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Treating Kuwait's oilfield water via conventional methods and membrane technology

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ABSTRACT

Kuwait is a desert country with scarce water resources and increasing population, which means that more water sources should be tapped, not only for irrigation but also to provide for the citizens of the country. Oilfield waters are produced at increasing levels in Kuwait, being a foremost oil producer in the gulf region. It contains lots of contaminants that, if left untreated, will pollute the surrounding areas when disposed of improperly. This paper examines the possibility of treating oilfield water to be used as an additional resource for irrigation and for improving its treatment prior to proper disposal. The water treatment concept being introduced was performed through several treatment stages including biological treatment combined with nitrification and denitrification (sedimentation), chemical treatment (flocculation and coagulation), reverse osmosis, and disinfection using ultraviolet process as the final treatment process. This was accomplished through the combination of conventional and membrane technology process. After the treatment, the water samples were tested and compared with the parameters set by the Kuwait Environment Public Authority (KEPA) for irrigation, as well as disposal. The results indicated that the treatment methods are efficient in treating oilfield water as the treated samples showed significant reduction in original concentration, such as to name a few, total suspended solids, total dissolved solids, ammonia, total Kjeldahl nitrogen, sulfide, turbidity, phosphate and biological oxygen demand with a reduction percentage of 94.23%, 95.86%, 76.47%, 80.39%, 94.59%, 98.0%, 54.54%, 80.19%, respectively. Grease, oil and chemical oxygen demand level can be lowered from the treated water by further treatment. Oilfield water can, therefore, be utilized for irrigation and eventual allowable discharge to sewage network conventional wastewater treatment methods combined with membrane technology.

Keywords: Oilfield produced water; Irrigation; Injection; Membrane treatment

1. Introduction

Oilfield water is produced as a byproduct along with the production of hydrocarbons from underground reservoirs, as there is always accompanying water with oil and gas during the extraction. Produced water is now considered as the largest waste stream generated in oil and gas industries [1,2]. The global amount of wastewater co-produced in oil and gas exploration is about 210 million barrels/d, three times higher than the produced oil [3]. The outcome and effect of discharging produced water on the environment or its alternative use for irrigation has lately become a significant issue of environmental concern, uncontrolled discharge can lead to the environmental damage, killing

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the life of water and plants [1,4]. One of the most critical problems is the improper and mismanagement of direct disposal of this water into disposal wells or into water bodies [5]. This water must meet specific standards for proper disposal into water bodies so as not to harm the marine ecosystems [6]. Produced oilfield water contains a lot of hazardous chemicals, which might include inorganic salts, several metals, and a wide variety of organic chemicals [7]. Minimizing the impact of the produced oilfield water on the environment should be considered in its treatment process [8].

Produced water as a consequence of oilfield activities is usually disposed of via re-injection after treatment, which should meet several requirements imposed by environmental regulations [9,10]. Due to the presence of microbial flora in oilfield water, which can introduce microbiologically influenced corrosion, studies have been done to inhibit the growth of these microorganisms to avoid corrosion in the pipes where the re-injection is being made [11]. However, it does not envision any other need or utilization for the produced water, except for its previously identified means of disposal alone, and that is ultimately it is just intended for re-injection.

Kuwait is a major oil producer in the Middle East with an oil production reaching three million barrels/d. Kuwait was the world's 10th largest producer of petroleum and other liquids in 2015 [12]. The increased oil production will certainly result in more produced water that requires even more handling and treatment. Due to the huge amount of water produced in the oilfield, it is very important for it to be treated and checked for its use in irrigation or disposal [13]. Prior to using oilfield water for either irrigation or disposal, it must be treated to match the standards set by Environmental Protection Agency (EPA) [14].

Wastewater, in Kuwait, is treated using conventional methods of treatment such as chemical treatment (flocculation, coagulation), biological treatment, disinfection (ultraviolet treatment), and reverse osmosis [14–16]. In this study, these treatments have been used on pre-treated oilfield water with some additional unconventional treatments as well, including, sand filter, carbon filter, reverse osmosis, and ultraviolet to improve its quality.

This paper aims to test the efficacy of conventional wastewater treatment methods combined with membrane technology for the treatment of produced pre-treated oilfield water and to check its suitability for irrigation purposes and its eventual disposal.

2. Experimental setup

2.1. Materials and methods

All chemicals obtained for this investigation are from Sigma-Aldrich (Aldrich Chemical Co., LLC, Millipore Sigma, 6000 N Teutonia Ave, Milwaukee, WI, 53209-3645 United States). All bottles and other containers were treated with 1 M HNO_3 solution before being washed with deionized water and dried.

The pH of the samples was measured using a pH meter (Senso-direct, Lovibond) that was previously calibrated. The pH meter was rinsed before measuring and was left to stabilize with the sample before recording the value.

The total suspended solids (TSS) of the samples was measured by filtering 50 mL of each water sample using a vacuum filter, except for the clarifier sample in which only 15 mL was filtered through a glass fiber filter and then weighed. Once finished, the filter papers were placed in an oven (Fisher Scientific Isotemp oven) for 1 h at 105°C ± 3°C. The mass increase divided by the water volume filtered is equal to the TSS in mg/L.

The total dissolved solids (TDS) of the sample was measured by taking 10 mL of the filtrate in heatproof crucibles after weighing it, then placing those crucibles in an oven (Fisher scientific Isotemp oven) at 105°C ± 3°C until completely evaporated. The crucible weight was taken after cooling it in a desiccator. The mass increase divided by the water volume filtered is equal to the TDS in mg/L.

Chemical oxygen demand (COD) was measured using Spectrophotometer (DR 3900, HACH Company World Headquarters: Loveland, Colorado, USA). 2 mL of each sample was taken in a prepared test tube with chemical reagents LCK 514 (100–2,000 mg/L) and LCK 314 (15–150 mg/L). The tubes are then placed in a COD reactor (Lovibond ET125) for 2 h at 150°C. After those 2 h, the COD was measured with HACH Spectrophotometer (DR 3900, HACH Company World Headquarters: Loveland, Colorado, USA).

The dissolved oxygen (DO) of each sample was measured using a DO meter (HQ30d Flexi), where the sensor was rinsed with distilled water before measuring the DO of each sample. The measurement was recorded once the value has been stabilized.

Ammonia and phosphate were measured by Hach spectrophotometer (DR 3900, HACH Company World Headquarters: Loveland, Colorado USA) and the concentration of the chemical constituents was measured in mg/L. Hydrogen sulfide in traditional water samples has been measured using the Hach modified methylene Blue Method (USEPA method 8131). The quality of the collected wastewater was tested in Kabd Wastewater Treatment Plant (WWTP) laboratories according to American Public Health Association (APHA) international standard [17].

BOD_5 test was conducted using 300 mL incubation glass bottle having a ground glass stopper and a flared mouth. The bottles were cleaned with a detergent, rinsed thoroughly, and drained before use, to obtain satisfactory water seals, and then water was added to the flared mouth of special BOD_5 bottles, after which, it was transferred to a plastic cup over the flared mouth of the bottle to reduce evaporation of the water seal during incubation. The samples were placed in an incubator (LabLine Instruments, Kalbadevi, Mumbai, Maharashtra 400002, India) at 20°C ± 1°C for 5 d [18]. The DO was then measured using Hach DO meter (model HQ30D Flexi) before and after the incubation period.

Turbidity was measured using turbidity meter (Hach 2100Q). The turbidity is recorded in NTU.

Hydrex 6451 polymer stock solution (600 mL of 3.5 g/L) is prepared for addition in three doses (each dose 200 mL). Hydrex 6451 polymer is a highly effective cationic flocculant, that condition off the solids for dewatering operations and aid in the water clarification processes. Hydrex (6541) polymer used is a high molecular weight, cationic, water soluble, flocculant polymer, designed to increase floc density, enhance clarity, improve settling characteristics and dewater sludge. Around four spoons of (each 4.14 g) poly-aluminum chloride (PAC, CAS No.:1327-41-9 EINECS No.:215-477-2, white powder), 25% of sodium hydroxide (NaOH). The polymers, poly aluminum chloride and sodium hydroxide, were purchased from Hydrotek Engineering Company in Kuwait.

The untreated oilfield water underwent a process with different stages which included both conventional processes and the proposed membrane technology. The stages of treatment include biological chemical treatment, sedimentation, and disinfection.

2.2. Purifier membrane specification

Membrane (Smartflo water purifiers, Pentair, Pentair Water India Pvt. Ltd., Verna Industrial Estate, Verna, Goa-403722) with UV Lamp (11W), was purchased from Hydrotek Engineering company in Kuwait [19]. Purification is undertaken up to 15 L/h, with acrylonitrile butadiene styrene body material using a wall-mounted type apparatus with dimension of 537 mm × 420 mm × 168 mm (H × W × D in mm). The minimum inlet water pressure is 5 psi and the maximum is 35 psi, whereas the inlet water temperature is from 2°C to 49°C. Total tank volume is about 7 L with membrane type classified as a thin layer composite. Booster pump voltage is set at 240 V DC with main voltage at 160–270 V AC. In the purifier, the water will pass through the four membrane stages (sedimentation cartridge, carbon filter, ultraviolet treatment, and a reverse osmosis) where, the water will exert pressure on a semi-permeable membrane and the purified part enter through the pores of the membranes to give the purified treated water, while the rejected water is diverted to the drain.

2.3. Kabd experimental water treatment method

Schematic diagram of the instrument used is shown in Fig. 1. Fig. 2 illustrates the actual designed setup apparatus for the treatment. The untreated oilfield water samples used were collected from a well in Kuwait that has been pre-treated by Kuwait National Petroleum Company (KNPC). KNPC water used for pre-treatment is sour water that contains 12,000 ppm of H_2S and 6,000 ppm of ammonia, which were both removed through the collection tank, stripper and separator to reduce H_2S and ammonia to 10 and 34 ppm, respectively. The pre-treatment stage also included a screen chamber and a skimming tank to reduce the amount of oil and grease present in the produced water. In the pre-treatment stage, the heavy materials, such as large debris and solids, are already removed from the wastewater. This stage also included several other operations such as screening, floatation, and grit removal.

Following the pre-treatment stages of KNPC, the untreated oilfield water samples were further treated following the process illustrated in Fig. 2. Untreated water (18.9 L or 5 gallons) was aerated using an air compressor for 24 h to ensure efficient biodegradation and to maintain DO level (2–3 mg/L) in tank 1 (Fig. 2). Then the aerated water (around 9 L) was pumped to the mixing tank (Tank 2) shown in Fig. 2, to undergo flocculation. The retention time was kept at around approximately 6–8 h. In this tank, the pH is reduced from 7 to 4 by gradually adding around 4 spoons of (each 4.14 g) PAC with continuous mixing. The purpose of PAC is to speed up the flocculation and settling of suspended solids. Once the pH has stabilized at 4, 75 mL of 25% of sodium hydroxide (NaOH) was added gradually with continuous stirring to bring back the pH to 7. Once the pH has stabilized at 7, 600 mL of 3.5 g/L nonreactive polymer (cationic polymer, Hydrex 6451) was added gradually in three doses (each dose 200 mL) with continuous stirring to enhance flocculation, coagulation, and settling of the suspended solids by increasing the amount of positive charge and therefore creating particles that are larger, heavier, and settle easily. Then, the water sample was stirred with a rod for 20 min and left to settle in 45 min. For large-scale applications

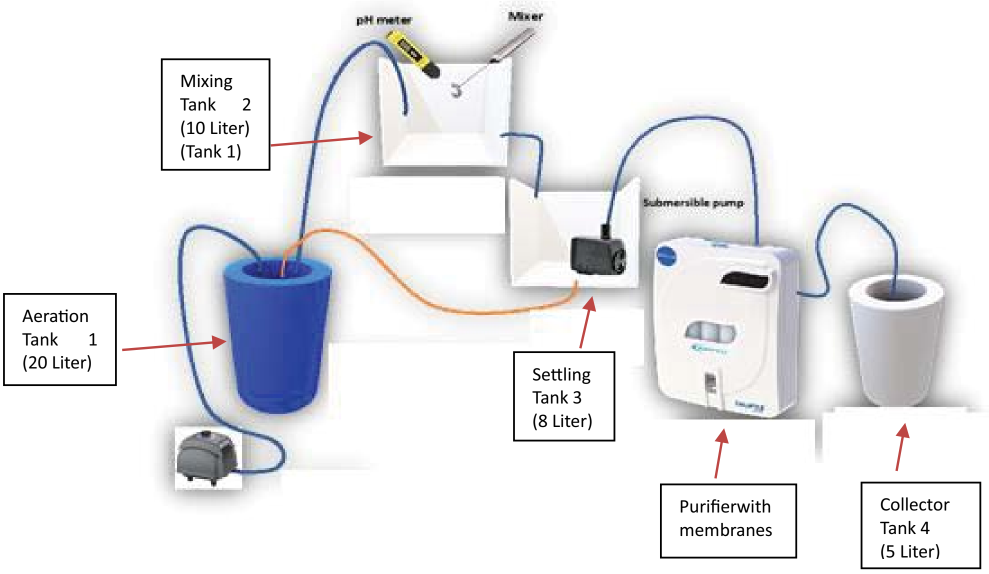

Fig. 1. Schematic diagram of the produced water treatment.

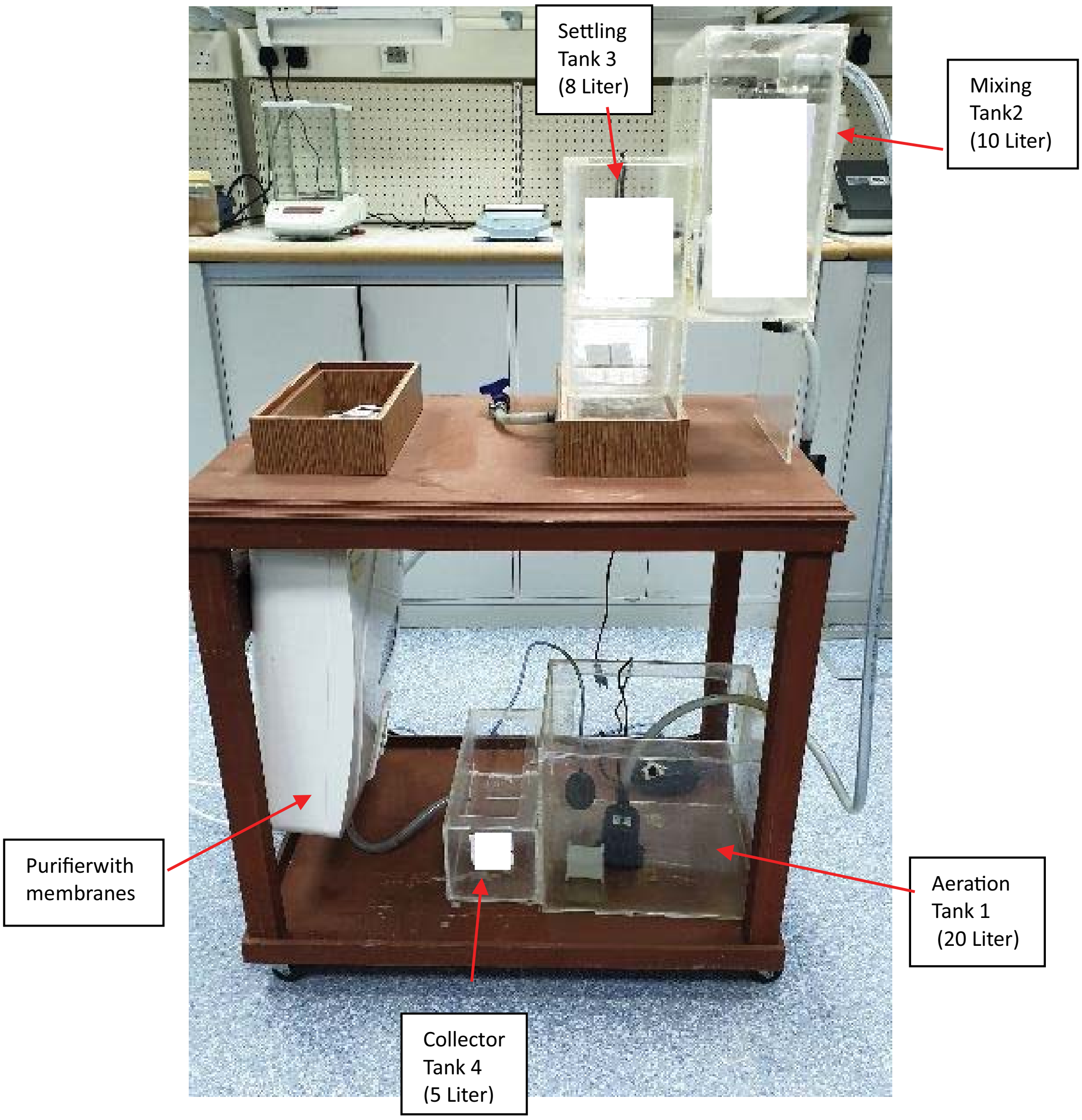

Fig. 2. Designed apparatus for produce water treatment.

such as the (KNPC plant), it is recommended to have about 4–6 h of sedimentation, depending on the solid levels present. The amount of NaOH and PAC depended on waste content present in the raw pre-treated water sample.

Fig. 3 shows the untreated water (Tank 1) and flocculation, coagulation, and settling setup. Once the solids have settled, the surface water is pumped to tank 3 to allow for any more solids to settle out of the water for 30 min. The water is then pumped to a water purifier that contains the membrane. In the purifier, remaining solids, intensity of odor and color, TDS, and bacteria will be further reduced. The treated water sample was then collected in tank 4, while the rejected water is diverted to the drain.

The untreated and treated samples (after purifier) were collected in containers that were cleaned thoroughly and sent for investigation at the Australian College of Kuwait Oil and Gas Laboratory. The samples were then tested at the Kabd WWTP following the standard analysis methods. The purification process was repeated three times prior to the final trial.

Two liters of both samples (untreated and treated, the former serving as control sample) were taken for analysis to Kabd WWTP. The water analyses conducted on the samples were pH measurement, TSS, TDS, COD, DO, ammonia-nitrogen, nitrate-nitrogen, nitrite-nitrogen, and sulfate. The results of these analyses are compared with standards set by Kuwait Environmental Public Authority (KEPA) limits for irrigation [19].

3. Results and discussion

The pre-treated Kuwait oilfield water was treated with the combination of conventional and membrane technology.

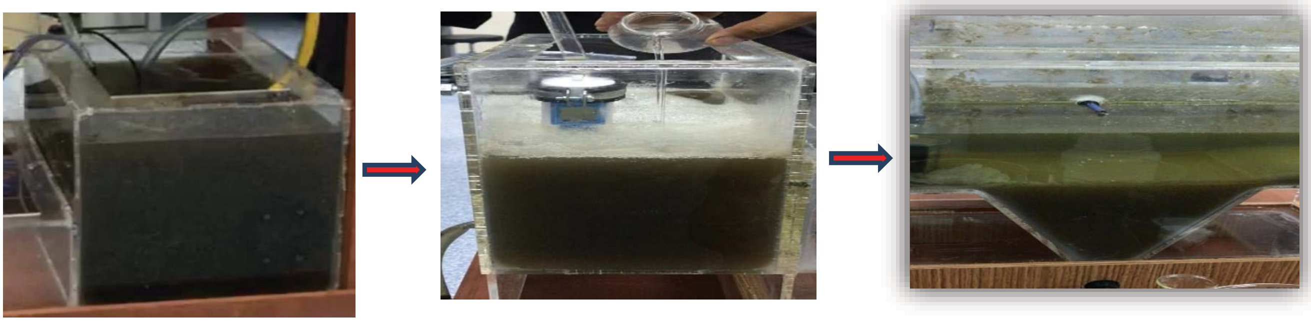

Fig. 3. Untreated water and settling of organic matter stages: (a) tank 1 (untreated water), tank 2 (mixing tank) (b), tank 3 (settling tank).

Chemical characteristics of both first and second sample in this study are presented in Table 1. The first sample was the untreated water sample after the pretreatment from KNPC. The second sample was the treated water sample after passing through the purifier containing the membrane. The results of the treated water were compared with KEPA standards to verify its suitability for irrigation purposes, or to be disposed of in an environmentally safe manner into water bodies [20].

Figs. 4a–f, Figs. 5a–f and Table 1 indicated the change in the analysis results from the untreated to the treated sample. Fig. 4a illustrates that the pH for both water samples fell within the range set by KEPA. The TSS results (Fig. 4b) showed (94%) significant decrease in value from 156 to 9 mg/L. TDS results (Fig. 4c) showed decrease in its value, similar to the TSS, from 7,100 to 294 mg/L with a 95.9% reduction. On the other hand, COD results reduced slightly from 859 to 840 mg/L (Fig. 4d) with 2.2% reduction, where the COD was beyond the limit of the standard limits for irrigation and disposal set by KEPA and therefore recommended further treatment. Future recommendations for lowering COD concentration is by (1) adding hydrogen peroxide to the water in small concentrations (300–500 mg/L) and (2) subjecting it to UV treatment. This combination of processes may oxidize organic and inorganic matter present in the water [21].

The DO results (Fig. 4f) showed an increase in DO concentration 0.83 to 3.36 mg/L post the membrane treatment. For further treatment, it is recommended to control the flow rate using flow meter. Extra aeration and reverse osmosis could be the reason for the increase of DO levels in the treated water. Well-maintained and adequately calibrated DO meters could be suggested to be used for controlling DO level [22].

The results for the ammonia analysis (Fig. 4f) showed a great reduction (76.47%) from 34 to 8 mg/L. The TKN results (Fig. 5a) showed a great reduction (80.39%) from 51 mg/L for the untreated sample to 10 mg/L after membrane treatment. Excessive amount of nitrogen will accumulate in the edible parts of the treated water and will affect the

Table 1
Results for the water analysis

Test	Untreated	Membrane	Reduction rate	KEPA maximum standard limits for irrigation	KEPA maximum standard limits for disposal	Uncertainty
pH	7	7.5	NR	5.5–8.5	6–8	±0.2
TSS, mg/L	156	9	94.23	15	10	±0.5
TDS, mg/L	7,100	294	95.86	1,500	1,500	±2.1
COD, mg/L	859	840	2.21	100	200	±1.9
DO, mg/L	0.83	3.36	NR	2	>2	±0.11
Ammonia, mg/L	34	8	76.47	15	30	±1.2
TKN, mg/L	51	10	80.39	35	5	±1.1
Oil and grease, mg/L	41	14	65.85	5	5	±1
Sulfide, mg/L	3.7	0.2	94.59	0.1	0.5	±0.001
Turbidity, NTU	204	4	98	50	30	±0.02
Phosphate, mg/L	36.3	16.5	54.54	30	2	±0.08
BOD_5, mg/L	101	20	80.19	20	30	±0.4

NR: no reduction; TSS: total suspended solids; TDS: total dissolve solids; COD: chemical oxygen demand; DO: dissolve oxygen; BOD_5: biological oxygen demand.

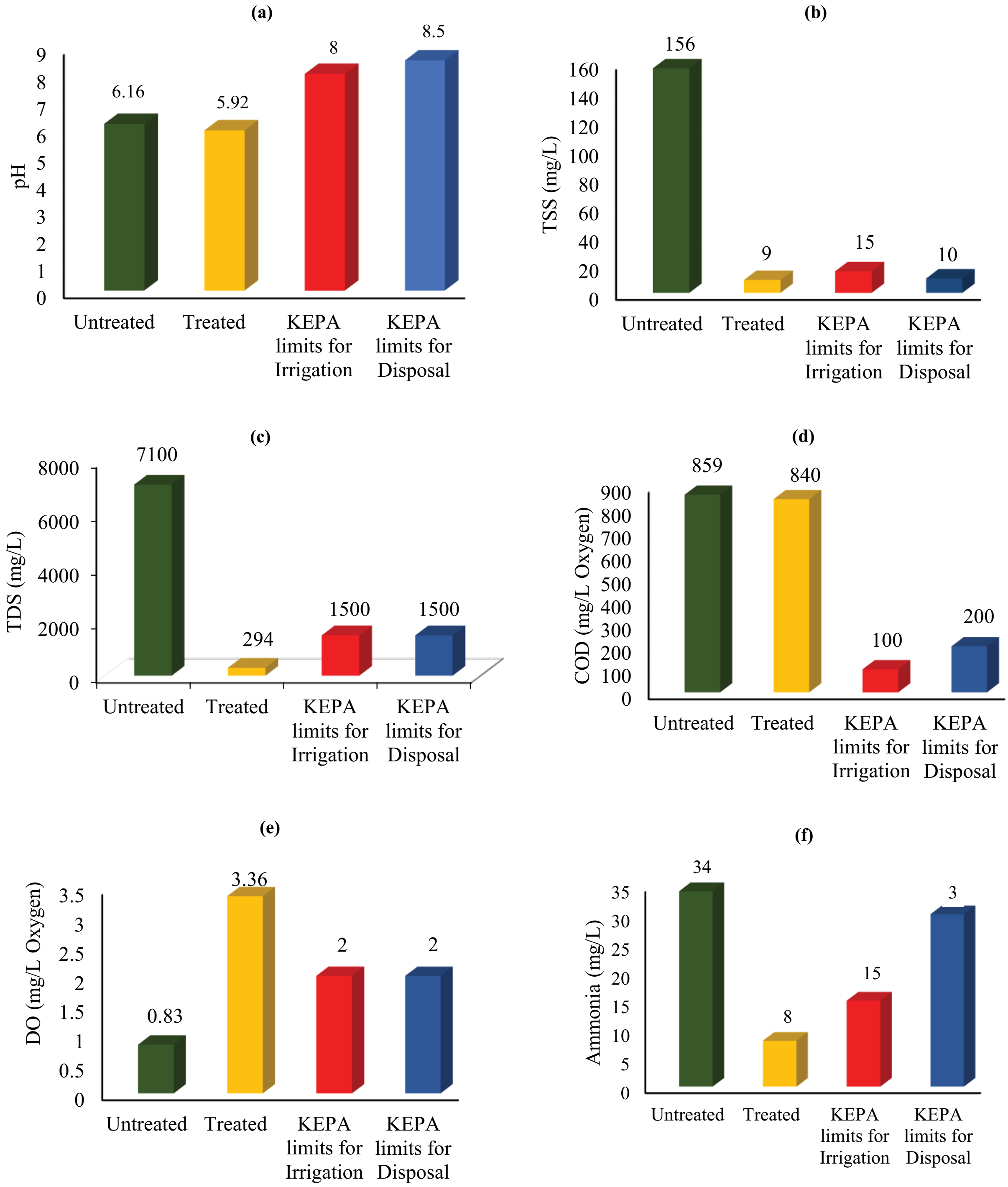

Fig. 4. Water analysis for the untreated and treated (after membrane) samples with KEPA standard limits: (a) pH, (b) TSS, (c) TDS, (d) COD, (e) DO, and (f) ammonia.

vegetative growth of the plants [23]. The results for the pH, TSS, TDS, and ammonia were within the KEPA standard limits for both irrigation and disposal.

Oil and grease analysis (Fig. 5b) showed that the concentration was decreased from 41 to 14 mg/L with 65.85% reduction percentage. The result was higher than the limits for both the irrigation and disposal standard. This is most likely due to the low retention time in the original settling tank or the separator in which the water was originally separated from the hydrocarbons. Organic toxic waste (oil and grease) can cause ecological damages to aquatic organisms and requires further treatment using enzyme and adsorption units [24]. Further treatment is required to lower the COD, oil and grease concentration.

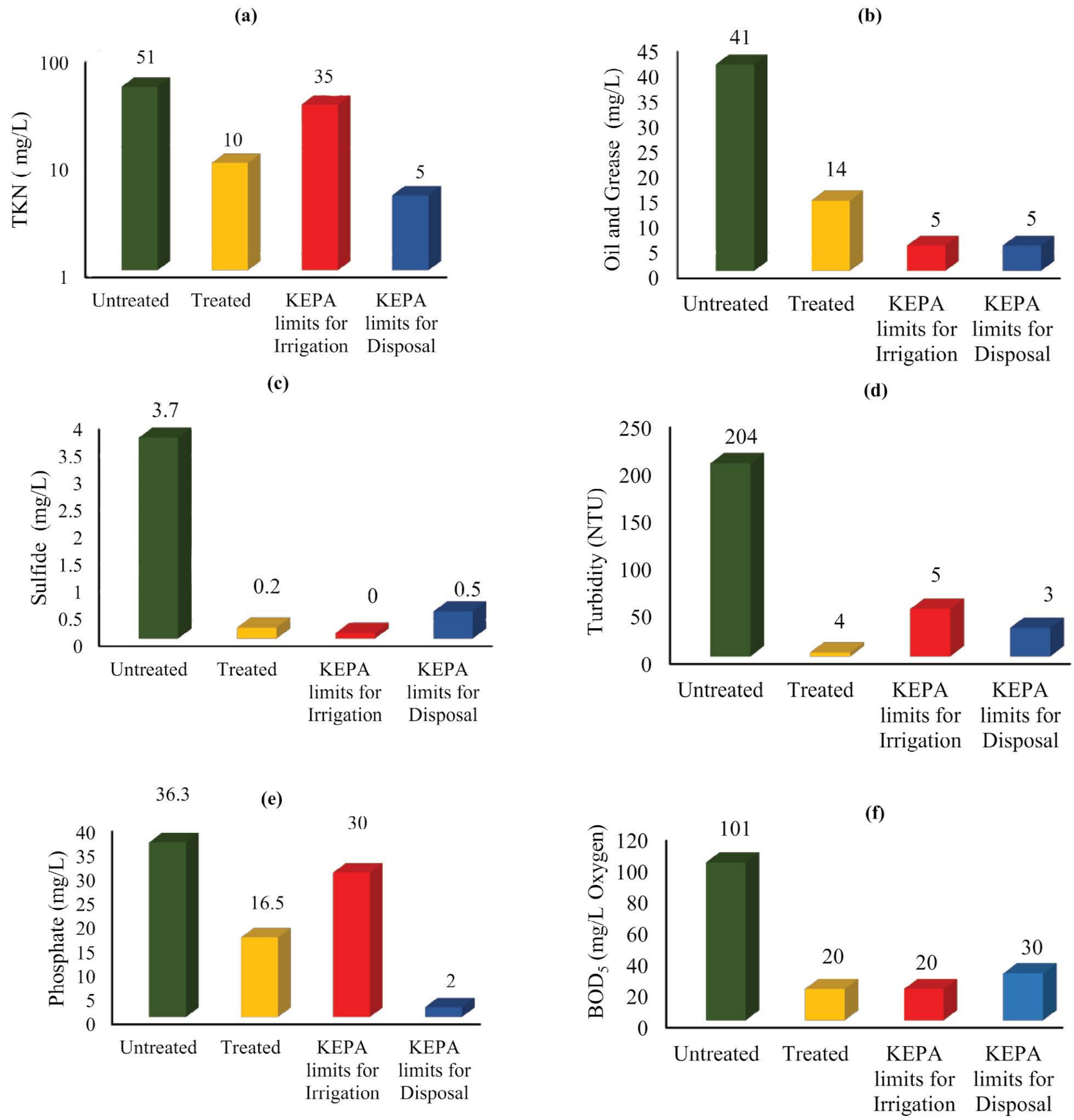

Fig. 5. Water analysis for untreated and treated (after membrane) samples with KEPA standard limits: (a) TKN, (b) oil and grease, (c) sulfide, (d) turbidity, (e) phosphate, and (f) BOD_5.

Table 1 shows that the sulfide analysis results (Fig. 5c) reduced from 3.7 to 0.2 mg/L with 94.6% reduction. However, the sulfide concentration for the treated water is 0.2 mg/L, which is slightly greater than the KEPA standard for irrigation. Turbidity analysis results (Fig. 5d) show that the turbidity decreased by 98% from 204 to 4 mg/L. The results for sulfide and turbidity were less than KEPA limits for irrigation and disposal. Phosphate (Fig. 5e) showed a 54% decrease in values from 36.3 to 16.5 mg/L. Phosphate result was lower than the irrigation limit whereas slightly higher than disposal limit. BOD_5 (Fig. 5f) showed an 80.19% decrease in value from 101 to 20 mg/L for treated sample. The BOD_5 result was quite similar for irrigation limit and much less than disposal limit.

Fig. 6 shows the water quality for three samples: sample (a) represents the untreated produced water; sample (b) is taken after the settling tank; and sample (c) is the sample after the membrane treatment. The results indicate an obvious clarity of the treated sample after the treatment, with the four stages of membrane being applied for treatment on the oilfield water.

The standard limits set by KEPA are based on the safe and efficient growth of crops in Kuwait and the values cannot exceed them. KEPA limit for pH is given in a range between 5.5 and 8.5. Too low of a pH can lead to adverse growth symptoms, particularly when it comes to nutrition; highly acidic water can lead to the acidification of soil. Alkaline irrigation water usually has a high concentration of carbonates and bicarbonates which lead to the precipitation of magnesium and calcium; this, in turn, affects the growth of plants because the precipitate will affect the absorption of important trace elements such as zinc [25]. Increasing TSS in irrigation water can lead to blockages in irrigation lines that would prevent the water from reaching target irrigation area. Turbidity is also a measure of the suspended solid in terms of the intensity of light that can pass through a sample; higher turbidity is an indicator of high TSS. Higher turbidity and TSS lead to the accumulation of solids on the surface of the soil as well as affect its ability to transmit and hold water [26]. High TDS is an indicator of dissolved ions in the water which also gives a high conductivity reading. High conductivity is an indicator of dissolved salts; higher conductivity means a higher salt content. Higher salts in irrigation water lead to water and nutrient absorption issues due to the imbalances in the said nutrients [27]. COD is an indicator of the concentration of organic matter that is chemically oxidized. COD can be a good parameter in irrigation water as increasing organic matter helps the soil retain water; however, it cannot be too high above the standards set [28]. Increasing concentrations of nitrogen, in the form of ammonia, nitrate, and nitrite, do not adversely harm crops; however, it can seep into the groundwater below and affect the water table [29]. Sulfide also has the added effect of depleting DO to form sulfate ions that further reduce availability of phosphorous to crops. Dissolved oxygen is required to be kept at concentrations of above 2 mg/L as the oxygen serves to improve nutrient absorption rates and overall plant growth. Dissolved oxygen is also necessary to allow for aerobic decomposition of organic matter instead of anaerobic decomposition as the latter produces harmful gases [22]. Oil and grease in irrigation water will coat the soil particles as a hydrophobic layer that prevents the water from hydrating the soil and reaching the crops. This can be reduced using enzyme and adsorption unit [30].

As for disposal, under KEPA's standards, the treated water sample is suitable for disposal barring the COD results. To deal with the COD, hydrogen peroxide can be added to the water in small concentrations (300–500 mg/L) and subject it to UV treatment. This combination of processes may oxidize organic and inorganic matter present in the water [21]. COD can be also reduced by coagulation and flocculation or by microbial action [31].

4. Conclusions

The effect of a combination of conventional treatment with membrane technology was investigated for the untreated (pre-treated) oilfields wastewater. Untreated and treated water samples were tested and compared with the parameters set by the Kuwait Environment Public Authority (KEPA) to verify its suitability for irrigation and disposal. The following conclusions can be drawn based on the results of this study:

- High percentage of reduction was shown for TSS, TDS, ammonia, TKN, sulfide, turbidity, phosphate, and BOD_5 with a reduction percentage of 94.23%, 95.86%, 76.47%, 80.39%, 94.59%, 98.0%, 54.54%, 80.19%, respectively. The results obtained were within KEPA standard limits for irrigation, as well as disposal.
- COD showed high concentration after the treatment that requires further treatment by utilizing hydrogen peroxide and UV treatment.
- Dissolved oxygen concentration was higher than KEPA standard limits in the treated water. Extra aeration and reverse osmosis could be the reason for the high level. It is recommended to control the flow rate using well-maintained and adequately calibrated dissolved-oxygen meters to control its level for the eventual proper operational management of produced water.
- Combination of conventional and membrane technology with RO will increase the overall systems recovery and can provide investment savings due to smaller intake

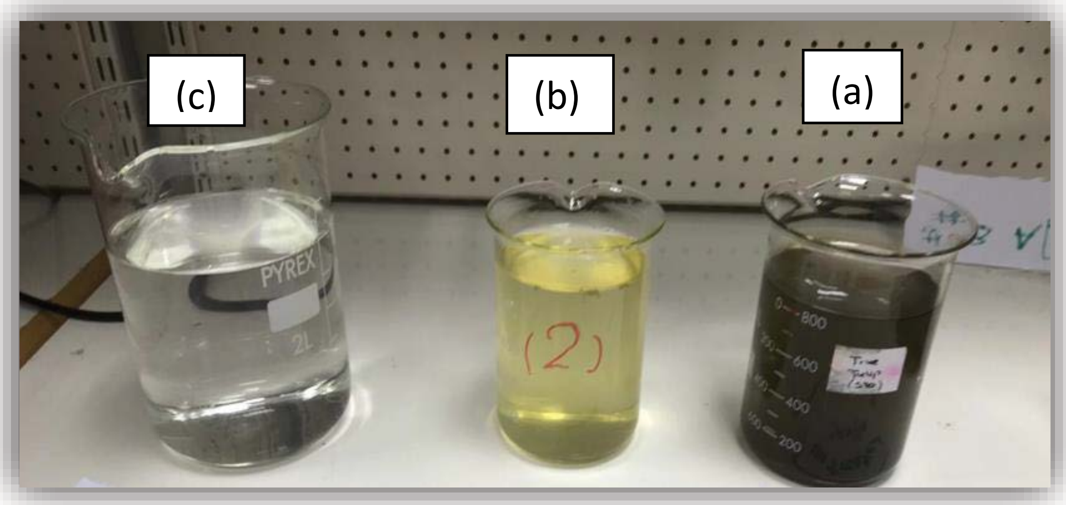

Fig. 6. (a) Untreated water, (b) water after clarifier, and (c) water after the membrane treatment.

systems, less space, and operational savings due to lower pumping requirements.
- Membrane has to be an integral part of the oilfield treatment process which underwent pre-treatment procedures normally undergone by wastewater, in combination with the conventional treatment method.

Declarations

We confirm that this manuscript has not been published elsewhere and is not under consideration in whole or in part by another journal. All authors have approved the manuscript and agree with submission to the journal Sustainable Environment Research. The authors have no conflicts of interest to declare.

Availability of data and materials

All data generated or analyzed during this study are included in this published article.

Competing interests

The authors declare that they have no competing interests.

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Authors' contributions

RM designed, analyzed, and interpreted the results, and was a major contributor in writing the manuscript. SM enhanced and edited the manuscript for final publication. ANS, AMA, and MB conducted the experiments. All authors read and approved the final manuscript.

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