



Optical particle size distribution and petroleum hydrocarbon analysis of offshore produced water from the Bohai Sea

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ABSTRACT

A comprehensive estimation of the contributions of particle size distribution and chemical composition of produced water (PW) samples collected from an offshore wastewater treatment plant to chemical oxygen demand (COD) is provided. The particle size distribution in the wastewater was investigated, and the COD contributed by each part estimated. The results showed that the COD distribution of the raw PW was 59.6% for the molecular weight cut-off of <1 kDa, indicating that the majority of COD originates from soluble carbonyl compounds of low molecular weight. The linear correlation coefficient R^2 between COD and UV_{254} reached 0.96 in the COD range of 24–226 mg/L, which was higher than that between COD and UV_{205} . The soluble parts of PW have three average fluorescence lifetimes, of 1.2, 5.6 and 17.1 ns, with respective contributions of 21.0%, 44.1% and 34.9%. Petroleum hydrocarbons, including 164 aromatics (i.e., naphthalenes, phenanthrenes, thiophenes, biphenyls, furans, chrysenes, pyrenes, fluorenes, triaromatic steroids, anthracenes) and 17 alkanes, were identified in the PW and quantified by gas chromatography–mass spectrometry analysis.

Keywords: Produced water; COD composition; Particle size distribution; Fluorescence analysis; GC–MS

1. Introduction

Produced water (PW) is a by-product of oil and gas exploitation, and represents the largest waste stream generated by the oil industry. This water is trapped together with oil under the earth's surface and extracted from crude oil above ground by an oil/water separator. Following separation, PW is treated for reuse or discharged to the surface [1]. As the oil well ages, large volumes of water are injected into the reservoir to maintain pressure and enhance the efficiency of oil recovery by polymer injection at offshore oil fields [2–4]. In some instances, the water content is greater than 90% [5,6].

The decision for reuse of PW usually depends on its quality following treatment. The physical and chemical properties of PW vary considerably depending on local field variables, the geological formation from which it comes, and the type of hydrocarbon product being produced [7]. As

a result of the serious environmental impacts of PW, many countries, including China, have implemented very stringent regulatory standards for PW discharges, and therefore there is a need for the oil and gas industry to develop environmental and economic technologies for PW treatment. As the composition and optical characteristics of offshore PW change according to its origin, without fundamental knowledge of these variations, development of regulations and guidelines for treatment and safe discharge will not be possible [8,9].

PW must be analyzed from a micro-perspective rather than the more common macro-perspective, based on chemical oxygen demand (COD), total organic carbon, biochemical oxygen demand, etc [10]. The particle size distribution, that is, the molecular weight distribution, of pollutants in PW helps evaluation of appropriate treatment technologies and optimization of the performance of PW treatment systems by providing information on the physical characteristics of pollutants in PW [11–14]. Previous studies have focused on analysis of the COD,

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toxicity and environmental impacts of PW [5,8,10,15–17]. Some studies have attempted to assess the influence of specific classes of chemicals on COD in PW [18]; however, most results have been described qualitatively [19–21]. Few investigations are available regarding the chemicals that contribute to COD in PW [22], although recent studies have utilized particle size distribution analysis as an alternative method for assessing different COD fractions [13,14,23–27]. The analysis involved a sequence of different-sized filtrations and ultrafiltrations, ranging from 2 to 1,600 nm [28].

In addition, there is limited knowledge on the specific chemical composition and fate of organic matter in PW at various stages of the treatment process [8]. It is necessary to understand the main components of PW to take full advantage of treatment technologies [29,30]. Organic compound classes identified in PW include polycyclic aromatic hydrocarbons (PAHs); benzene, toluene, ethylbenzene and xylenes (BTEX), phenols, biphenyls and aromatic amines [31,32]. Concentrations of individual organic compounds in PW samples are low, ranging from 18 µg/L to 100 s of ng/L [22,32], and PAHs were the group most commonly observed in PW, with concentrations of individual PAH compounds varying greatly due to the different solubilities of the compounds in aqueous solution [8,33]. However, there are many more compounds in PW that have not yet been identified, and more investigative work is needed.

The overall objective of the present work was to characterize the chemicals contributing to COD in a PW treatment system in the Bohai Sea. The results could allow comprehensive estimation of the chemical components contributing to COD and optical absorbance. The emission spectral characteristics of the soluble components were measured based on both stationary and time-correlated fluorescence analysis, and petroleum hydrocarbon distributions in PW samples were also obtained.

2. Materials and methods

2.1. Sample information

The wastewater samples were collected from an offshore PW treatment plant located in SZ 36-1 Oilfield in Bohai Bay (Tianjin Branch Company of China National Offshore Oil Corporation [CNOOC], East China), in May 2016. The characteristics of the PW samples, including the COD, pH, oil and suspended solids (SS) contents, color, total nitrogen (TN), total phosphorus (TP) and ammonium nitrogen (NH₃-N) content are listed in Table 1. COD was determined using a closed reflux titrimetric method based on the standard method using a Hach DR3000 spectrophotometer (Loveland, CO, USA) [34]; the analysis results for the other parameters are listed in Table 1, with the analysis being conducted according to Environmental Protection Agency (EPA) Standard Analytical Methods [35].

2.2. Sequential filtration for molecular weight analysis

Knowledge about the distribution of molecular sizes is very important for understanding the basic chemistry

of organic compounds of different molecular weights in PW and their degradation during treatment progress. The molecular size distribution of the PW was determined by sequential ultrafiltration for improved physical segregation. Specifically, the experiment was carried out on PW using gradient membrane separation via an ultrafiltration apparatus [36,37] (Fig. 1); all ultrafiltration experiments were conducted under positive pressure (0.6–1.8 atm with N₂ as the inert gas) in a continuously stirred cell with a volumetric capacity of 400 mL using an SCM-type ultrafilter (Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai, China). Briefly, PW samples were initially filtered using a 0.45 µm cellulose ester membrane, and then gradient-separated by polyether sulfone membranes with nominal molecular weight cut-offs (MWCOs) of 50, 10, 5 and 1 kDa. Each PW fraction was analyzed for its COD and UV₂₅₄ value.

Table 1
Characteristics of the produced water samples used in the present work

Parameter	Value
COD (mg/L)	226
pH	7.05
Oil (mg/L)	12.2
Salinity (mg/L)	9,374
Cl ⁻¹ (mg/L)	5,436.3
SS (mg/L)	27.6
Color (Pt-Co unit)	16
Conductivity (µs/cm)	16.8
TN (mg/L)	43.7
TP (mg/L)	0.06
NH ₃ -N (mg/L)	33.6

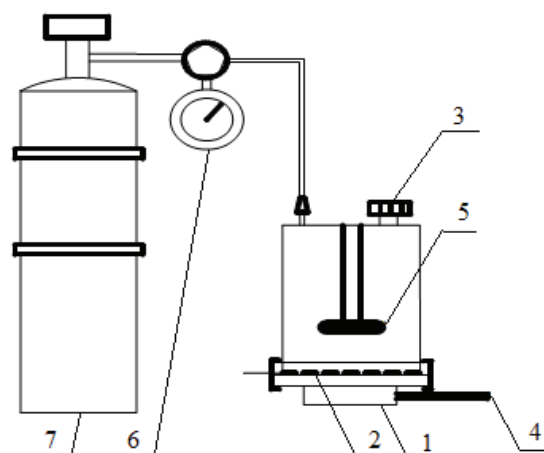


Fig. 1. Schematic diagram of the SCM-type ultrafilter used in the study (1, Ultrafilter cup; 2, membrane; 3, feed inlet; 4, outlet; 5, stirrer; 6, pressure gauge; 7, nitrogen tank).

2.3. Analysis methods

2.3.1. Absorption spectra of produced water

The absorption spectra of PW were recorded on an ultraviolet–visible (UV-vis) spectrometer (TU1810-PU; Shimadzu, Tokyo, Japan) at $20^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$. The optical length was 1 cm.

2.3.2. Steady and time-correlated fluorescence study of produced water

Steady-state fluorescence spectra were recorded on a Hatch F4500 fluorimeter (Hitachi, Tokyo, Japan) at $20^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$. Samples for fluorescence measurements were placed in $1\text{ cm} \times 1\text{ cm}$ quartz cells. All samples were excited at 250 nm and the fluorescence spectra were recorded at between 290 and 500 nm for PW samples. The bandpass for the excitation and emission monochromator was ca. 2 nm.

Time-resolved fluorescence measurements were performed with a FluoTime 200 (PicoQuant GmbH, Berlin, Germany) time-correlated single-photon counter at a constant temperature ($20^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$). The experiments were performed using a picosecond light emitting diode (PLS-280; PicoQuant) as the excitation source. The excitation and emission wavelengths were 280 and 375 nm, respectively. The maximum intensity for all samples was 5,000 counts. The instrument response function was recorded using Ludox solution by scattering the light at 280 nm.

The fluorescence decays were fitted to Eq. (1) using PicoQuant software (Fluofit; PicoQuant) so that the lifetimes (τ_i) and pre-exponential factors (A_i) could be determined. The χ^2 statistic and visual inspection of the residuals were used to determine how well the calculated decay fitted the experimental data. Fits were considered acceptable when the χ^2 value was between 0.9 and 1.1. A monoexponential function was first applied to fit the experimental data. If the residuals were not random, two or more exponentials were used until an acceptable fit was obtained.

$$I(t) = I_0 \sum_{i=1}^n A_i e^{-t/\tau_i} \quad (1)$$

2.3.3. Gas chromatography–mass spectrometry analysis

A 440 mL PW sample was initially extracted with 30 mL of CH_2Cl_2 (HPLC grade) under neutral conditions using a separating funnel. Each extraction was done five times. The combined extract (about 150 mL) was dehydrated and concentrated at 40°C by rotary evaporation. Residues of 5.0 mg were weighed accurately into a standard chromatographic bottle, and then 1 mL chromatographic grade isoctane was added together with external recovery standards of anthracene- d_{10} (0.124 mg/L) and α -androstane (0.110 mg/L). Hydrocarbons in the resulting samples were identified and quantified by gas chromatography–mass spectrometry (GC–MS, 5975C; Agilent, Palo Alto, CA, USA). Specifically, HP-5MS (30 m \times 0.25 mm \times 0.25 μm ; Agilent) and UIHP-5MS columns (60 m \times 0.25 mm \times 0.25 μm ; Agilent) in series were used for separation. Helium was the carrier gas (flow rate of 34 mL/min) and the diversion ratio was 15:1. The GC injection port temperature was 250°C . The column temperature

was fixed at 50°C for 1 min, ramped from 50°C to 100°C at $20^{\circ}\text{C}/\text{min}$, and then from 100°C to 315°C at $3^{\circ}\text{C}/\text{min}$, before being held for 28.5 min. The mass spectrometer conditions were as follows: ionization mode, electron impact ionization; electron energy, 70 eV; interface temperature, 280°C ; solvent delay, 3 min; ion source temperature, 230°C ; quadrupole temperature, 150°C ; and mass scan range: 50–550 AMU.

3. Results and discussion

3.1. Particle size distributions of produced water

The COD and UV absorbance at 254 nm (UV_{254}) were calculated to describe the distribution of different molecular weight components in PW. Fig. 2 shows changes in the corresponding COD fractions and UV_{254} for PW samples via sequential filtration. The COD distribution of the raw PW was 21.0% for MWCs $> 0.45\ \mu\text{m}$, indicating that particulate COD contributed relatively little to the total COD. The COD proportion was 5.2% for components between 50 kDa and $0.45\ \mu\text{m}$, while intermediate components between 10 and 50 kDa had the smallest proportion of COD (approximately 0.9%). Subsequent components with MWCs between 5 and 10 kDa, and between 1 and 5 kDa, contributed 2.4% and 10.9% of the total COD, respectively. The remaining components with MWCs smaller than 1 kDa contributed 59.6% of the total COD, indicating that soluble components with molecular weights of less than 1,000

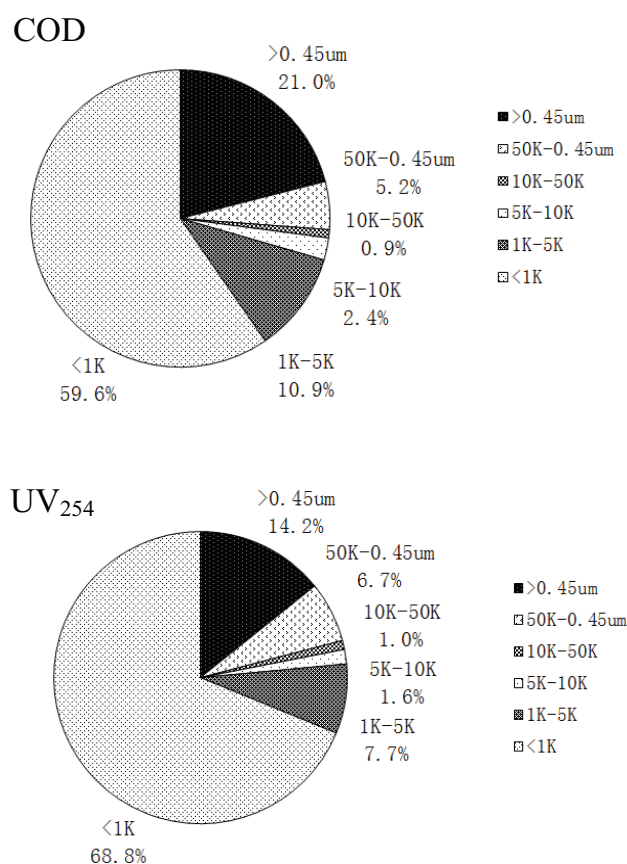


Fig. 2. Distribution of the chemical oxygen demand (COD) and UV_{254} of the produced water fractions based on molecular weight (MW).

made a larger contribution to the COD than other components; most of these were colloids, polymers and soluble small molecular components [38]. Similar results for MWCO distribution in mature PW have been reported by others [39,40].

UV₂₅₄ refers to the UV absorbance at a wavelength of 254 nm, which is associated with reflection of aromatic hydrocarbons in water; specifically, higher values indicate a higher concentration of aromatic hydrocarbons. As expected, the correlation between particle size distribution and UV₂₅₄ was analogous to the relationship between particle size distribution and COD. According to the relative molecular mass distribution of pollutants, the UV₂₅₄ distribution of the raw PW was 68.8% for the MWCO < 1 kDa. In contrast, the UV₂₅₄ proportion for MWCOs between 1 and 50 kDa was only 10.3%. Particles with >0.45 μm in size, and components with relatively larger MWCOs (between 50 kDa and 0.45 μm) contributed 20.9% of the total UV₂₅₄.

These results indicate that the soluble phase, particularly with a small molecular weight, is the dominant component of PW. Flocculation processes are commonly used in engineering; however, such processes do not adequately treat components under the MWCOs of 1 kDa and, more recently, advanced oxidation technologies have been used for further treatment of such components in PW [7].

3.2. Correlation of ultraviolet absorption characteristics and COD

The organics in PW contain aromatic ring structures or conjugated double bond structures that can absorb UV light; the UV absorption bands of benzene derivatives and major oil components are close to 254, 225 and 205 nm [41,42]. Research shows that use of COD as a single indicator cannot accurately reflect the true organic matter concentration in water, and that the characteristic UV absorption value reflects the concentration of PAHs in water, which is not reflected by COD [43]. In this study, the trends of UV₂₅₄, UV₂₂₅, UV₂₀₅ and COD were consistent. The correlations among the test parameters were analyzed and the results are shown in Fig. 3.

The linear correlation coefficients of COD in the range 24–226 mg/L and UV₂₅₄, UV₂₂₅ and UV₂₀₅ were 0.960, 0.918 and 0.915, respectively. These results show that the correlations between UV₂₅₄ and COD and UV₂₂₅ and COD are stronger than that of UV₂₀₅ and COD, and the correlation between the UV absorption of extracted CCl₄ (extraction ratio, 1:1) at a peak of 266 nm and COD was not stronger than that between the UV absorption of raw PW and COD. This indicates that the extraction process may subject to errors when the COD of raw PW is low. UV₂₅₄ as an organic control indicator in water treatment, warrants further study. UV₂₅₄ and COD had a good linear correlation for the same water sample, and UV₂₅₄ analysis is simple and cheap compared with determination of COD. In addition, UV₂₅₄ analysis creates no secondary pollution and may be considered as an indirect index of PW pollution.

3.3. Fluorescence spectra of the soluble phase of PW

As shown in Fig. 4, there was a broad emission peak from 300 to 480 nm with a maximum of around 370 nm in the influent water samples. PW contains many PAHs, and PAHs such as anthracene, pyrene, benz[*a*]anthracene and dibenz[*a,h*]

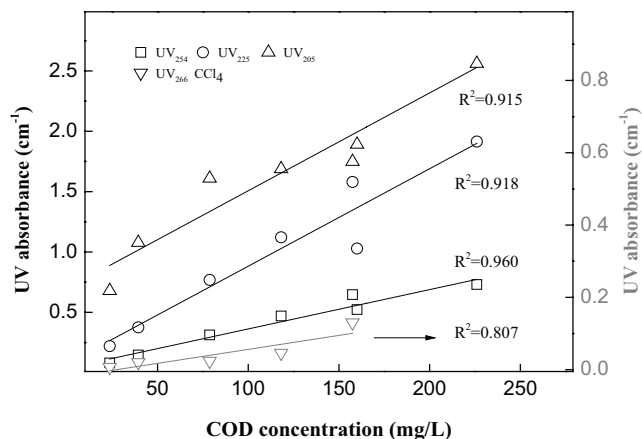


Fig. 3. Relationship between the ultraviolet (UV) absorption values and chemical oxygen demand (COD).

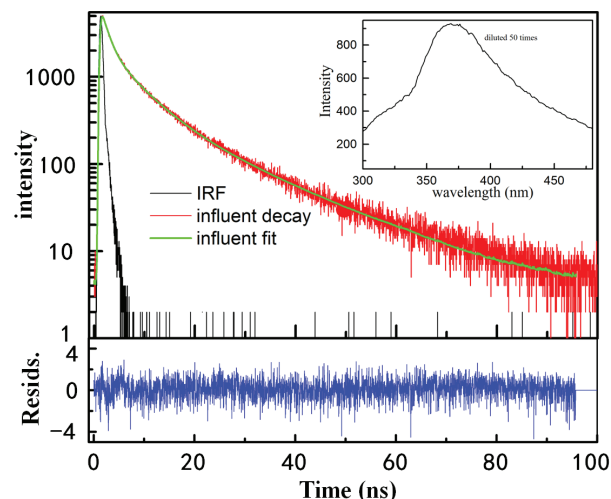


Fig. 4. Decay of fluorescence in a produced water (PW) sample after filtration by a 0.45 mM membrane (red); the green curve corresponds to the fit of the data to Eq. (1). The instrument response function (IRF) is shown in black. The residuals between the experimental data and the fits are shown in the lower panel. The inset shows the stationary fluorescence spectra of PW influent diluted 50 times.

anthracene all possess a high emission intensity from 350 to 500 nm. Therefore, the broad emission band of PW may result from PAHs. The relatively lower emission peak from 300 to 350 nm may be due to the contribution of single ring aromatic compounds.

The fluorescence lifetimes of the PW sample were also measured. Fluorescence decays in water are not monoexponential (Fig. 4), because of the complicated compositions. There were three average fluorescence lifetimes in the PW samples of 1.2, 5.6 and 17.1 ns. The respective contributions were 21.0%, 44.1% and 34.9%.

3.4. Petroleum hydrocarbons in PW

The species and concentrations of organic pollutants in the PW were analyzed by GC–MS of CH₂Cl₂ extractions. Various

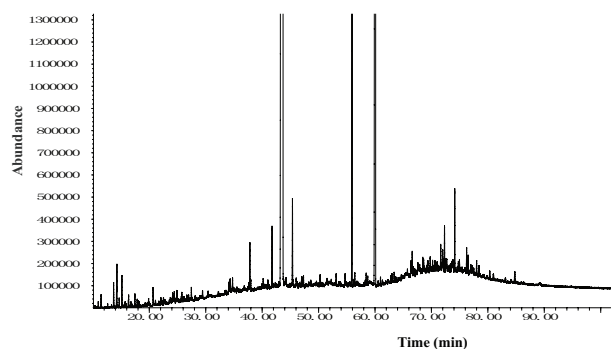
groups of organic components were identified on the basis of their mass spectra and GC retention times, and by comparison with the National Institute of Standards and Technology mass spectra library. Peak areas of the total ion chromatograms (TICs) were calculated using the real time execution integrator contained in the Agilent enhanced ChemStation software. The chromatograms were all determined under the same conditions; the abundances of the peaks detected were compared and an estimated removal giving the peak areas of some target compounds with SI > 85% by GC–MS in the PW samples.

The TIC of the PW sample is shown in Fig. 5. The chromatogram showed the presence of at least 164 aromatics with a total content of 125.96 $\mu\text{g/L}$, and 17 linear hydrocarbons with a total content of 4.52 $\mu\text{g/L}$. The ratio between the total content of aromatic organic compounds to the total detected organic matter was as high as 96.54%. Specifically, the detected aromatic compounds included 36 naphthalenes, with a total content of 18.30 $\mu\text{g/L}$, 29 phenanthrenes, with a total content of 36.48 $\mu\text{g/L}$, 20 thiophenes, with a total content of 5.43 $\mu\text{g/L}$, 9 biphenyls, with a total content of 1.96 $\mu\text{g/L}$, 9 furans, with a total content of 2.10 $\mu\text{g/L}$, 14 chrysenes with a total content of 10.46 $\mu\text{g/L}$, 6 pyrenes, with a total content of 5.39 $\mu\text{g/L}$, 13 fluorenes, with a total content of 5.80 $\mu\text{g/L}$, 5 triaromatic steroids, with a total content of 14.90 $\mu\text{g/L}$, 4 anthracenes, with a total content of 1.13 $\mu\text{g/L}$, and 19 other types of compound with a total content of 24.01 $\mu\text{g/L}$. Many of these compounds have complicated structures, and are refractory and have unfavorable impacts on the environment.

PAHs are among the most important compounds in PW with respect to the environment and human health. Higher molecular weight PAHs (4–6 rings), and especially those with structural embayment (e.g., benzo[*a*]pyrene and dibenzo[*a,l*]pyrene), may be carcinogenic. Although PAHs were not identified in all PW samples, the PAHs that were observed were mostly of low molecular weight (naphthalene, azulene, phenanthrene, anthracene, and fluorene and their derivatives) [22]. As listed in Table 2, different PAHs were detected among the PW samples. It has been reported that the concentration of total PAHs typically ranges from about 0.040 to 3 mg/L in PW [1]. The concentration of phenanthrene and its derivatives in the PW from the Bohai Sea was 36.48 $\mu\text{g/L}$ in this study, making phenanthrene the predominant PAH species.

In contrast, the concentration of the pyrene series was only approximately 5.39 $\mu\text{g/L}$. The World Health Organization (WHO) recommends a concentration limit for the sum of six PAHs of 0.2 $\mu\text{g/L}$ in drinking water vs. 0.01 $\mu\text{g/L}$ for benzo[*a*]pyrene alone [44]. The US EPA sets a maximum allowable concentration of 0.028 $\mu\text{g/L}$ for benzo[*a*]pyrene vs. 0.2 $\mu\text{g/L}$ for total PAHs [22].

(a) aromatic hydrocarbons



(b) alkanes

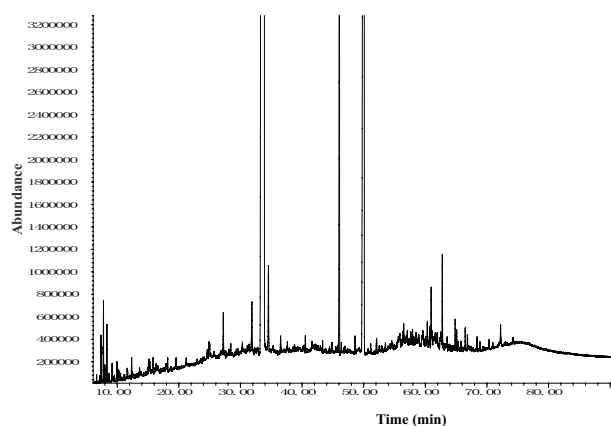


Fig. 5. Total ion chromatogram of the PW sample. (a) Aromatic hydrocarbons and (b) alkanes.

Table 2

Concentrations of various aromatic hydrocarbons in produced water collected from SZ36-1 terminal sewage

No.	Name	Number of compounds	Value ($\mu\text{g/L}$)	Proportion (%)
1	Naphthalenes	36	18.30	14.5
2	Phenanthrenes	29	36.48	29.0
3	Thiophenes	20	5.43	4.3
4	Biphenyls	9	1.96	1.6
5	Furans	9	2.10	1.7
6	Chrysenes	14	10.46	8.3
7	Pyrenes	6	5.39	4.3
8	Fluorenes	13	5.80	4.6
9	Triaromatic steroids	5	14.90	11.8
10	Anthracenes	4	1.13	0.9
11	Other compounds	19	24.01	19.1
Total		164	125.96	

Table 3
Concentrations of various alkanes in produced water collected from SZ36-1 terminal sewage

No.	Name	Retention time	Area	Concentration (µg/g)	Raw oil concentration (mg)	Sample volume (µL)	Value (µg/L)
1	nC14	14.3	185,046	2.50	5	40	0.11
2	nC15	17.7	279,315	3.77	5	40	0.16
3	nC16	21.2	275,607	3.72	5	40	0.16
4	nC17	24.7	531,615	7.17	5	40	0.31
5	nC18	28.1	388,081	5.23	5	40	0.22
6	nC19	31.4	547,522	7.38	5	40	0.32
7	nC20	34.6	434,269	5.86	5	40	0.25
8	nC21	37.6	533,849	7.20	5	40	0.31
9	nC22	40.5	583,401	7.87	5	40	0.34
10	nC23	43.3	590,710	7.96	5	40	0.34
11	nC24	46.1	1,452,438	19.58	5	40	0.84
12	nC25	48.6	546,057	7.36	5	40	0.32
13	nC26	51.1	423,189	5.71	5	40	0.25
14	nC27	53.5	327,653	4.42	5	40	0.19
15	nC28	55.9	273,017	3.68	5	40	0.16
16	nC29	58.1	224,826	3.03	5	40	0.13
17	nC30	60.3	193,726	2.61	5	40	0.11
Total							4.52

Furthermore, several alkane pollutants, such as docosane, hexadecane, tetracosane, octadecane, eicosane and tetradecane, were identified in the present study (Table 3), which are on the Black List of preferred controlled pollutants, as determined by the US and China EPA. Conversely, BTEX were not detected in the PW samples, mainly because the samples were obtained from a viscous oil exploitation site and had been treated by flocculent precipitate. It is clear that the PW need further advanced treatment before discharge into the environment.

4. Conclusions

The particle size distribution of the wastewater was investigated, and the COD contributed by each part estimated. The results showed that the COD distribution of the raw PW was 21.0% for the MWCO of 0.45 µm and 59.6% for the MWCO of 1 kDa. The majority of COD originated from soluble low-molecular-weight carbonyl compounds in the PW. There were three average fluorescence lifetimes of the soluble organic matter. The COD of PW had a good correlation with its UV absorbance at 254 nm. Approximately 164 aromatics and 17 alkanes, including some organic pollutants belonging to the group of preferred controlled pollutants, were detected and quantified in the PW by GC–MS analysis. Because of the strict discharge release standards of the China EPA, PW requires further treatment in addition to oil recovery and flocculent precipitate.

Acknowledgments

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References

- [1] J. Neff, K. Lee, E.M. DeBlois, Produced Water: Overview of Composition, Fates, and Effects, K. Lee, J. Neff, Eds., Produced Water: Environmental Risks and Advances in Mitigation Technologies, Springer New York, New York, NY, 2011, pp. 3–54.
- [2] E.T. Igundu, G.Z. Chen, Produced water treatment technologies, *Int. J. Low Carbon Technol.*, 9 (2014) 157–177.
- [3] L. Yu, M. Han, F. He, A review of treating oily wastewater, *Arab. J. Chem.*, 10 (2017) S1913–S1922.
- [4] A.A. Olajire, Review of ASP EOR (alkaline surfactant polymer enhanced oil recovery) technology in the petroleum industry: prospects and challenges, *Energy*, 77 (2014) 963–982.
- [5] H.Z. Ma, B. Wang, Electrochemical pilot-scale plant for oil field produced wastewater by M/C/Fe electrodes for injection, *J. Hazard. Mater.*, 132 (2006) 237–243.
- [6] J.R. Lu, X.L. Wang, B.T. Shan, X.M. Li, W.D. Wang, Analysis of chemical compositions contributable to chemical oxygen demand (COD) of oilfield produced water, *Chemosphere*, 62 (2006) 322–331.
- [7] F.R. Ahmadun, A. Pendashteh, L.C. Abdullah, D.R.A. Biak, S.S. Madaeni, Z.Z. Abidin, Review of technologies for oil and gas produced water treatment, *J. Hazard. Mater.*, 170 (2009) 530–551.
- [8] T.I.R. Utvik, Chemical characterisation of produced water from four offshore oil production platforms in the North Sea, *Chemosphere*, 39 (1999) 2593–2606.
- [9] G.T. Tellez, N. Nirmalakhandan, J.L. Gardea-Torresdey, Performance evaluation of an activated sludge system for removing petroleum hydrocarbons from oilfield produced water, *Adv. Environ. Res.*, 6 (2002) 455–470.
- [10] Q. Zaib, O.D. Aina, F. Ahmad, Using multi-walled carbon nanotubes (MWNs) for oilfield produced water treatment with environmentally acceptable endpoints, *Environ. Sci. Process Impacts*, 16 (2014) 2039–2047.

- [11] I. Arslan-Alaton, T. Olmez-Hanci, E. Dulekgurgen, D. Orhon, Assessment of organic carbon removal by particle size distribution analysis, *Environ. Eng. Sci.*, 26 (2009) 1239–1248.
- [12] R. Bande, B. Prasad, I. Mishra, K. Wasewar, Oil field effluent water treatment for safe disposal by electroflotation, *Chem. Eng. J.*, 137 (2008) 503–509.
- [13] G. Li, B. Bai, K.H. Carlson, Characterization of solids in produced water from wells fractured with recycled and fresh water, *J. Pet. Sci. Eng.*, 144 (2016) 91–98.
- [14] S. Kumar, C. Guria, A. Mandal, Synthesis, characterization and performance studies of polysulfone/bentonite nanoparticles mixed-matrix ultra-filtration membranes using oil field produced water, *Sep. Purif. Technol.*, 150 (2015) 145–158.
- [15] B.H. Diya'uddeen, S.R. Pouran, A.R.A. Aziz, S.M. Nashwan, W. Daud, M.G. Shaaban, Hybrid of Fenton and sequencing batch reactor for petroleum refinery wastewater treatment, *J. Ind. Eng. Chem.*, 25 (2015) 186–191.
- [16] P. McCormack, P. Jones, M.J. Hetheridge, S.J. Rowland, Analysis of oilfield produced waters and production chemicals by electrospray ionisation multi-stage mass spectrometry (ESI-MSn), *Water Res.*, 35 (2001) 3567–3578.
- [17] S.B. Henderson, S.J.W. Grigson, P. Johnson, B.D. Roddie, Potential impact of production chemicals on the toxicity of produced water discharges from North Sea oil platforms, *Mar. Pollut. Bull.*, 38 (1999) 1141–1151.
- [18] M.Y. Yang, B. Jing, W.J. Chen, Q. Li, X.Q. Yin, Experimental study on COD composition and electrochemical degradation of wastewater in offshore oilfields, *J. Chin. Chem. Soc.*, 64 (2017) 73–79.
- [19] S. Deng, G. Yu, Z. Chen, D. Wu, F. Xia, N. Jiang, Characterization of suspended solids in produced water in Daqing oilfield, *Colloids Surf., A*, 332 (2009) 63–69.
- [20] Z.F. Lu, F.T. Zhan, Z.X. Wang, S.D. Zhang, Separation and composition characterization of acidic components in water produced by polymer flooding in Gudao Oilfield, *J. Fuel Chem. Technol.*, 36 (2008) 588–593.
- [21] M.J. Zhu, J. Yao, W.B. Wang, X.Q. Yin, W. Chen, X.Y. Wu, Using response surface methodology to evaluate electrocoagulation in the pretreatment of produced water from polymer-flooding well of Dagang Oilfield with bipolar aluminum electrodes, *Desal. Wat. Treat.*, 57 (2016) 15314–15325.
- [22] W.H. Orem, C.A. Tatu, H.E. Lerch, C.A. Rice, T.T. Bartos, A.L. Bates, S. Tewalt, M.D. Corum, Organic compounds in produced waters from coalbed natural gas wells in the Powder River Basin, Wyoming, USA, *Appl. Geochem.*, 22 (2007) 2240–2256.
- [23] M. Campagna, M. Cakmakci, F.B. Yaman, B. Ozkaya, Molecular weight distribution of a full-scale landfill leachate treatment by membrane bioreactor and nanofiltration membrane, *Waste Manage.*, 33 (2013) 866–870.
- [24] F.B. Yaman, M. Cakmakci, D. Karadag, B. Ozkaya, V. Bali, B. Dora, Molecular weight distributions in cotton-dyeing textile wastewaters, *Desal. Wat. Treat.*, 57 (2016) 12684–12691.
- [25] T. Ngoc Han, N. Huu Hao, T. Urase, K.Y.-H. Gin, A critical review on characterization strategies of organic matter for wastewater and water treatment processes, *Bioresour. Technol.*, 193 (2015) 523–533.
- [26] H. Svensson, Y. Jani, W. Hogland, M. Marques, Particle size characterization of oak wood leachate: chemical oxygen demand and toxicity distribution within different fractions, *Water Sci. Technol.*, 70 (2014) 502–509.
- [27] S. Dogruel, E.U. Cokgor, O. Ince, S. Sozen, D. Orhon, Potential of ultrafiltration for organic matter removal in the polymer industry effluent based on particle size distribution analysis, *Environ. Sci. Pollut. Res.*, 20 (2013) 340–350.
- [28] S.M. Hocaoglu, D. Orhon, Particle size distribution analysis of chemical oxygen demand fractions with different biodegradation characteristics in black water and gray water, *Clean (Weinh)*, 41 (2013) 1044–1051.
- [29] Y. Nergis, M. Sharif, M.A. Farooq, A.A. Mahmood, Chemical oxygen demand (COD) fractions characterization of Karachi metropolitan wastewater, *J. Chem. Soc. Pak.*, 32 (2010) 711–716.
- [30] A. Reyhani, H.M. Meighani, Optimal operating conditions of micro- and ultra-filtration systems for produced-water purification: Taguchi method and economic investigation, *Desal. Wat. Treat.*, 57 (2016) 19642–19654.
- [31] S.J. Maguire-Boyle, A.R. Barron, Organic compounds in produced waters from shale gas wells, *Environ. Sci. Process Impacts*, 16 (2014) 2237–2248.
- [32] H.S. Dorea, J.R.L. Bispo, K.A.S. Aragao, B.B. Cunha, S. Navickiene, J.P.H. Alves, L.P.C. Romao, C.A.B. Garcia, Analysis of BTEX, PAHs and metals in the oilfield produced water in the State of Sergipe, Brazil, *Microchem. J.*, 85 (2007) 234–238.
- [33] G.T. Tellez, N. Nirmalakhandan, J.L. Gardea-Torresdey, Comparison of purge and trap GC/MS and spectrophotometry for monitoring petroleum hydrocarbon degradation in oilfield produced waters, *Microchem. J.*, 81 (2005) 12–18.
- [34] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, *Standard Methods for the Examination of Water and Wastewater*, 20th ed., American Public Health Association (APHA), American Water Works Association, Water Pollution Control Federation, Washington, D.C., USA, 1999.
- [35] SEPA of China, *Standard Monitoring and Analytical Methods for the Examination of Water and Wastewater*, 4th ed., China Environmental Science Press, Peking, China, 2002.
- [36] Z.Y. Lou, Y.C. Zhao, Size-fractionation and characterization of refuse landfill leachate by sequential filtration using membranes with varied porosity, *J. Hazard. Mater.*, 147 (2007) 257–264.
- [37] H. Zhang, X.G. Wu, X.W. Li, Oxidation and coagulation removal of COD from landfill leachate by Fered-Fenton process, *Chem. Eng. J.*, 210 (2012) 188–194.
- [38] K.S. Ashaghi, M. Ebrahimi, P. Czermak, Ceramic ultra- and nanofiltration membranes for oilfield produced water treatment: a mini review, *Open Environ. Sci.*, 9 (2007) 1–8.
- [39] M. Ebrahimi, D. Willershausen, K.S. Ashaghi, L. Engel, L. Placido, P. Mund, P. Bolduan, P. Czermak, Investigations on the use of different ceramic membranes for efficient oil-field produced water treatment, *Desalination*, 250 (2010) 991–996.
- [40] M. Cakmakci, N. Kayaalp, I. Koyuncu, Desalination of produced water from oil production fields by membrane processes, *Desalination*, 222 (2008) 176–186.
- [41] A.P. Carpenter, Determination of tocopherols in vegetable oils, *J. Am. Oil Chem. Soc.*, 56 (1979) 668–671.
- [42] J.L. Weishaar, G.R. Aiken, B.A. Bergamaschi, M.S. Fram, R. Fujii, K. Mopper, Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon, *Environ. Sci. Technol.*, 37 (2003) 4702–4708.
- [43] A. Blasberger, E. Behar, H.B. Perets, N. Brosch, A.G.G.M. Tielens, Observational Evidence linking interstellar UV absorption to PAH molecules, *Astrophys. J.*, 836 (2017) 173.
- [44] World Health Organization (WHO), *Guidelines for Drinking-Water Quality, Health Criteria and Other Supporting Information*, Vol. 2, World Health Organization, Geneva, 1984.