MS, GC-PID	0.051–399.84
Fluoranthene <sup>e</sup>	GC-MS	0.0027–0.0062
m+p-Xylenes <sup>e</sup>	GC-PID	0.194–0.242
Naphthalene <sup>e</sup>	GC/MS	0.0099–0.0107
o-Xylene <sup>e</sup>	GC-PID	0.089–0.103
Perylene <sup>e</sup>	GC-MS	0.0016–0.0026
Phenanthrene <sup>e</sup>	GC-MS	0.0022–0.0024
Phenol <sup>g</sup>	GC-MS	0.53–1.90
Pyrene <sup>e</sup>	GC-MS	0.0009–0.001
Toluene <sup>c,d,e,f</sup>	GC-MS, GC-PID	0.10–5.979
Total oil and grease (TOG) <sup>c,g,i</sup>	Partition-gravimetric method	2.74–195
Total organic carbon (TOC) <sup>d,f,j</sup>	TOC analyzer	21.9–971
Total petroleum hydrocarbons (TPH) <sup>g,i</sup>	GC-MS	125–2,301

<sup>a</sup> Analysis methods utilized by the correspondent references

<sup>b</sup> Concentration observed in the oil field-produced water by the correspondent references

<sup>c</sup> EPA (2000)

<sup>d</sup> Khan et al. (2016)

<sup>e</sup> Dórea et al. (2007)

<sup>f</sup> Gabardo et al. (2011)

<sup>g</sup> Ozgun et al. (2013)

<sup>h</sup> Almaraz et al. (2020)

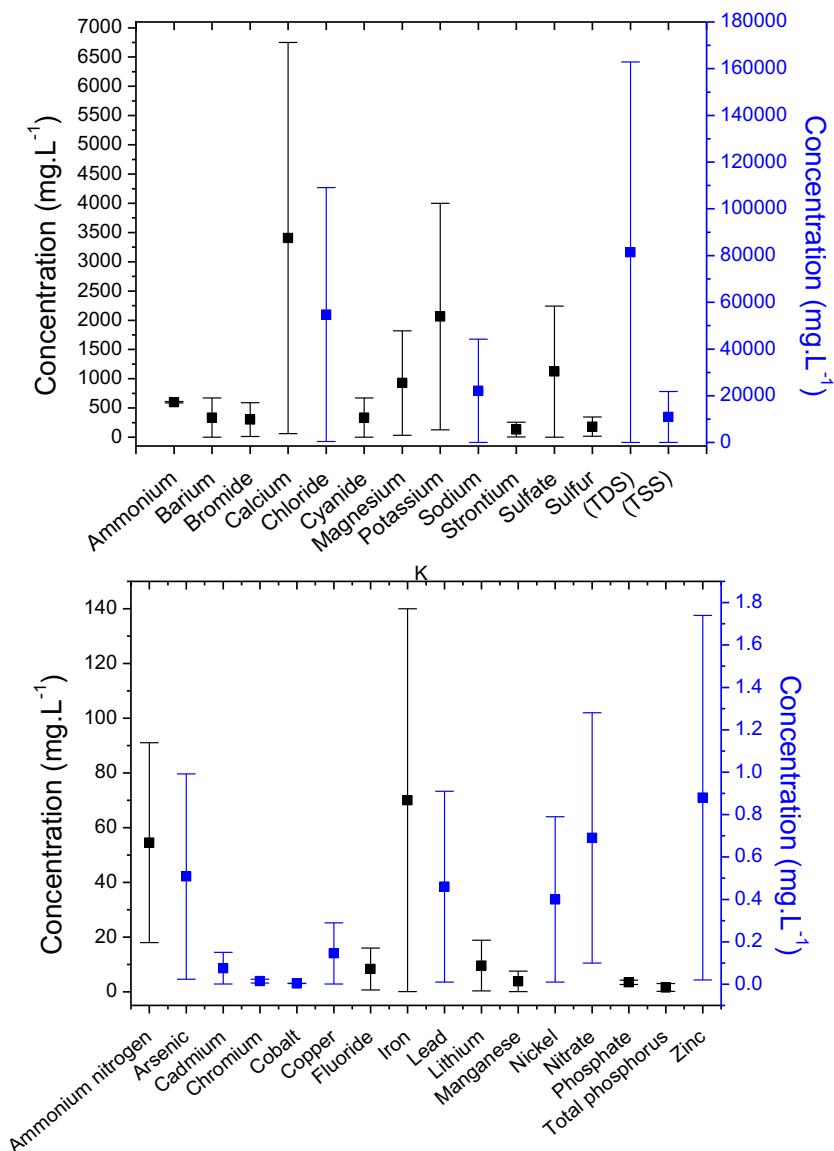
<sup>i</sup> Kose et al. (2012)

<sup>j</sup> Hu et al. (2020)

and 1 mg L<sup>-1</sup> of naphthalene were also added. Silva et al. (2015) obtained the synthetic effluent from the dispersion of crude oil in a solution containing different salts (17 mg L<sup>-1</sup> NaNO<sub>3</sub>, 4229 mg L<sup>-1</sup> NaCl, 204 mg L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>, 1497 mg L<sup>-1</sup> KCl, 2.35 mg L<sup>-1</sup> AlCl<sub>3</sub>, 1506 mg L<sup>-1</sup> MgCl<sub>2</sub>, and 4875 mg L<sup>-1</sup> CaCl<sub>2</sub>), whose concentrations were retrieved from the average values found in the literature for real produced waters. The synthetic effluent used by Jiménez

et al. (2017) was obtained from the emulsification of 100 mg L<sup>-1</sup> of gasoline lubricant and 50 mg L<sup>-1</sup> of olive oil in filtered marine water, using Triton-X as an emulsifying agent. Also, 5 mg L<sup>-1</sup> of phenol, which was chosen as a representative compound of the organic compounds dissolved in a real produced water, was added. Al-Malack and Al-Nowaiser (2018) characterized a real effluent supplied by the oil and gas company

**Fig. 2** Concentration range of the main inorganic compounds in real produced water samples



Saudi Aramco and prepared a synthetic produced water with similar characteristics.

### Photochemical systems aspects

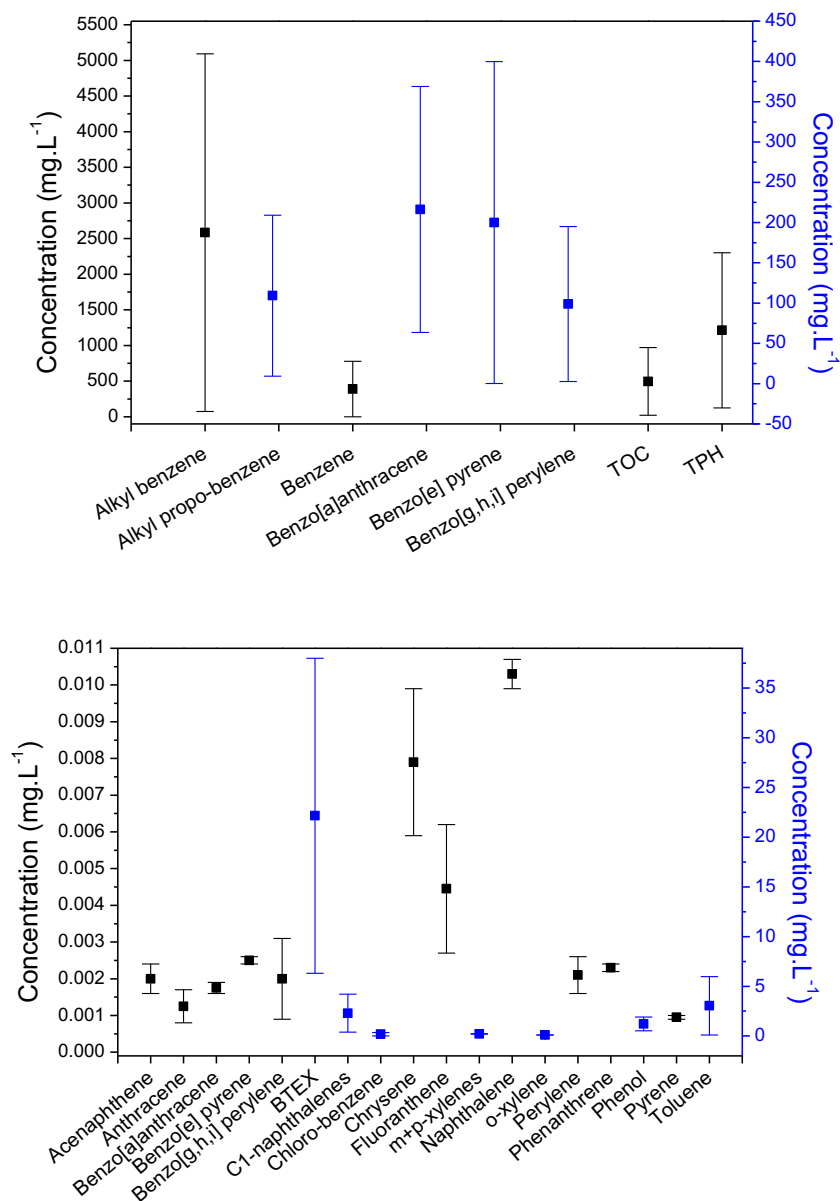
The complex chemical composition of oil field-produced water associated with the presence of recalcitrant organic pollutants makes this effluent difficult to remediate by conventional treatment methods. Advanced oxidation processes (AOPs) appear as chemical procedures capable of degrading these pollutants that are resistant to the primary treatment, constituting secondary/tertiary or polishing techniques. Thus, AOPs target the degradation of toxic constituents, allowing industrial effluents to meet safety and environmental discharge limits (Vaiano et al. 2020). This section presents the general aspects of AOPs for organic pollutant degradation, focusing on the

photochemical parameters as light source, phase aspects, and reactor configuration, as shown in Fig. 4.

AOP techniques are based on the generation of reactive species with high oxidative capacity, such as hydroxyl radicals (HO<sup>•</sup>), which are responsible for the degradation and even the mineralization of the target pollutant. AOP reactions can occur through the addition of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), considered the simplest form, through the process of ozonolysis, sonolysis, electrolysis, Fenton, or photolysis. The latter might be also associated with the previous techniques, constituting the applied photochemistry (Khan and Tahir 2019). The most common AOPs and their respective paths are show in Table 4.

Since the discovery of the possibility of using sunlight as an irradiation source to promote chemical reactions such as the generation of hydrogen from water, new applications have been sought, especially for the degradation of persistent contaminants such as dyes, drugs, aromatics, and other organic

**Fig. 3** Concentration range of the main organic compounds in real produced water samples



pollutants. The application of solar irradiation combined with processes such as Fenton, sonolysis, ozonolysis, and other AOPs allows the use of a low-cost energy source (Rueda-Marquez et al. 2020).

The main techniques using solar or artificial energy (UVA, UVB, UVC) are homogeneous (photolysis included) and photocatalytic, capable of generating oxidizing or reducing radicals responsible for the degradation of contaminants (Molinari et al. 2020). Figure 5 presents five main topics to elucidate the effectiveness of photochemical processes (Wang et al. 2020a): (1) light source, (2) input species, (3) impact factors, (4) mechanisms, and (5) pathways and products.

The light source plays a major role in supplying the necessary energy for the occurrence of photolysis or the excitation of electrons from the valence band to the conduction band, in

the case of photocatalysis. In general, the application of the light source will lead to the occurrence of any of the following processes: (i) photolysis, which transforms molecules only by irradiation (UV, solar, etc.); (ii) photooxidation, which generates radicals such as hydroxyl (HO<sup>•</sup>), sulfate (SO<sub>4</sub><sup>-•</sup>), and chlorine (Cl<sup>•</sup>) responsible for the degradation of pollutants; (iii) photoreduction, which generates radicals such as hydrated electron (e<sub>aq</sub><sup>-•</sup>) and hydrogen atom (H<sup>•</sup>) (Ossai et al. 2020). The most common sources for application in photochemistry are sunlight, low-pressure mercury lamp-induced ultraviolet (LPUV), low-pressure mercury lamp-induced vacuum ultraviolet (LPVUV), medium-pressure mercury lamp-induced ultraviolet (MPUV), and fluorescent light, each of them with a specific spectral irradiance and intensity.

**Table 3** Standard methods used for produced water characterization (Liden et al. 2019; Jiang et al. 2021)

Type of analysis	Standard protocols <sup>a</sup>
Alkanity	EPA 310.1; 310.2
Turbidity	EPA 180.1 (rev. 2.0) SM 2130 B-2011 ASTM D1889-00 USGS I-3860-85
Carbon	SM 5310B ASTM D7573 EPA 415.1
Nitrogen	ASTM D8083
pH	EPA 150.1
Solids	SM 2540 (A-F) ASTM D5907-13 USGS I-3750-85; I-1750-85; I3753-85
Metals or cations	EPA 200.7; 200.8; 130.1 SM 3120B; 3125 ASTM D1971; D1976; D5673; D1126 USGS I-4020-05
Anions	SM 4110 EPA 300.0; 300.1 ASTM D4327 USGS I-4020-05
Nonvolatile organic compounds	EPA 605; 610
Semivolatile and volatile organic compounds	EPA 1659; 8015; 8260B; 1625; 8015D 8021; 624; 1664B
Electrophilic compounds	EPA 525.2; 8015; 8260B
Bacteria	MALDI-MS EPA 1600, 1603, 1680, 1681, 1682
Naturally occurring radioactive materials	EPA 900.0, 903.0, 903.1, 901.1

<sup>a</sup>EPA Environmental Protection Agency, SM standard methods; ASTM American Society for Testing and Materials; USGS United States Geological Survey; MALDI-MS matrix-assisted laser desorption/ionization mass spectrometry

Another important factor about light source is its oxidant activation capacity in the photochemical process. In the case of H<sub>2</sub>O<sub>2</sub>, which represents the oxidant with greater application in photochemical processes, photons may activate the hydrogen peroxide, which drives the HO· generation inducing the pollutant degradation. Cunha-Filho et al. (2019) reported that H<sub>2</sub>O<sub>2</sub> optimized excess may enhance the generation of HO· radicals, achieving the highest mineralization rate for the organic pollutant acetylsalicylic acid at the shortest times. However, the oxidant dose can also affect the generation of transformation products, which consists in intermediates formed by organic pollutants not completely mineralized, adding risks to humans and the environment (Wang et al. 2018).

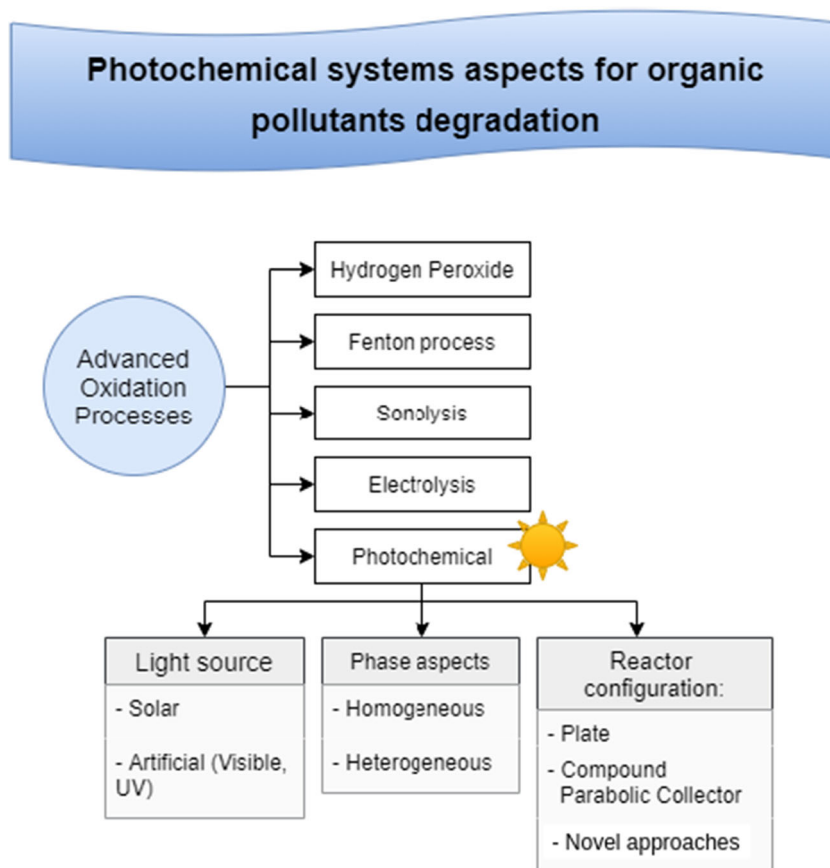
Since photons exhibit a particular behavior such as wave-particle duality, their characteristics differ from the nature of matter corresponding to H<sub>2</sub>O<sub>2</sub> and catalysts. Thereby, the residence time for photochemical reactors is directly affected not

only by reactor hydrodynamics, but also by optical thickness, reactant absorption, radiant flux, and incident radiation. Cassano et al. (1995) investigated the radiant energy transport fundamentals for the modeling of a continuous flow annular reactor. The authors observed that due to optical thickness, different intermediates were generated in different equipment regions, as well as different residence times for each region.

Light sources represent an important investment in the development of photochemical processes for countries located in the sunbelt. Brazil, for example, is in the region of latitude ± 35° of the equator and presents the highest solar radiation. Some studies using a combination of different AOPs with solar irradiation have been reported for the removal of several compounds (Reina et al. 2020). For instance, the degradation of N-acetyl-to-aminophenol was evaluated by using a solar-galvanic Fenton-like process (Castañeda-Juárez et al. 2020). Phenol was degraded by the heterogeneous catalysts TiO<sub>2</sub>/activated carbon and ZnO/activated carbon irradiated by UV



**Fig. 4** Photochemical systems aspects for effluent treatment



(Lee et al. 2019) and by a sono-photo-Fenton-like process using persulfate as an oxidizing agent (Yazdanbakhsh et al. 2020). The treatment of cooling water in an oil refinery was studied by means of heterogeneous photocatalysis using  $\text{TiO}_2$  under UV irradiation (254 nm) (Haolat et al. 2018). Figure 6 presents a simplified scheme of the reactor design aspects. The AOP technique should be considered together with the reactor configuration in order to successfully achieve the degradation of contaminants.

In addition to the choice of the AOP technique that is suitable to degrade the contaminants present in the effluent, especially in secondary treatment or polishing steps, the choice of

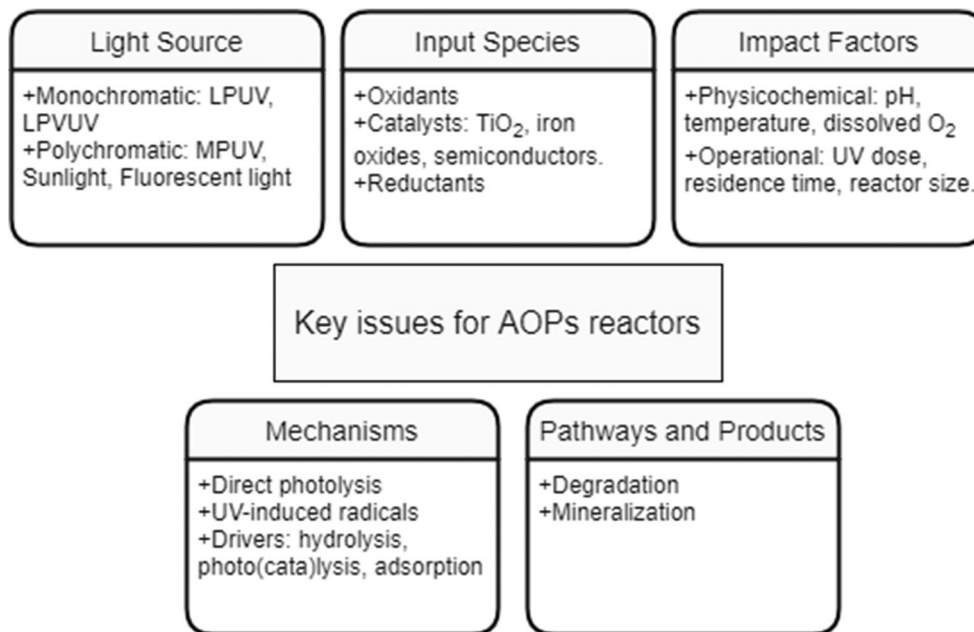
the type of reactor will also be linked to the process feasibility. Batch, plug flow, fixed bed, and slurry reactors are the most common in the literature, as they have a wide applicability for both homogeneous and heterogeneous processes. Other reactor types are described by some authors as promising alternatives, such as annular and thin film, mainly for photochemical processes (photolysis, UV-peroxide, and photo-Fenton-like), with increasing application of solid catalysts (Mazierski et al. 2015).

The configuration of the reactor, operational conditions, recycle streams, and the presence of packing material contribute to the existence of multiple units of phase equilibrium,

**Table 4** Advanced oxidation processes and their respective paths

Process	Paths	Reference
Homogeneous Fenton	$\text{H}_2\text{O}_2 + \text{Fe}^{2+/3+}$	Vaiano et al. (2020)
Heterogeneous Fenton	$\text{H}_2\text{O}_2 + \text{Fe@solid support}$	Vaiano et al. (2020)
Sonolysis	$\text{H}_2\text{O} + \text{Ultrasound}$	Vaiano et al. (2020)
Electrochemical	$\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$	Brillas (2020)
UV-hydrogen peroxide	$\text{H}_2\text{O}_2 + h\nu$	Vaiano et al. (2020)
Photolysis	Pollutant + $h\nu$	Stefan (2018)
Photo-Fenton	$\text{H}_2\text{O}_2 + \text{Fe}^{2+/3+} + h\nu$	Brillas (2020)
Photocatalysis	Semiconductor + $\text{H}_2\text{O} + h\nu$	Khan and Tahir (2019)

**Fig. 5** Key issues about reactor design for AOP processes. Adapted from Wang et al. (2020a)



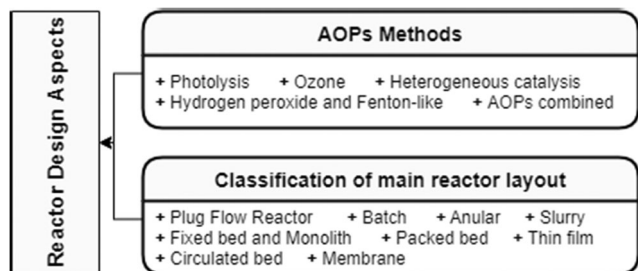
mass transfer and chemical activity, important factors for the development of faster processes, with lower cost and close to continuous operations. All these parameters and mechanisms need to be evaluated on bench scale in order to proceed to pilot scale, and then on full scale (Khan and Tahir 2019). However, it was verified that there is a gap of studies addressing the issue of different reaction systems’ aspects on pilot scale for produced water treatment, or other petrochemical effluents. Furthermore, the coexistence of different inorganic and organic species represents the greatest difficulty in the application of AOPs for produced water treatment, especially photocatalysis. This occurs due to the possibility of radiation competition between different contaminants and the interference in the formation of oxidative radicals and consequent reduction in the efficiency of the catalytic process (Wang et al. 2020b).

Fang et al. (2020) evaluated UV/H<sub>2</sub>O<sub>2</sub>, UV/chlorine, and UV/persulfate processes for the oil sand process water (OSPW) treatment, including degradation of dissolved organic matter (DOM) and naphthenic acid (NA) removal. The UV/persulfate showed the highest NA removal (81.2%), followed by UV/chlorine (71.0%), UV/H<sub>2</sub>O<sub>2</sub> (70.9%), and UV

photolysis (22%, without oxidant), considering the initial NA concentration of 35.58 mg L<sup>-1</sup>, an incident irradiance set at 3.50 mW cm<sup>-2</sup>, using 1 kW medium-pressure mercury lamp, with emission range from 200 to 530 nm, and reaction time of 40 min.

A photolysis process for the degradation of a mixture of anthracene and benzo[a]pyrene at ultra-trace levels in water was studied by Rubio-Clemente et al. (2020). UV photolysis was performed in batch mode using an annular photoreactor, four mercury low-pressure (6 W, 254 nm) lamps, and black light lamps (8 W, 365 nm), at 25 ± 1 °C. The authors achieved a 99% removal efficiency for both contaminants with 15 min, 4 UVC LP lamps, and UV irradiance of 0.63 mW cm<sup>-2</sup>. PAH compounds, such as anthracene and benzo[a]pyrene, are known for their tolerance to biodegradation, which enlists photocatalysis as an alternative to petrochemical wastewater treatment.

Ziulli and Jardim (2003) evaluated the effect of photolysis and photocatalytic processes for an accelerated degradation of water-soluble fraction (WSF) of crude oil in marine waters. The irradiation tests consisted of a quartz reactor with a 125-W high-pressure mercury lamp (366 nm) and the use of TiO<sub>2</sub> at 0.1% (w/v) for the photocatalytic experiments. Gas chromatography-mass spectrometry analysis was performed to quantify generated products. For the photolysis tests, the authors verified a subtle reduction of some peaks observed after 24 h under photolysis, but after 6 days of photolysis the chromatogram did not exhibit significant differences. Furthermore, no mineralization occurred during photolytic experiments of crude oil WSF in marine waters. On the other hand, the photodegradation in the presence of TiO<sub>2</sub> resulted in a complete oxidation for the crude oil soluble part (WSF-D



**Fig. 6** Schematic representation of reactor designs for AOP applications

sample) after 24 h of irradiation and after 4 days for the WSF-A sample. Considering the recalcitrant aspect of the organic compounds present in crude oil, the heterogeneous process rises as a promising alternative for petrochemical wastewater and produced water treatment.

## Performance of photochemical reactors

The development of new photoreactors for oil field-produced water treatment, or petrochemical effluents, usually apply model molecules as a way to evaluate the potential for photodegradation and optimization of hydrodynamics, residence time, and other parameters for system design. Among the most common model molecules for use in preparation of synthetic effluents are phenol, BTEX mixtures (benzene, toluene, ethylbenzene, and xylenes), and chlorinated hydrocarbons, in concentrations close to those found in real petrochemical effluents (Silva et al. 2012; Mota et al. 2018; Carvalho et al. 2019; Al-Ghouti et al. 2019).

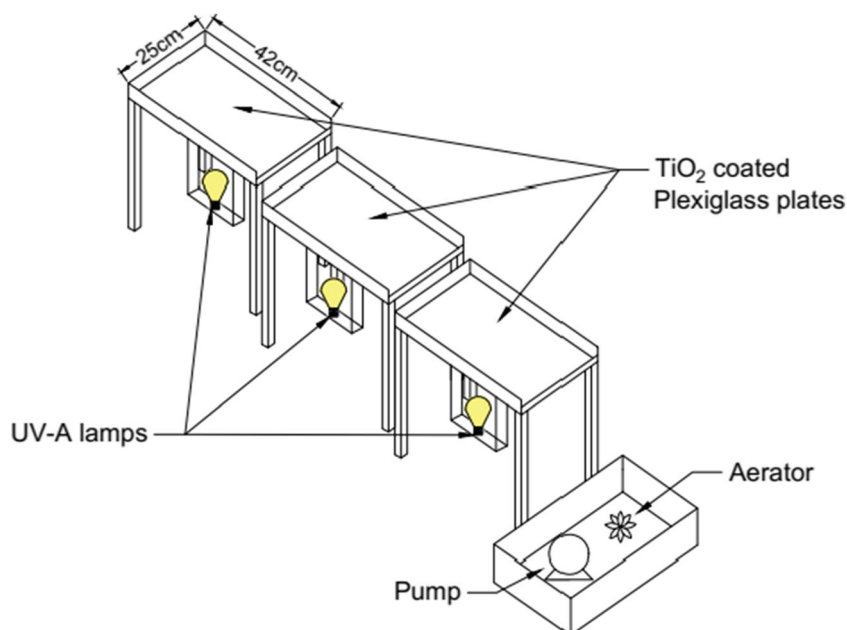
Haolat et al. (2018) used an annular quartz reactor, with a UV light source ( $\sim 254$  nm) and solid catalysts formed by silica beads coated with  $\text{TiO}_2$ , for the cooling water treatment from an oil refinery. The effluent characterizations showed chemical and biological contamination, resistant to conventional treatments, with  $\sim 160$  mg  $\text{L}^{-1}$  TOC. The system showed 17% degradation (72 h) of TOC and 100% reduction ( $\sim 600$  s) of biological contamination.

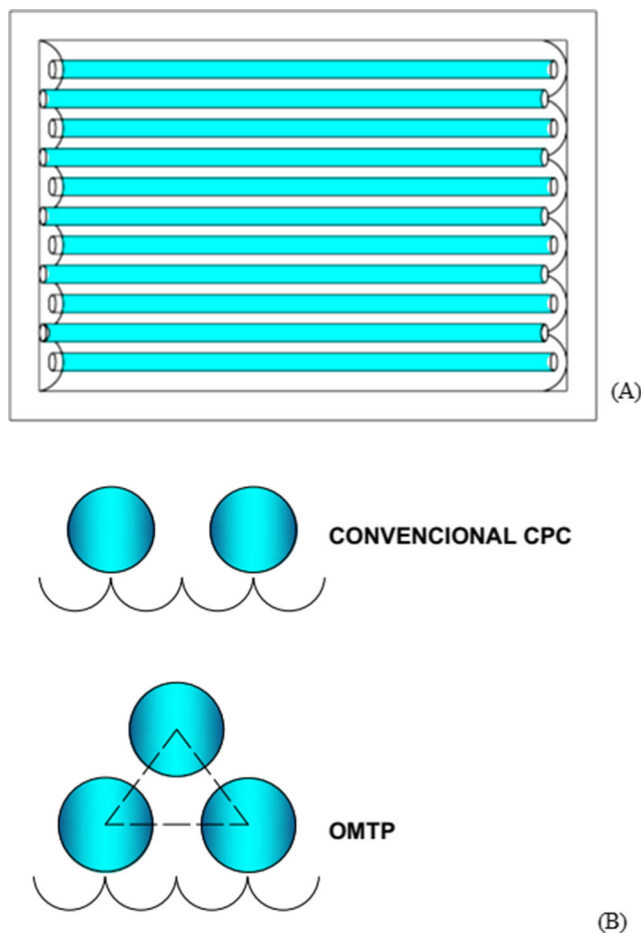
Using phenol as the target molecule for degradation, Khaksar et al. (2017) developed a cascade reactor (Fig. 7) with  $\text{TiO}_2$  nanoparticles immobilized over the reactor surface. The photocatalytic reactor configuration consisted of three

rectangular plates ( $450 \times 250 \times 2$  mm) arranged in series, with three walls with 4 cm of height and a smaller wall (2 cm) that allows the film to flow from a plate to the next one. The liquid film on each plate was 2 cm, with a flow rate of  $4$  L  $\text{min}^{-1}$ . The plates were made of transparent Plexiglass immobilized by  $\text{TiO}_2$  nanoparticles using an epoxy concrete sealer. Phenol photocatalysis was investigated considering factors such as initial concentration,  $\text{TiO}_2$  amount, turbidity, and medium pH, using UVA lamps with a wavelength of 350 nm as the light source. Degradation of 88% of phenol was achieved for an initial concentration of  $50$  mg  $\text{L}^{-1}$ , reaction time of 3 h, pH = 9, and  $80$  g  $\text{m}^{-2}$  of  $\text{TiO}_2$  per plate. The reported photocatalytic reactor configuration builds a major contribution to the development of new projects that will allow photocatalytic processes to operate in continuous mode, especially for the treatment of effluents from the petrochemical industry.

A modification of the compound parabolic collector (CPC) solar reactor was proposed by Ochoa-Gutiérrez et al. (2018), consisting of additional tubes in the intersection spaces occupied by the reflective plates. The prototype Offset Multi Tubular Photoreactor (OMTP) (Fig. 8) developed by the authors was evaluated in the degradation of contaminants such as phenol, dichloroacetic acid (DCA), and 4-chlorophenol (4CP), using  $\text{TiO}_2$  nanoparticles dispersed as solid catalyst with 21.5 nm and solar irradiation. The new tube configuration showed an increase of 1.8 times in the residence time of the fluid and an increase of 44% in the solar energy absorbed by the system, resulting in an increase in the degradation efficiency of phenol, DCA, and 4CP of 242, 125, and 118%, respectively, when compared to the CPC system. The arrangement modification in the tubes proposed by the authors allowed greater absorption of solar irradiation, reducing the

**Fig. 7** Cascade reactor with immobilized  $\text{TiO}_2$  nanoparticles. Adapted from Khaksar et al. (2017)





**Fig. 8** Offset multi tubular photoreactor, **A** top view; **B** compound parabolic collector (CPC) front view, and OMTP front view. Adapted from Ochoa-Gutiérrez et al. (2018)

required size of the equipment, contributing to the economic and technical feasibility in oil platforms and refineries, where space may be limited.

The efficiency of a photocatalytic process is intrinsically related to the reactor configuration used, assessed by means of parameters such as the incidence of photons on the system and photonic efficiency. Manassero et al. (2017) investigated the influence of three types of photocatalytic reactor configurations, using  $\text{TiO}_2$  as a catalyst. The evaluated configurations were as follows: (i) slurry reactor, with the dispersed catalyst, (ii)  $\text{TiO}_2$  film immobilized on the reactor surface, and (iii) fixed bed reactor with  $\text{TiO}_2$  immobilized in glass beads. The light incident on the system came from a UV/Vis lamp in the 350- to 410-nm range. The performance of the reactors, for the conditions studied by the authors, follows the order of efficiency: slurry > fixed bed > film, when the photonic and quantum efficiencies were evaluated. The suspension of the catalyst in solution of the system (i) favors a higher incidence of photons, increasing the photocatalytic activity and the reaction rate, in contrast to the configurations with the immobilized  $\text{TiO}_2$  (systems ii and iii). However, from the

process point of view, the immobilization of the catalyst allows the intensification of the system, so that a new stage for the separation of  $\text{TiO}_2$  from the aqueous medium is not necessary. In this way, the development of new configurations of photocatalytic reactors that uses immobilized catalysts associated with enhanced conversion efficiencies is a goal to be sought.

In addition to the reactor configuration and the type of AOP applied, parameters such as pH, concentration of pollutant, and presence of salts can also affect the degradation and mineralization kinetics of the contaminants. In this way, Tolosana-Moranchel et al. (2020) reported the effect of the salts  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  on the photocatalytic degradation ( $\text{TiO}_2$  P25 and Hombikat UV-100 as catalysts) of phenol. The loss of photoactivity observed for P25 catalyst occurred mainly due to the pH change in the brine solution, since no effect on  $\text{HO}\cdot$  radical formation was reported. In the case of Hombikat catalyst, the salt ions enhanced the photoactivity and induced a faster radical formation. Thereby, for a produced water containing a buffer agent to regulate the pH, the semiconductor application as photocatalyst may enhance the degradation of recalcitrant contaminants as phenol.

### Combined processes on petroleum wastewater treatment

Several biological, chemical, and physical processes have been proposed for the treatment of produced water in order to remove free and dispersed oils, grease, metals, suspended solids, sand, bacteria, dissolved gases, radioactive compounds, and dissolved salts (Fakhru'l-Razi et al. 2009; Nasiri et al. 2017). These techniques include adsorption, coagulation, flocculation, flotation, filtration, chemical and biological oxidation, activated sludge, and membrane, among others (Al-Ghouti et al. 2019). As oil field-produced water has an overly complex composition, most of the mentioned methods are useful in removing or degrading only certain groups of compounds (Jiménez et al. 2018). In this context, the need of combined processes is recommended to increase the overall efficiency of the treatment and ensure that the required quality levels are achieved (Kusworo et al. 2018; Silva et al. 2015).

For instance, flotation is very efficient in separating dispersed oil, but such technique is not able to remove dissolved compounds (Younker and Walsh 2014). With the application of biological treatments, it is possible to remove soluble components. However, biological methods should not be used in effluents containing high concentrations of recalcitrant compounds that may be toxic to the microorganisms used (Diya'uddeen et al. 2015). Thus, a preliminary treatment step must be performed. Membrane filtration systems are very efficient at removing various compounds present in produced

water. Nevertheless, previous treatment steps must be carried out in order to reduce the load of contaminants present in the effluent aiming at the reduction of membrane fouling (Kusworo et al. 2018).

Many studies employing the integration of different treatment techniques have been investigated. A schematic representation of different treatment combinations of oil field-produced water or effluents from oil refineries developed in recent years are listed in Fig. 9. More detailed information about these processes can be seen in Table 5 and in the following paragraphs.

Zhao et al. (2014) evaluated the application of a previous electrocoagulation stage before the reverse osmosis membrane system in order to remove hardness, COD (chemical oxygen demand), and turbidity from produced water. The authors observed that the addition of the previous electrocoagulation step reduced the fouling and scaling associated with the precipitation of oil and calcium, which is efficient concerning the increase of the membrane life cycle.

Silva et al. (2015) evaluated the integration of flotation and photo-Fenton techniques for the treatment of synthetic produced water (Fig. 10). The authors obtained a 99% TOG removal after 10 min of flotation followed by 45 min of photo-Fenton. Although the combined process is very efficient, homogeneous photo-Fenton reactions require the acidification of the medium to prevent the precipitation of iron. Besides, Brazilian legislation establishes a maximum limit of 15 mg L<sup>-1</sup> (0.27 mM) of dissolved iron for the discharge of effluents (CONAMA 2011). The optimum iron concentration found in this work was higher than the allowed value. Consequently, further steps are necessary both to neutralize the medium and to remove the dissolved iron. Overall, techniques that use immobilized iron in solid supports are desirable in order to overcome these limitations.

Diya'uddeen et al. (2015) employed a Fenton process as a prior step to a sequencing batch reactor (SBR) to treat the effluent from an oil refinery. Fenton process was able to remove 95% of the phenol present in the effluent, which is desirable for the treatment system in question, as this compound decreases the efficiency of the biological reactor due to its high toxicity to the microorganisms. After the two stages of treatment, COD and TOC were reduced to values below the discharge limits, which reveals the satisfactory efficiency of the combined system for the petroleum wastewater treatment.

Estrada-Arriaga et al. (2016) studied the integration of an AOP (Fenton reaction or solar photo-Fenton using ferrioxalate), followed by an ultrafiltration membrane stage for the treatment of oil refinery wastewater with a high concentration of phenol (200 mg L<sup>-1</sup>). The presence of chlorides and sulfates in the effluent affected the performance of the Fenton reaction, with a maximum COD removal efficiency of 55%. By using photo-Fenton with ferrioxalate and ultrafiltration membrane, an overall COD removal of 94% was

achieved. However, membrane fouling was observed due to the deposition and precipitation of Fe<sup>2+</sup> and Fe<sup>3+</sup> ions on the membrane surface for both AOPs employed, and by the deposition of small remaining floccules from the photochemical reaction using ferrioxalate.

El-Naas et al. (2016) studied the use of a pilot plant consisting of three stages for the treatment of an oil refinery effluent: electrocoagulation, biological treatment in a spouted bed bioreactor (SBBR), and adsorption with granular activated carbon. Different configurations of the three units were tested. The authors found that the application of electrocoagulation as a first step resulted in a better performance of the process, since this operation was able to reduce the suspended solids and the COD from the effluent. Thus, the subsequent steps (bioreactor and adsorption) had their efficiencies increased.

Kose-Mutlu et al. (2016) analyzed the effects of applying a treatment step before the passage of produced water by filtration membranes. Different techniques were evaluated, including combinations of microfiltration unit systems and powdered activated carbon (PAC) or granular activated carbon (GAC), as shown in Fig. 11. Such methods were used before nanofiltration and reverse osmosis treatments. The combined techniques of GAC, microfiltration, and reverse osmosis showed the best efficiencies in reducing the effluent electrical conductivity and heavy metal concentrations.

The degradation of phenolic compounds from an oil refinery effluent was studied by Hernández-Francisco et al. (2017) using electrocoagulation (EC) associated with Fenton or photo-Fenton reactions. When EC was combined to photo-Fenton, TOC and total phenols removal of 88% and 100% were achieved, respectively. According to the authors, most of the remaining TOC is attributed to the presence of short-chain carboxylic acids, which are non-toxic and biodegradable.

A system combining electrocoagulation and membrane bioreactor has been proposed by Al-Malack and Al-Nowaiser (2018) to treat synthetic produced water. High COD and TOG removals were obtained for the integrated treatment. In addition, the authors did not observe membrane fouling during the 60 days of operation, which was attributed to the application of the previous electrocoagulation step.

Al-Kaabi et al. (2019) evaluated the treatment of a real produced water sample using two integrated steps: sand filter and activated carbon (or activated carbon modified with microemulsion), as shown in Fig. 12. With the combined treatment, removal values of 100% were observed for most metals and more than 95% for BTEX. However, TOC removal efficiency was low.

Precipitative softening (PS), walnut shell filtration (WSF), and membrane distillation (MD) were used as integrated techniques to treat produced water from shale oil and gas fields (Zhang et al. 2019). Precipitative softening was able to reduce

**Table 5** Combined processes employed for the treatment of oil field–produced waters and refinery wastewaters

Combined process	Type of wastewater	Conditions	Inlet stream	Benchmark parameters	Reference
Electrocoagulation (EC) and reverse osmosis (RO)	Oilfield produced water	EC: pH = 7; current density = 5.56 mA cm <sup>-2</sup> ; time = 30 min RO: transmembrane pressure = 20 bar; flow rate = 0.8 L min <sup>-1</sup>	COD = 280 mg L <sup>-1</sup> Turbidity = 135 NTU Hardness = 300 mg L <sup>-1</sup>	COD removal = 66% Turbidity removal = 92% Hardness removal = 85%	Zhao et al. (2014)
Flotation and AOP (photo-Fenton)	Synthetic produced water	Flotation: pH = 7.0; air flow = 3.209 cm <sup>3</sup> min <sup>-1</sup> ; flotation time = 10 min AOP: pH = 3.0; [H <sub>2</sub> O <sub>2</sub> ] = 10 mM; [Fe <sup>2+</sup> ] = 0.44 mM; reaction time = 45 min	TOG = 300 mg L <sup>-1</sup>	TOG removal = 99%	Silva et al. (2015)
AOP (Fenton) and sequencing batch reactor (SBR)	Refinery wastewater	AOP: pH = 3; [H <sub>2</sub> O <sub>2</sub> ] = 222 mM; [Fe <sup>0</sup> ] = 22.2 mM SBR: pH = 6.5–7.5; air rate = 1 mL min <sup>-1</sup> ; reaction volume = 4.8 L; treatment time = 10 h	COD = 1259 mg L <sup>-1</sup> TOC = 186 mg L <sup>-1</sup> [Phenol] = 14.7 mg L <sup>-1</sup>	COD removal = 76.5% TOC removal = 45% Phenol removal = 96%	Diya'uddeen et al. (2015)
AOP (solar photo-Fenton) and ultrafiltration (UF0)	Refinery wastewater	AOP: pH = 5; [H <sub>2</sub> O <sub>2</sub> ] = 500 mg L <sup>-1</sup> ; [Fe <sup>2+</sup> ] = 20 mg L <sup>-1</sup> ; reaction time = 2 h UF: pressure = 8.5 psi; flow rate = 8.8 mL min <sup>-1</sup>	COD = 400 mg L <sup>-1</sup> [Phenol] = 200 mg L <sup>-1</sup>	COD removal = 94% Phenol removal = 100%	Estrada-Arriaga et al. (2016)
Electrocoagulation (EC), spouted bed bioreactor (SBBR) and adsorption (AD)	Refinery wastewater	EC: current = 65 A; T = 30–35 °C; capacity = 1.48 m <sup>3</sup> h <sup>-1</sup> SBBR residence time = 1 h; T = 30 °C; pH = 7; working volume = 1 m <sup>3</sup> (AD) average particle size = 1.5 mm; total bed volume = 0.5 m <sup>3</sup>	COD = 3970 – 4745 mg L <sup>-1</sup> [Phenol] = 8 – 10 mg L <sup>-1</sup>	COD removal = 96% Phenol removal = 100%	El-Naas et al. (2016)
Microfiltration (MF), adsorption (GAC), and reverse osmosis (RO)	Oil and gas field produced water	MF: transmembrane pressure = 1 bar; effective filtration area = 155 cm <sup>2</sup> GAC: carbon bed height = 1 m; contact time = 20 min; downflow velocity = 100 mL min <sup>-1</sup> RO: operating pressure = 40 bar	COD = 532 mg L <sup>-1</sup> Conductivity = 40.01 mS cm <sup>-1</sup> [Fe] = 3 mg L <sup>-1</sup> [Sr] = 152.9 mg L <sup>-1</sup>	COD removal = 90% Conductivity removal = 99% Fe removal = 99% Sr removal = 98%	Kose-Mutlu et al. (2016)
Electrocoagulation and AOP (photo-Fenton)	Refinery wastewater	EC: current density = 40 mA cm <sup>-2</sup> ; time = 20 min; pH = 7 AOP: [H <sub>2</sub> O <sub>2</sub> ] = 306 mg L <sup>-1</sup> ; [Fe <sup>2+</sup> ] = 19.8 mg L <sup>-1</sup> ; pH = 3; reaction time = 1 h	TOC = 248.7 mg L <sup>-1</sup> [Total phenols] = 123.5 mg L <sup>-1</sup>	TOC removal = 88% Total phenols removal = 100%	Hernández-Francisco et al. (2017)
Electrocoagulation and membrane bioreactor (MBR)	Synthetic produced water	EC: current density = 30 mA cm <sup>-2</sup> ; time = 120 min MBR: permeate flux = 12 L m <sup>-2</sup> h <sup>-1</sup>	TOG = 100 mg L <sup>-1</sup> COD = 1600 mg L <sup>-1</sup>	TOG removal = 95% COD removal = 97%	Al-Malack and Al-Nowaiser (2018)
Filtration (F) and adsorption (AD)	Gas field produced water	F and AD: flow rate = 0.3 m <sup>3</sup> h <sup>-1</sup>	TOC = 2405 mg L <sup>-1</sup> [Benzene] = 11.17 mg L <sup>-1</sup> [Fe] = 4.14 mg L <sup>-1</sup> [Ni] = 7.08 µg L <sup>-1</sup>	TOC removal = 31.07% Benzene removal = 99.93% Fe removal = 100% Ni removal = 100%	Al-Kaabi et al. (2019)
Precipitative softening (PS), filtration, and membrane distillation (MD)	Shale oil and gas produced water	PS: pH = 10; [alum] = 15 mg L <sup>-1</sup> ; mixing time = 1 min; settling time = 30 min F: flow rate = 4.5 L min <sup>-1</sup> MD: crossflow velocities = 0.4 L min <sup>-1</sup> ; T(feed) = 60 °C; T(distillate) = 20 °C	Alkalinity = 555 mg L <sup>-1</sup> [Ba] = 42.1 mg L <sup>-1</sup> [Ca] = 878 mg L <sup>-1</sup> [Benzene] = 9 mg L <sup>-1</sup> Turbidity = 322 NTU	Alkalinity removal = 67% Ba removal = 65% Ca removal = 32% Benzene removal = 95% Turbidity removal = 94%	Zhang et al. (2019)
Electrocoagulation and filtration	Oilfield produced water	EC: current density = 6.66 mA cm <sup>-2</sup> ; time = 12 min F: flow rate = 20 mL min <sup>-1</sup> ; empty bed contact time = 19 min	TOC = 83.1 mg L <sup>-1</sup> Turbidity = 53.4 NTU [Iron] = 11 mg L <sup>-1</sup>	TOC removal = 74% Turbidity removal = 93% Iron removal = 100%	Rodriguez et al. (2020)
Solid phase extraction (SPE) and microfiltration (MF)	Oilfield produced water	SPE: flow rate = 2.5 mL min <sup>-1</sup> ; resin dose = 10 g	TOC = 148.5 g L <sup>-1</sup> Turbidity = 121 NTU	TOC removal = 100%	Abdel-Shafy et al. (2020)

**Table 5** (continued)

Combined process	Type of wastewater	Conditions	Inlet stream	Benchmark parameters	Reference
		MF: mean pore size = 200 nm; transmembrane pressure = 1 bar	TDS = 66 g L <sup>-1</sup>	Turbidity removal = 98.02% TDS removal = 20%	
Electrochemical oxidation (EO) and bioelectrochemistry (BE)	Synthetic produced water	EO and BE: current density = 71 mA cm <sup>-2</sup> ; time = 4 h	TPH = 700 mg L <sup>-1</sup> COD = 4600 mg L <sup>-1</sup> TDS = 17.5 g L <sup>-1</sup>	TPH removal = 89% COD removal = 89.57% TDS removal = 34.3%	Mohanakrishna et al. (2021)

several scale-forming species concentrations, like alkalinity, dissolved barium, and calcium while filtration was efficient in removing organic compounds, with removal values higher than 95%. The application of the pretreatment steps (PS and WSF) improved the membrane reusability, allowing three consecutive cycles with satisfactory performance.

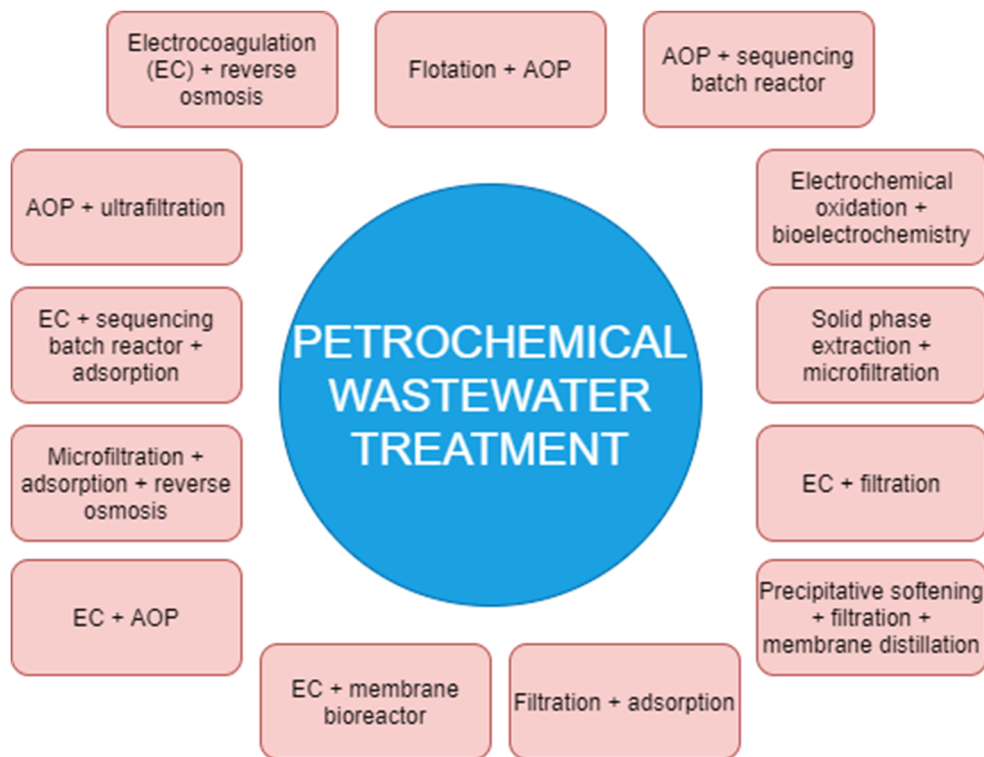
Rodriguez et al. (2020) proposed the combination of chemical coagulation or electrocoagulation followed by filtration for the treatment of a real sample of oil field–produced water. Although more efficient when compared to chemical coagulation, electrocoagulation has a higher operating cost, being 1.2 or 1.7 times more expensive than chemical coagulation using ferric chloride or aluminum sulfate as coagulants, respectively. Thereafter, the previously electrocoagulated effluent was submitted to filtration. Different filter media were

tested, including agricultural residues, such as pecan nutshell, nutshell and biochar, and granular activated carbon. Turbidity removal values of 94, 95, and 97% were obtained using biochar, activated carbon, and nutshell, respectively.

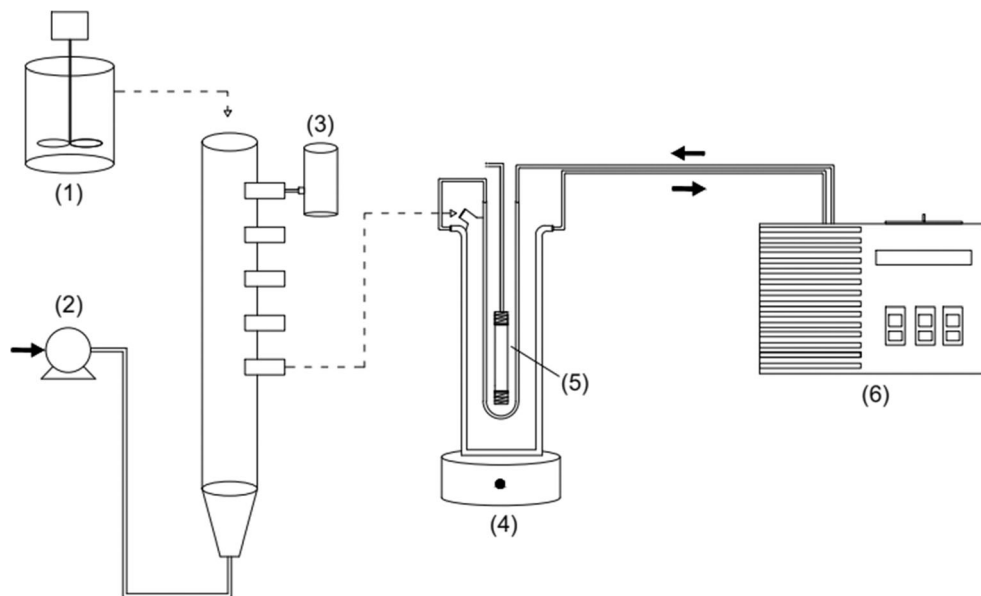
Solid-phase extraction (SPE) using a porous resin composite coupled to microfiltration was applied for the treatment of a real produced water sample (Abdel-Shafy et al. 2020). According to the authors, the composite, which is a mixture of phenyl epoxy, poly(vinyl)pyrrolidone (PVP), and Fe<sub>3</sub>O<sub>4</sub>, presented both adsorption and catalytic activity. SPE promoted high efficiency of oil removal (99%). When the previously treated effluent was fed to a microfiltration unit, total removal of the oil was obtained.

Mohanakrishna et al. (2021) evaluated the combination of electrochemical and bioelectrochemical steps for treating

**Fig. 9** Schematic representation of different treatment methods combinations for treating produced waters or petrochemical effluents found in the literature



**Fig. 10** Schematic representation of a combined treatment system composed by flotation and photo-Fenton in an annular photoreactor. (1) Mixing tank with synthetic oil field-produced water; (2) compressed air; (3) foam collector; (4) magnetic stirrer; (5) mercury vapor lamp; (6) thermostatic. Adapted from Silva et al. (2012)



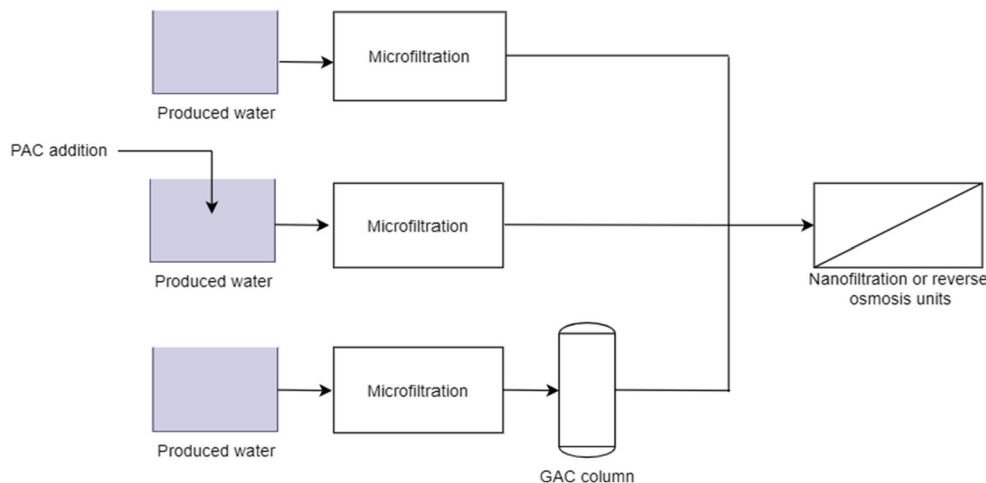
synthetic produced water. Initially, the wastewater was submitted to an electrochemical cell in order to partially degrade dissolved organic contaminants. Then, the previously treated effluent was fed to a microbial fuel cell aiming to simultaneously remove the remaining organics and generate electricity. The integrated system promoted high removal efficiencies.

Application of technologies such as filtration, bioremediation, hydrocyclone, adsorption, and flotation that are usually applied in the oil field effluent treatment steps allow the removal of large amounts of dispersed and emulsified oil, and organic and inorganic pollutants. However, the difficulty in both reducing the recalcitrant compounds' concentrations below the discharge limits and removing oil droplets with smaller sizes are disadvantages of these methods (Li et al. 2021). Thereby, combined process such as those that include AOPs are reported as promising to achieve the specification of an oil field effluent for correct disposal.

### Conclusions

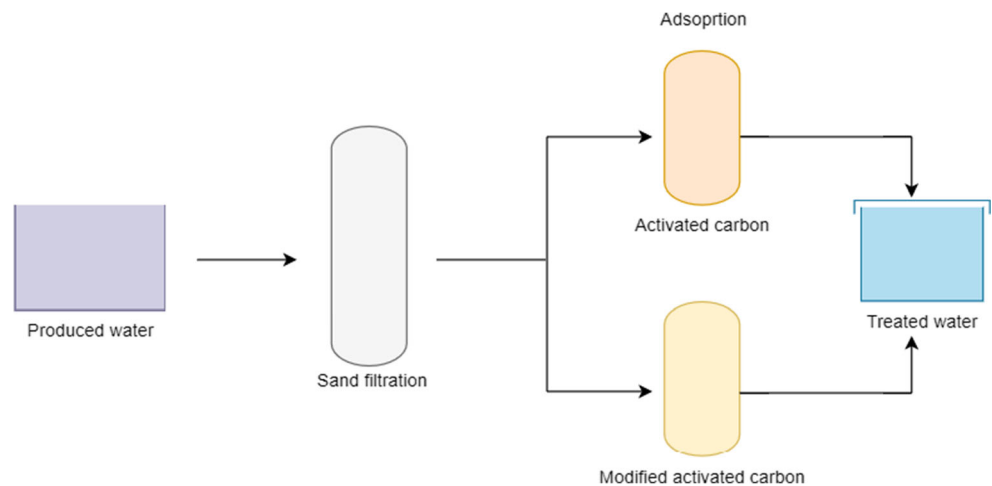
This review manuscript presents an overview on three themes involving the treatment of oil field-produced water. Firstly, an informative description is provided for the analytical methods employed to quantify several organic and inorganic species in different produced water samples reported in the literature. The report also contains relevant aspects about photochemical reaction systems including different homogeneous and heterogeneous (catalytic) processes applied to oil field-produced water. In particular, insights about details of photochemical reactors employed for the abatement of organic substances in produced water are highlighted. A review of the literature addressing combined processes to efficiently treat produced water is discussed. In fact, the combination of more than one technique is found necessary and it is important to compile the main characteristics and results.

**Fig. 11** Schematic representation of a combined treatment system composed by microfiltration, adsorption and reverse osmosis or nanofiltration units. Adapted from Kose-Mutlu et al. (2016)





**Fig. 12** Schematic representation of a combined treatment system composed by filtration and adsorption columns. Adapted from Al-Kaabi et al. (2019)



**Author contribution** Conceptualization: L. R. Hollanda; methodology: S. B. F. Santos; formal analysis and investigation: J. G. A. A. Faustino; writing—original draft preparation: L. R. Hollanda, E. L. Foletto; writing—review and editing: G. L. Dotto, E. L. Foletto; funding acquisition: O. Chiavone-Filho; supervision: O. Chiavone-Filho. All authors read and approved the final manuscript.

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**Data availability** The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

## Declarations

**Ethical approval** Not applicable.

**Consent to participate** Not applicable.

**Consent to publish** Not applicable.

**Competing interests** The authors declare no competing interests.

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