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Case Report

Characterization and assessment of process water from oil and gas production: A case study of process wastewater in Qatar

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A B S T R A C T

This study characterized and assessed three different process water (PWWs) (S-1, S-2, and S-3) from oil and gas production in Qatar. The wastewater generated in various processing stages contains many harmful components including polyaromatic hydrocarbons, phenol, heavy metals, ammonia, and other hydrocarbons and non-hydrocarbons. The results revealed that S-2 had higher pH (8.5) followed by S-3 (8.3) and S-1 (7.8). Lastly, S-1 reported the highest concentration of gasoline range organics (GRO) and extractable petroleum hydrocarbons (EPH), and polycyclic aromatic hydrocarbons (PAHs) followed by S-2 and S-3. In addition, biological oxygen demand (BOD) was the highest in S-1 44,300 mg/L followed by S-2 and S-3 26,300 and 14,600 mg/L, respectively. Moreover, salinity was also the highest in S-3 at 260 ppt, followed by S-2 at 38.2 ppt and S-1 at 38.9. Overall, S-1 reported the highest concentration of GRO, EPH, and all PAHs followed by S-2 and S-3. Additionally, the PWWs consisted of high organic containing wastes. The results also revealed that all three PWWs were enriched with zinc and iron, and sixteen different hydrocarbon compounds were identified, amongst which acenaphthene, acenaphthylene, fluorene, anthracene, phenanthrene, benzo(a)anthracene, and pyrene were dominating in all three samples.

1. Introduction

The oil and gas sector is a huge complex industry that has three key stages; upstream, midstream, and downstream to generate valuable petroleum products [1]. The upstream process involves the exploring of natural gas fields or crude oil fields and the drilling of the wells to recover oil and gas. The midstream process includes the transporting, storage, and various processes of oil and gas. When oil and gas reserves are discovered or recovered, they should be transported to a refinery that may be in a different geographic region. Transportation includes all transporting activity from tanker ships to pipelines and trucking fleets. The downstream process refers to transforming raw materials including refining crude oil and natural gas into valuable petroleum products such as diesel oil, petrol, gasoline, asphalt, liquefied petroleum gas (LPG), heating oil, and others [2]. The downstream process can be considered as the major source of commercialization for a country. Consequently, due to the growth in population and worldwide economic development, a significant demand for petroleum products has also seen exponential growth. It is also expected that by 2035, the global energy demands will increase by 37% from the current level with a significant portion of the energy-dependent on petroleum products [3]. Oil and gas production processes consume and generate large quantities of water, which results in the production of significant amounts of petroleum wastewaters (PWWs) [4]. The use of water by the energy sector may vary depending on the type of fuel, the extraction method, the level of processing, and the climate of the location under development. On the other hand, limitations on water availability affect the selection of technology in the industry, site selection, and other phases of resource development. It has been estimated that amount of PWWs produced is around 0.4 to 1.6 times the crude oil produced [5]. It is noteworthy that although many processes of the oil and gas industry use water, not each process necessarily required raw or treated water. A certain amount of the used water within the oil and gas refinery can be cascaded and continually reused or recycled within the same plant, while a large amount requires management [6]. Hence, the petroleum sector faces significant challenges due to a lack of water resources and concerns about environmental pollution [7]. From the point of view of sustainable development in such an industry, the connection between water and petroleum energy generation is now widely established. To aid the petroleum sector development while also protecting the environment, well-developed

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water management and wastewater treatment technologies are critically required [8]. The industrial processes should be innovative, well balanced, and optimized to achieve efficient and sustainable water resources use and to eliminate the negative impact on the environment by the treatment system. Radelyuk et al. [8] described sustainable water use in the industry through three pillars and their interaction: social, economic, and environmental. Economic factors are the industrial processes that use efficient and cost-effective technologies to treat the process water and reuse it in a safe manner, while the environmental factors are related to the quality and quantity of used water and the wastewater disposal site. The interaction between economic and environmental factors allowed reducing the negative impact of oil industrial activities on water bodies and increasing the water viability for the consumer. The social factor is public health and safety, which are primarily regulated by the government [8]. The sources of PWWs are generated from the production activities such as vapor condensation, spent caustic, and process water. In addition, PWWs can be generated from a cooling tower, surface runoff, or spilled petroleum products [9]. These different types of PWWs can be combined or segregated during treatment practices based on the water management strategies [7]. These different sources of water can vary in their constituents and characteristics. PWWs generated by refineries are usually highly concentrated with hydrocarbons and other major constituents of petroleum. However, the amount and the quality of the different types of PWWs rely on the time, location, human activities, and governmental laws and regulations [10]. Consequently, the composition and the quantity of the hazardous pollutants in the PWWs can extensively vary based on the operation practices, the type and efficiency of the treatment and its processing equipment, and the operating regulation protocol employed for minimization of wastes [11]. Characterization of PWWs parameters is useful in determining wastewater management alternatives in the petroleum industry sector through designing the best collection and treatment practices, reuse options, and environmental management acts. Additionally, these data are beneficial to building up further investigations of industrial wastewater's impact on the environment and its contamination characteristics including pollutants of emerging concern and toxicity [5,12,13]. The refined oil features can be varied from one to geographic site. Several chemical, physical, and biological processes, collectively called weathering affect the physicochemical properties of the PWWs. Qatar is regarded amongst the top three countries to have the largest gas reserves in the world, and is described by its arid area and weather [6]. Since the 1990s, Qatar has undergone a drastic transformation into a natural gas-driven emerging economy as a result of carefully constructed plans created and implemented in close collaboration with potential natural gas suppliers, technology providers, and investors [4]. Qatar produced 75.354 million tons of oil equivalent (mtoe) of crude oil [14].

This paper presented the physiochemical properties of three PWWs, which were collected from oil and gas industry sites in Qatar and are denoted as S-1, S-2, and S-3. To point out the potentialities of facing the continuous increase of the discharge of PWWs by their recycling after treatment, the main objective of this study is (i) to identify the possible sources of the collected PWWs (ii) characterization of the collected PWWs, and (iii) to incorporate a brief case study for characterizing one of the PWWs in Qatar. This study briefly emphasizes the sources of various wastewater streams and highlights some of the main parameters that are present and used to evaluate the quality of the PWWs, which helps in determining treatment strategies and the viability of recycling or reusing the wastewaters.

2. Sources of wastewater streams in the oil and gas industry

Generally, oil and gas industry processes are highly dependent on water supply. However, the quantity of water required is dependent on various factors including the complexity of the operation, size of the plant, oil type, and the products and chemicals used for treatment. During the refining process, a large amount of wastewaters is produced which is commonly known as process water [15]. Since a large amount of water is required during the refinery process, thus a significantly high volume of wastewaters is generated which can reach up to 0.4–1.6 times the amount of crude oil process [16]. In addition, the process water comes into direct contact with hydrocarbons, causing pollution by certain hydro-soluble oil components. Thus, process water can be divided into several major groups. Table 1 summarizes some of the major groups of wastewater streams that are generated in a typical petroleum refinery.

From Table 1, it can be deduced that it is an obligation to identify the source or stream of the generated wastewater in the oil and gas industry to understand the types of hazardous pollutants that may be present, which can aid in designing the best treatment practices, reuse options, and environmental management acts [27]. For instance, sour water contains compounds and substances that damage the biological treatment units [28].

2.1. Petroleum wastewater quality and disposal standards

Petroleum effluents are composed of numerous amounts of hazardous compounds including organic pollutants and inorganic pollutants such as petroleum hydrocarbons and heavy metals [29]. The characteristics of PWWs depend on various factors including types of refined oil, the operation conditions, and the sources of the PWWs pollutants [30,31]. The PWWs parameters used to characterize the water quality are mainly total dissolved solids (TDS), total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total petroleum hydrocarbons (TPH), oil and grease (O&G), total organic carbon (TOC) and total metals and ions such as ammonia, nitrates, sulfides, and others [3,32]. Other scientists also consider other specific parameters such as cadmium, lead, and mercury as well as certain organics like cyanides, benzene, toluene, ethylbenzene, and xylene (BTEX), as well as inorganics such as phosphates, chlorides, and other micropollutants. In some cases, physical parameters of the PWWs are used as an indicator of the water quality such as pH (acids, alkalis), turbidity, color, and odor. Various environmental organizations such as the United States Environmental Protection Agency (USEPA) and the World Bank Group (WBG) have set regulatory limits for the disposal of treated petroleum effluents to surface water, marine water, and agricultural fields due to the high concentrations of different contaminants in PWWs and their potential toxicological implications [33,34].

2.1.1. pH

pH is one of the essential parameters, which directly affects the PWWs' treatability. It also has an influence on the mobility of pollutants such as heavy metals' leachability. The pH value of PWWs reveals the proteinaceous matter composition and ammonia compounds emission. The normal pH range to use wastewater for irrigation purposes is between 6.5 and 8.4. A small change in pH can lead to a change in the concentration of certain substances in the surrounding environment [35]. Król et al. [36] stated that the solubility of anions increases in alkaline waters while the solubility of cations increases in acidic waters. In addition, acidic effluents impact the dynamics of the bacterial community in the environment by lowering the bacterial diversity and causing a shift in their populations [37]. The pH level in PWWs from gas operations usually is more acidic (ranging between 3.5 and 5.5) than PWWs from oil field operations (ranging between 6 and 7) [18].

2.1.2. Total dissolved solids (TDS), electric conductivity (EC), and salinity

TDS represents all dissolved matter in PWWs including inorganic salts and organic matter. EC measures the ability of a liquid to conduct an electric charge, which depends on the concentration and strength of the dissolved ions. Hence, EC is correlated to TDS, and both are indicators of salinity level [38]. Salinity represents the salt in PWWs, which is an inorganic matter that is typical of the concept of TDS. Ahmad

Table 1
Different wastewater streams generated in the oil and gas industry.

Type of PWWs	Description	Type of contaminants present
Produced water	Produced water is the largest oilfield wastewater produced during the oil extraction process or deep well injection process [17].	The most common contaminants present in produced water are total soluble solids (TSS), chemical oxygen demand (COD), total organic carbon (TOC), hydrocarbons, and heavy metals [18].
Desalter effluent	A desalter in an oil refinery is usually the first process where the salt is removed from heated crude oil by washing with feed water and additive chemicals. The water generated from the washing step to desalt the crude oil is the desalter effluent [19].	The most common contaminants present in desalter water are TSS, COD, hydrocarbons, Ammonia, and sulfides. Their concentrations are varied depending on the type of feed water in the desalter unit.
Stripped sour water	Steam is utilized in various refinery operations as a stripping medium in distillation as well as a diluent in catalytic cracking and other processes to lower the hydrocarbon partial pressure. The steam condenses into an aqueous phase, which is then removed as sour water. Because this steam condenses in the presence of hydrocarbons containing hydrogen sulfide (H_2S) and ammonia (NH_3), these constituents are absorbed into the sour water at amounts that usually need treatment [21].	The most common contaminants present in sour water are COD, phenols, cyanide, sulfides, and ammonia. The composition of stripped sour water highly depends on the production source of sour water in the refinery [20].
Tank bottoms water	Water and sediments are commonly found in raw crude oil when it is collected up when oil is recovered from wells. This is referred to as bottom sediment and water. When oil is stored in huge tanks, the bottom sediment and water settle to the bottom and must be regularly removed to avoid accumulation and end up in a loss of storage capacity. Usually, these bottom tanks' sludge is transferred for separation or to the wastewater treatment units [22].	The common contaminants present in tank bottoms water are COD, hydrocarbons, TSS, and sulfides. High COD and organic contents are usually found in water as it is in direct contact with raw crude oil.
Spent caustic effluent	Spent caustic is produced when acidic components from hydrocarbon streams are extracted. These acidic compounds include residual H_2S, organic acids, phenol, cyanide, and CO_2 [23].	The common contaminants present in spent caustic are sulfides, phenols, cyanide, H_2S, and RSH (mercaptans). Depending on the manufacturing process, spent caustic effluents vary in their composition [23].
Condensate blowdown	Condensate can be lost in oil refineries from boiler systems, steam generators, or steam traps. A portion of the condensate is removed from the system to maintain the acceptable level of dissolved solids [24].	The volume of generated process condensate usually is the lowest among all types of wastewater streams in a refinery. The main component of this condensate is TDS, silica, and COD.
Cooling water blowdown	Cooling tower systems in PR are used to cool down the process water for reusing and absorbing the heat. To avoid an accumulation of dissolved solids in a cooling tower, a portion of the circulating water is rejected as blowdown [24].	The cooling tower effluents vary in their composition depending on the pretreatment of the cooling tower and the quality of feed water. However, the common contaminants present are TSS, TDS, BOD, COD, and chemical additives such as biocides, anti-scale, and corrosion inhibitors [7].
Ballast water	When a vessel is traveling empty to pick up oil or after unloading oil, ballast water is carried on board to preserve stability [25].	The most common contaminants present are COD, TDS, and TOC. It is noteworthy that the most common pollutants that can be occurred in ballast water are introducing invasive species through introducing invasive species to new habitats during traveling [26].

et al. [39] reported the typical TDS concentration in produced water between 1000–400,000 mg/L. Additionally, Al-Ghouti et al. [17] stated that the salinity of petroleum effluents range from a few part per thousand (ppt) to 300 ppt, which is much higher than the salinity of seawater. High TDS indicates hard water that leads to scaling and fouling in the treatment system, which consequently reduces the treatment *performance* and increases the overall maintenance costs [8].

2.1.3. Total suspended solids (TSS)

TSS refers to non-soluble or suspended solids in effluents such as sediments, sand, and biological matter [40]. The range of TSS in petroleum effluents largely varies based on the streams and pollutants present in the PWWs. Typically, the TSS concentrations in petroleum effluents range from 5 mg/L to 5800 mg/L [18].

2.1.4. Oil and grease (O&G)

The term O&G parameter in PWWs refers to a broad range of chemical compounds such as fats, wax, and oils from petrochemical sources. The concentration of dispersed O&G in PWWs is an important parameter to evaluate water quality and safety [41]. Releasing PWWs with a high concentration of O&G can highly impact the surrounding habitat and organisms by coating plants and animals and suffocating them through oxygen depletion [42]. Kusworo et al. [43] reported the range of dissolved O&G in petroleum wastewaters, to be between 500 mg/L to 3000 mg/L. Generally, the concentrations of O&G in petroleum effluent vary from 40 mg/L to as much as 9000 mg/L. The maximum limit of O&G in discharge wastewater is 5 mg/L [42].

2.1.5. Total organic carbon (TOC), biochemical oxygen demand (BOD), and chemical oxygen demand (COD)

The organic intensity of any petroleum effluent is generally measured in three ways, namely TOC, COD, and BOD. TOC in petroleum effluents represents the organic matter from petroleum hydrocarbons and biological sources [44]. It involves the dissolved and particulate organic carbon forms. Hence, high TSS can affect the reliability of TOC as it reduces the homogeneity of the WW [45]. COD represents the oxygen demand required to oxidize all the OM in the PWWs. COD involves the oxygen demand required for biodegradable and non-biodegradable substances. In other words, COD measures the amount of organic compound, which will be oxidized, and TOC measures the amount of carbon bound to organic substances [46]. Consequently, there is a directly proportional relation between TOC and COD. BOD represents the oxygen required for the biological decomposition of the organic matter in PWWs by microorganisms. The greater the organic contamination in the sample, the greater oxygen amount will be needed by the organisms, the lower PWWs quality, with the consideration of the biodegradability of the organic matter. BOD is an indirect measurement of the organic pollution in WW [47]. However, BOD does not represent all the OM present in the PWWs but only the biochemically degradable OM.

Therefore, COD values are larger than BOD. Dawoud et al. [18] reported that the typical concentration of TOC in produced water is 45 mg/L - 71 mg/L. However, according to studies reported by El-Naas et al. [48]; Janson et al. [49]; Lahlou et al. [50]. The concentration of COD in different petroleum effluents was 64 mg/L, 5300 mg/L, and 1572 mg/L respectively. Kusworo et al. [43] reported that the range of COD and BOD in petroleum wastewaters is 750–1600 mg/L and 300–1000 mg/L respectively. The value of BOD, COD, and TOC are vital in determining the efficient treatment technology as they are directly linked to biodegradation treatment by microbes. If the value of BOD, COD, and TOC are very low in wastewater, microbial degradation is not a suitable treatment as microbes will not be able to thrive with a low supply of carbon source impacting overall their performance in the treatment plant. On the other hand, too much organic matter can increase the microbial biomass leading to several treatment challenges reducing the effluent quality such as bio-clogging and bad odor [51].

2.1.6. Metals

Different studies reported the presence of various metals in petroleum effluents with different concentrations [52]. Metals such as lead (Pd), zinc (Zn), iron (Fe), manganese (Mn), and barium (Ba) are present in petroleum effluents at large concentrations. Other metals such as cadmium (Cd), nickel (Ni), copper (Cu), chromium (Cr), and mercury (Hg) are present in trace amounts in petroleum effluents [53]. The concentration of heavy metals in produced water from natural gas including Ba, Cd, Cu, Cr, Fe, Ni, Mn is 60.51 ppb, 0.05 ppb, 0.62 ppb, 30.31 ppb, 4144 ppb, 7.08 ppb, and 268.3 ppb, respectively [54]. The standard limits of some metals of water reuse for different applications are represented in Table 2 [55].

2.1.7. Total petroleum hydrocarbons (TPH) and BTEX

Total petroleum hydrocarbons refer to hydrocarbon amounts in PWWs mainly involving carbon and hydrogen. TPH consists of dissolved petroleum hydrocarbons form and suspended form. They are generally divided into three categories, namely saturated, unsaturated, and aromatics [56]. TPH is a combination of volatile and extractable petroleum hydrocarbons consisting of benzene, toluene, ethylbenzene, and xylenes (BTEX), which are volatile aromatic hydrocarbons, phenols, polycyclic aromatic hydrocarbons (PAHs), methyl tertiary butyl ether (MTBE), and naphthalic acids [57]. Phenols are expected to be founded at a high level in some petroleum streams such as spent caustic streams [58]. Phenol is harmful and produces other harmful byproducts during the chlorination of marine water [59]. Table 3 shows the characteristics of major petroleum hydrocarbon compounds present in petroleum effluents. Jain et al. [2] reported that desalter water contains benzene, phenol, and oil levels of approximately 1 mg/L - 100 mg/L, and 20 mg/L - 200 mg/L, respectively. Additionally, oil levels in desalter water and tank bottoms water are 100 mg/L - 300 mg/L and up to 5000 mg/L, respectively.

2.1.8. Total nitrogen (TN) and ammonium

Total nitrogen in PWWs includes both organic nitrogen (Kjeldahl nitrogen) and inorganic nitrogen. It represents all forms of nitrogen compounds including organically bound nitrogen, ammonia (NH_3–N), nitrates (NO_3–N), and nitrites ((NO_2–N) in PWWs [71]. Kjeldahl nitrogen is the total amount of organic nitrogen and ammonia-nitrogen (NH_3–N) in the wastewater. Ammonium is the most common nitrogen substance available in petroleum effluents [72]. Alzarooni & Elshorbagy

Table 2
Standard limits of metals for water reuse for different applications [55].

Metals / Application	Fe (mg/L)	Cu (mg/L)	Cr (mg/L)	Zn (mg/L)
Agricultural reuse	≤5	≤0.2	≤0.1	≤2
Restricted urban reuse	N.A.	N.A.	N.A.	N.A.
Industrial application	≤0.02–0.05	≤0.01	N.A.	N.A.

Table 3
Characteristic of major petroleum hydrocarbon compounds present in petroleum effluents.

PWWs parameters	Concentration in various Petroleum effluents	Characteristics	Environmental impact	Maximum concentration level
PAHs	• Total PAHs in tank bottoms is 1265.75 mg/L [22]. • Naphthalene concentration in condensate flare in a petroleum refinery is 70 ppm [60]. • Naphthalene, Acenapthylene, and Fluorene concentration in caustic spent is 20 mg/l, 11.8 mg/L and 0.39 mg/l respectively [60].	Hydrophobic, colorless, high melting and boiling points. Common PAHs in petroleum effluents are naphthalene, anthracene, Phenanthrene, fluorine, pyrene, and benzo(e)pyrene [61].	Genotoxic, cariogenic, and mutagenic [62].	The maximum level for PAHs in drinking water is 0.2 ppb by USEPA [61].
BTEX	• Al-Kaabi et al. [63] reported the concentration of benzene, toluene, ethylbenzene, and xylene in produced water is 11.17 mg/L, 0.27 mg/L, 4.64 mg/L, and 1.157 mg/L respectively. • Ishak & Malakahmad [64]. reported the concentration of benzene, toluene, ethylbenzene, and xylene in petroleum wastewater is 33.85 mg/L, 39.83 mg/L, 1.85 mg/L, and 31.54 mg/L, respectively.	Volatile organic compounds have different flashpoints, different water solubility, and different odors. Ethylbenzene is a highly flammable liquid [65].	Benzene considers a carcinogenic compound. Other BTEX compounds have negative effects on the blood system, nervous system, and respiratory and kidney system [66]	The drinking water standards for benzene, toluene, ethylbenzene, and xylene (BTEX) are 0.005 g/m^3, 1 g/m^3, 0.7 g/m^3, and 10 g/m^3 [67,68].
Phenolic compounds	• Alzarooni & Elshorbagy [60], mentioned the phenol concentration in spent caustic is 21.7 ppm • Dawoud et al. [18] reported the phenol concentration in produced water from Qatar is 1.96.	Volatile, present in liquid or crystal. Common phenol compounds are phenol, 1-naphthol, and 2- methyl phenol [69]	Carcinogenic, ecotoxic, and phytotoxic [69]	USEPA limits the total phenol in industrial water discharge to 1 ppm [67,70].

[60]. mentioned that ammonium results in petroleum wastewater streams from two processes including NH_3 injection to neutralize H_2S and to hydrogenate the organic nitrogen when the crude is processed. The standard of TN for effluent discharge is 5 mg/L. High levels of TN are present in certain petroleum wastewater streams such as crude oil tank discharge and desalter water. The typical range of total nitrogen in produced water is 23 mg/L - 26 mg/L [18].

2.1.9. Sulfate

Sulfur is present in PWWs in various forms. Due to the presence of H_2S, mercaptans (RSH), and disulfide in crude oil, sulfur compounds are commonly present in almost all types of petroleum wastewater streams. Most of the sulfur compounds are removed during the refinery process to avoid corrosion in vessels and to prevent catalyst poisoning [73]. The end-products do contain sulfur which should meet the acceptable standard limits set by the environmental regulations which are 0.5 mg/L for sulfides as per the U.S. Environmental Protection Agency (USEPA) [74]. The typical range of sulfate radicals in produced water is 61 mg/L - 68 mg/L [18]. According to studies reported by Minier-Matar et al. [75] and Zhao et al. [76], the estimated sulfate concentration in produced and processed water is 349 mg/L and 347 mg/L respectively. Table 4 summarizes the characteristics of petroleum wastewater as reported by studies for various countries. In addition, it also mentions the environmental standards for their discharge as per the US-EPA.

Al-Kaabi et al. [53] and Janson et al. [49] reported acidic petroleum effluents with pH values of 4.43 and 4.3, respectively. The highest COD and TOC values were 10,497 mg/L and 2405 mg/L, respectively reported by Al-Kaabi et al. [54], while the highest TDS and SO_4 values were 10,465 mg/L and 336 mg/L, respectively reported by Lahlou et al. [50]. Furthermore, the highest phenol concentration reported was 185 mg/L by El-Naas et al. [48]. Different quality standards are reported for water reuse for different applications such as irrigation, urban reuse, and industrial reuse. Most of the pollutants present in industrial wastewaters are to be evaluated ecotoxicologically because of their physiochemical characteristics [44]. Some of these pollutants are classified as highly toxic persistent organic pollutants due to their chemical stability and resistance to oxidation and reduction in nature [62]. Living organisms, especially Humans are exposed to these pollutants by different routes such as skin contact, inhalation, or ingestion [77].

3. Materials and methods

3.1. PWWs sampling

Three PWWs were collected from a local petroleum refinery in Qatar. The PWWs were processed wastewater and named S-1, S-2, and S-3. The samples were regularly collected every alternate week for one month to have a homogenous and sufficient amount.

3.2. Chemical characterization

Various physical and chemical properties were investigated using a pH meter (HACH HQ 40d) by following the ASTM D4456-17 method. This method determined the samples' pH, conductivity, total organic carbon (TOC), total dissolved solids (TDS), total suspended solids (TSS), oil and grease content, chloride, and sulfate content. Additionally, the hydrocarbon was analyzed using gas chromatograph-mass spectrometry (GS-MS) (Agilent 7890B/5977B) by following USEPA 8015C method to determine benzene, toluene, ethylbenzene, and xylene concentrations while USEPA 5030C/8260C while the USEPA 3005A/6010C was performed to determine the total petroleum hydrocarbons and the USEPA 3510C/827 for polycyclic aromatic hydrocarbons (PAH). Heavy metals were analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES) (PerkinElmer Optima 3000V, or Shimadzu ICPS-7510 Sequential Plasma Spectrometer, Japan).

4. Results and discussion

4.1. Physiochemical analysis

The treatment option of the wastewater is dependent on the wastewater characteristics. Hence, the characterization of petroleum effluents is beneficial, as it will aid in determining the wastewater management strategies in petroleum refineries by planning the best collection and treatment practices and exploring the possibility of reusing wastewater. Moreover, the characterization data can highlight the environmental impact of these industrial wastewaters and focus on pollutants of emerging concern and toxicity. A full physiochemical analysis of the samples was performed, including pH, electric conductivity (EC), total saturated solid (TSS), total dissolved solids (TDS), oil and grease (O&G), salinity, chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC), total inorganic carbon (TIOC), hydrocarbons including [gasoline range organics (GRO) (<C5–C10), C10–C40], benzene, toluene, ethylbenzene and xylenes (BTEX), polyaromatic hydrocarbons (PAHs), and metals. The results are shown in Table 5, for the three different sites, namely sample 1 (S-1), sample 2 (S-2), and sample 3 (S-3) for pH, EC, TSS, TDS, O&G, Salinity, COD, BOD, TOC, and TIOC. Additionally, hydrocarbons contents in the three samples are presented in Table 6. It is apparent that the three samples varied in terms of their characteristics. For instance, S-1 reported the highest organic content. O&G was reported to be 9950 mg/L in S-1, followed by 1580 mg/L in S-2 and 623 mg/L in S-3. Additionally, the COD was

Table 4
Environmental standards for effluent discharge as per the US EPA and characteristics of different petroleum refinery effluents as reported in the literature of various countries.

Environmental standard for effluent discharge as per the USA EPA (mg/L)											
pH	COD	BOD	TOC	O&G	TSS	TDS	$N–NH_4$	Sulfides	Phenol	Reference	
6–8.5	125	15	N/R	5	20	N/R	40	0.5	0.35	[31,78–80]	
Studies											
pH	**COD mg/L**	**BOD**	**TOC**	**O&G**	**TSS**	**TDS**	**$N–NH_4$**	**SO_4**	**Phenol**	**Country**	**Ref**
8.6	3134	N.R.	N.R.	N.R.	N.R.	1503	N.R.	N.R.	855	Indonesia	[50]
4.43	10,497	1034	2405	N.R.	21.33	N.R.	N.R.	46.13	1.96	Qatar	[54]
N.R.	64	8.2	N.R.	N.R.	30	10,465	N.R.	336	N.R.	Qatar	[50]
9.2	8100	4047	N.R.	0.29	19.5	4761	N.R.	238.09	238.09	India	[5]
8.57	6444.93	1310	N.R.	N.R.	42	N.R.	N.R.	N.R.	34.95	Tunisia	[81]
7.5–8.5	3500–5300	N.R.	N.R.	N.R.	0.08	10	N.R.	14.5–16	160–185	Qatar	[48]
9	1800	620	N.R.	N.R.	420	2200	N.R.	N.R.	N.R.	Pakistan	[82]
4.3	1572	N.R.	491	47	N.R.	5189	11	54	N.R.	Qatar	[49]
7–9	300–600	150–350	N.R.	<50	<150	N.R.	10–30	N.R.	N.R.	China	[83]
N.R.	68–220	0.2–1.2	10.4–31.3	1.1–3.5	N.R.	N.R.	0.21–21.23	N.R.	0.85–3.75	KSA	[84]

Table 5
Various parameters of the three different petroleum process wastewaters.

Parameter	S-1	S-2	S-3
pH	7.8	8.5	8.3
Electric conductivity (EC) @ 25 °C (μS/cm)	58,200	143,000	227,000
Total suspended solid (TSS) (mg/L)	2010	940	2470
Total dissolved solid (TDS) (mg/L)	41,600	113,000	188,000
Oil and grease (O&G) (mg/L)	9950	1580	623
Salinity (ppt)	38.9	112	260
Chemical oxygen demand (COD) (mg/L)	74,800	46,000	26,700
Biological oxygen demand (BOD) (mg/L)	44,300	26,300	14,600
Total organic carbon (TOC) (mg/L)	5490	4730	3300
Total inorganic carbon (TIOC) (mg/L)	<0.3	<0.3	<0.3

Table 6
Hydrocarbon content in the three different PWWs.

Parameter		S-1	S-2	S-3
GRO (<C5–C10) mg/L		1.51	0.50	0.25
EPH(C10–C40) mg/L		7940	1470	934
BTEX (μg/L)	Benzene	<100	<100	<100
	Ethyl benzene	<100	<100	<100
	m-Xylene and p-Xylene	<200	<200	<200
	o-Xylene	<100	<100	<100
	Toluene	<100	<100	<100

almost double in S-1 (72,800 mg/L) while S-2 contained 46,000 mg/L, and the least was found in S-3 at 26,700 mg/L. The BOD was 44,300 mg/L in S-1 and 14,600 mg/L in S-3. Surprisingly, TOC content did not have a huge difference among the three samples; S-1 contains 5490 mg/L while S-2 and S-3 contain 4730 mg/L and 3300 mg/L, respectively. The reason for such differences in the concentrations could be the high hydrocarbons content present in S-1. Additionally, the results confirmed that S-1 had the lowest water quality with the highest BOD, COD, and TOC followed by the S- 2 and S-3. Remarkably, the COD and BOD values in all three samples investigated in this study are much higher than those from various countries, as reported in Table 4. For instance, Al-Kaabi et al. [54] reported the COD and BOD of 10,497 mg/L and 1034 mg/L, respectively for produced water. In Indonesia, the COD of 3134 mg/L was reported for petrochemical refinery wastewater. Here, it can be seen from Table 5 that the pH of the used PWWs in this study was alkaline and ranged between 7.8 and 8.5 (S-1 was 7.8, S-2 was 8.5 and, S-3 was 8.3). This can probably be due to various reasons including the nitrification process that is carried out to convert ammonia to nitrate in the wastewaters and the activity of the microorganism [81]. The TIOC in the three samples is undetectable which is not surprising since TIOC is usually traced in PWWs. Moreover, salinity was reported to vary amongst the three samples. S-1 shows the lowest salinity (38.9 ppt), while S-2 and S-3 are characterized by elevated salinity of 112 ppt and 260 ppt, respectively. Similarly, high EC and TDS were found in samples 2 and 3, which are correlated with salinity levels in both samples. It has been stated in different studies that the salinity of petroleum effluents ranges from a few part per thousand (ppt) to 300 ppt [17]. Elevated salinity negatively impacts the wastewater treatment process, which means additional treatment is required to reduce the salt concentration [85]. One of the primary reasons for the differences in the characteristic of wastewater could be the different types of wastewaters. For instance, this study investigated the PWWs while Al-Kaabi et al. [54], investigated produced water, and Kusworo et al. [43] investigated petroleum refineries wastewaters. According to Dawoud et al. [18], the characteristics of several processes and produced waters are to determine the proper treatment methods and viability to reuse water for irrigation or direct disposal without harming the surrounding environment. Singh & Kumar. [86], characterized pretreated petroleum refinery wastewater and found the pH of wastewater was 9.2, while the O&G was low at 0.29 mg/L, the COD reported was 8100 mg/L and TDS was 4761 mg/L. On the other Khatoon & Malik. [87], studied petroleum refinery wastewater that was combined with domestic sewage and reported the pH of the wastewater to be 7.82 similar to S-1, while the EC was 3460 μS/cm, salinity was 2.01 PSU, and TDS and COD as 1910 ± 54.5 and 310 ± 32.1, respectively.

4.2. Hydrocarbon analysis

Wastewaters generated from the oil and gas industry usually have a high content of aromatic and aliphatic petroleum hydrocarbons as well as other harmful compounds. These contaminated wastewaters need proper treatment and management strategies before disposing or being treated for re-use. In case of an accidental oil spill, these compounds accumulate and find their way to terrestrial and aquatic life. Over time, these compounds can pose a negative impact on the living and nonliving biota. These compounds are hydrophobic and thus persist in the environment for long periods. Thus, it is important to identify such compounds prior to any treatment. Likewise, the three PWWs samples were also analyzed for the hydrocarbons content including gasoline range organics (GRO) and extractable petroleum hydrocarbons (EPH), benzene, toluene, ethylbenzene, and xylenes (BTEX), and polycyclic aromatic hydrocarbons (PAHs). From Table 6 and Fig. 1, it can be seen that S-1 shows the highest concentration of GRO, EPH, and all PAHs followed by S-2 and S-3. In general, the BTEX compounds are less than 100 mg/L in all three samples. This is because BTEX compounds are volatile and unstable in nature. These results are in line with the data obtained for COD, TOC, and BOD (Table 5). A total of sixteen compounds were detected in all three influents as illustrated in Fig. 1. The effluent was found to contain mainly acenaphthene, acenaphthylene, fluorene, anthracene, phenanthrene, benzo(a)anthracene, and pyrene.

4.3. Heavy metal analysis of the collected samples

It is also essential to determine the presence of heavy metals as they are highly toxic and non-destructible. As these metals bioaccumulate and over time biomagnify in the food chain [88]. Which consequently affects the aquatic ecosystem directly or indirectly. Therefore, this study also analyzed the heavy metal composition in all three samples and the results are shown in Table 7. It can be seen that seven heavy metals were detected in the three-water effluents. It was found that all three effluents were rich in zinc and iron. Furthermore, S-3 had the highest concentration of copper, while nickel was only found in S-2. Cadmium, mercury, and lead were present in traces. Depending on contact time, toxicity level, and concentration, the presence of a high concentration of heavy metals gives rise to a detrimental impact on the environment and human lives. Wokoma & Edori [89] studied heavy metal concentration in oily wastewater discharged from an oil plant in Nigeria and concluded that Zn concentration varied between 0.206 and 0.330 mg/L, while Fe and Pb concentration was 0.231–0.275 mg/L and 0.018–0.135 mg/L. The finding of this study was in line with Al-Kaabi et al. [63] also reported similar results and found that the metals Zn, Cd, Cu, and Ni had the highest concentrations, 4.98 mg/L, 0.050 mg/L, 0.62 mg/L, and 7.080 mg/L, respectively. Khatoon & Malik [87]. and Rasheed & Saleh [90]. also reported high metal concentration in wastewater from a petroleum refinery.

5. Importance of wastewater characterization

Characterization of wastewater from the oil and gas industry is very important in planning the wastewater management alternatives through designing the best collection and treatment practices, reuse options, and environmental management acts. Additionally, these data are beneficial to building up further investigations of industrial wastewater's impact on the environment and its contamination characteristics including pollutants of emerging concern and toxicity. Different treatment approaches have been introduced and explored. Each treatment technology has its pros and cons, which may differ based on the characterization

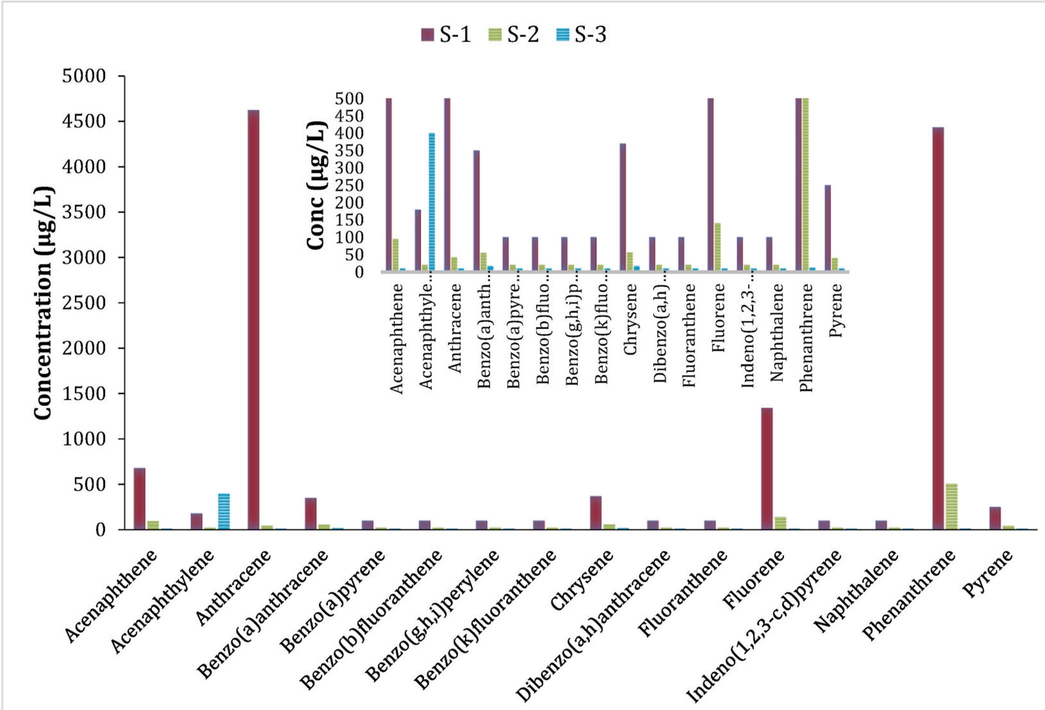

Fig. 1. PAH content in the three different PWWs.

Table 7
Heavy metals concentrations in the three different PWWs.

Metals (mg/L)	S-1	S-2	S-3
Zinc (Zn)	6.93	4.08	3.02
Cadmium (Cd)	<0.0001	<0.0001	<0.0001
Mercury (Hg)	<0.0001	<0.0001	<0.0001
Lead (Pb)	<0.0001	<0.0001	<0.0001
Iron (Fe)	17.0	8.57	11.0
Nickel (Ni)	<0.0001	0.176	<0.0001
Copper (Cu)	0.0527	0.0287	0.135

of wastewater. To plan an efficient treatment system, a full analysis should be provided including the properties and concentration of pollutants in wastewater, site description, and the proposed treatment plan. Hence, many recent research works are aiming at planning comprehensive strategies for wastewater management and treatment with focusing on their recycling and reusing options to reduce the consumed/generated wastewater. However, it is very obvious that this is a significant challenge for many oil and gas companies, especially in a country like Qatar due to the characteristics of the region, the oil production rate, the physicochemical properties and amount of wastewater, and the limited sources of natural water. Indeed, it is essential to characterize the composition of the local oil and gas industry effluents to offer an efficient, appropriate, and sustainable treatment process.

6. Conclusion

The current study revealed that the PWWs characteristic could vary on various parameters including the collected site, the operation conditions, the type of refined oil, and sources of generated wastewater. This is also evident in the case study that was carried out in this study. According to the findings, the BOD was highest in S-1 44,300 mg/L followed by S-2 and S-3 26,300 and 14,600 mg/L respectively. Moreover, salinity was also highest in S-3 at 260 ppt, followed by S-2 at 38.2 ppt and S-1 at 38.9. In addition, S-2 had higher pH (8.5) followed by S-3 (8.3) and S-1 (7.8). Lastly, S-1 reported the highest concentration of GRO, EPH, and all PAHs followed by S-2 and S-3.

The presence of harmful organic and inorganic pollutants in petroleum wastewater is attracting the interest of many scientists to find an effective treatment technology to treat these effluents. Hence, the characterization of wastewater is very critical before implementing or designing any treatment. For a country that is regarded as one of the most water-stressed countries with limited freshwater resources, it is essential for Qatar to strategically adopt PWWs treatment for the petroleum effluents in a way that the water can be reused and recycled. The study also revealed that Qatar wastewater from the oil and gas industry is characterized by very high concentrations of COD, BOD, TDS, and TSS. These results highlight the significance of designing effective, suitable, and sustainable treatment plans to implement the country's laws regarding the regulation of releasing or reusing, or recycling treated wastewater.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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