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Desalination of produced water from oil production fields by membrane processes

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Abstract

Water co-produced with oil and gas is termed produced water. Produced water is very difficult wastewater to treat and characteristics changes by well to well. In this study, treatability of produced water generated from oil production fields in Trakya region which is operated by National Oil and Natural Gas Company of Turkey was investigated. The aim of this study is to investigate the pre-treatment alternatives of reverse osmosis and nanofiltration membranes and find the most appropriate treatment combination. Management of produced water was also evaluated. Dissolved air floatation (DAF), acid cracking (AC), coagulation (CA) with lime and precipitation, cartridge filters (CDF) (5 and 1 μm), microfiltration (MF) and ultrafiltration (UF) were used as pre-treatment techniques, and nanofiltration (NF) and reverse osmosis (RO) were carried out to reduce salt content of produced water as a final treatment. Different combinations were tried to determine the best pre-treatment combination regarding both the best effluent water quality and high permeate flux. According to the experimental results, treatment combinations provided required treatment to reach discharge standard for COD which is 250 mg/L for petroleum industry in Turkey. However, different treatment combinations should be applied to reach the discharge standard for sodium.

Keywords: Oil production; Produced water; Desalination; Membrane treatment

1. Introduction

Oil is one of the main energy sources of worldwide and its production is a very essential issue. While oil is produced, some unfavourable effects in the environment occur. Produced water, which is produced during oil production, is one of the most important sources of unfavourable effects. Volume of this wastewater is around 70% of total wastewater produced during oil production [1]. In many instances, this waste stream is seven to eight times greater by volume than oil produced at any given oilfield [2,3]. Produced water is separated from oil or

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gas at the head of the production well. While 65% of this water is re-injected to the well for pressure maintenance, 30% of total is injected to deep well for final disposal in the case of proper aquifer conditions and the rest of the water is discharged to surface water. The water, which is not re-injected to the production well, has to be treated. Feeding groundwater, irrigation and maintaining wetland habitats are the potential options for reuse [4,5]. Additionally, the water re-injected to the well must also be treated due to effects on the reservoir composition. Sometimes an aquifer having appropriate formation conditions cannot be available.

Produced water has distinctive characteristics due to organic and inorganic matters. It includes largely salts and oil hydrocarbons which may be toxic to environment. Produced water is variable and can be very different by well to well. Besides, characteristics of produced water from oil and gas fields can also be very variable.

Many studies have been carried out on produced water from oil fields. Physical and chemical separation processes such as coagulation, acidification and membrane processes have been performed. However, these processes alone did not provide the petroleum waste discharge standards [6]. Successful treatment of produced water generally requires a series of pre-treatment operations to remove different contaminants. Separation techniques that have been tested for the removal of oil, grease, and suspended solids from produced water include walnut shell filtration, fiber ball media filtration, gravity-type cross flow pack separation, ceramic cross flow microfiltration and ultrafiltration [7]. Removal of organic compounds from produced water is carried out by electroflocculation, adsorption, bioreactors, wetlands, ultrafiltration, nanofiltration and reverse osmosis. After appropriate pre-treatment, the high total dissolved solids (TDS) can be removed from produced water by reverse osmosis [7].

There are about 40 oil and gas production wells which produce small amounts of produced water each day in the oil and gas production site (Trakya) which is at the northwest of Turkey. In this site, the portion of the produced water discharged to deep well for final disposal, is coming up to the ground level just after injected to well. This means that deep well injection cannot be a solution for final disposal of produced water in this site. For this reason, this wastewater should be treated before disposal to environment.

It is not possible to design appropriate treatment plant according to literature for produced water because of different characteristics of water. Detailed experimental investigation should be carried out before deciding the final treatment method. The aim of this paper is to compare different treatment methods, especially membrane technologies and determine the best pre- and final treatment systems.

2. Materials and method

2.1. Experimental setup

The experimental system supplied by Osmonics Inc. (Sepa CF lab-scale 316SS membrane cell) was used during membrane experiments. Detailed explanation of experimental set up is given in previous papers [8,9]. Schematic diagram of experimental setup was shown in Fig. 1. The concentrate stream was flowed back to the feed vessel while permeate stream was being collected separately. All experiments were carried out at constant temperature of 25 ± 1°C. Heat exchanger was used as cooling system. Tap water was flowed into thin spiral cooper pipe to keep constant temperature in the feed tank. Firstly, the water was passed from cartridge filter. Then, the water was pumped by high pressure pump to membrane unit. Permeate was collected in a beaker in order to determine the permeate flux.

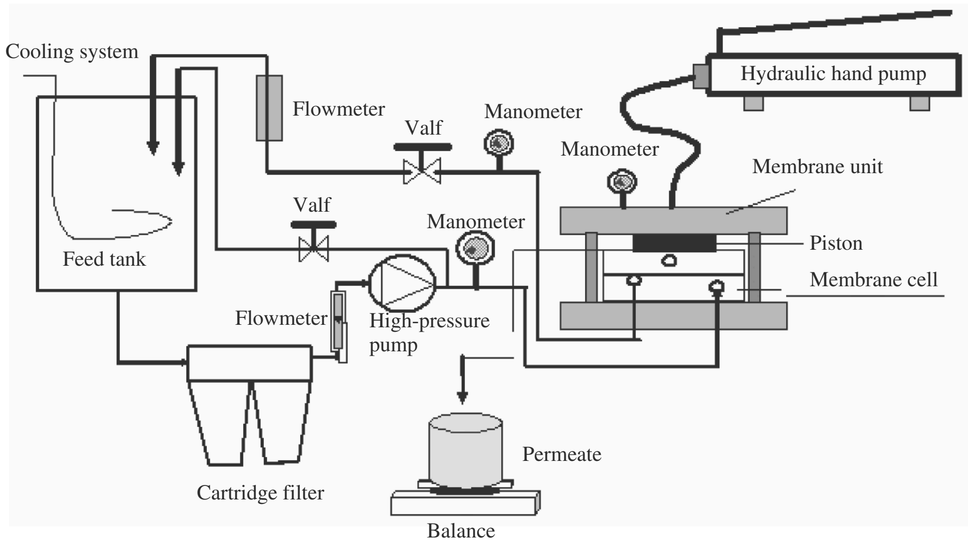

Fig. 1. Schematic diagram of experimental setup.

2.2. Membranes

Surface area of membrane was 155 cm^2. Technical information of membranes used in experiments is given in Table 1.

2.3. Parameters

Parameters in Turkish water pollution control regulation for oil industry: hydrocarbon production plants (TWPCR) [10] were used

Table 1
Technical information of membrane types

Parameters	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse osmosis (RO)	
				RO1	RO2
	–	MW	NF200	ST10	AG
Polymer type	Cellulose acetate	Ultrafilic	Polyamide thin film composite	Thin film composite	Thin film composite
Manufacturer	–	Osmonics	Film Tech	Osmonics	Osmonics
Surface area, cm^2	155	155	155	155	155
Flux/pressure, L/m^2 h/bar	–	190	7	37	44
Maximum pressure, bar	–	5	41	–	–
Operation pressure, bar	1	2	5–20	5–25	5–25
Maximum temperature, °C	50	–	45	50	50
pH	2–11	1–10	2–10	2–11	4–11
MWCO	0.2[a]	100,000	200–300	200	300
Removal efficiency, %	–		90 ($MgSO_4$)	98.2 (NaCl)	99.5 (NaCl)

[a]Pore size as μm.

during experiments. The experimental results of the study were compared with the standards in TWPCR. Flux, temperature, pH, conductivity, salinity, total dissolved solid (TDS), sodium, chloride and chemical oxygen demand (COD) were measured in raw and treated water. In addition to these parameters, the whole parameters in TWPCR were measured in raw wastewater.

2.4. Wastewater characterization

Two different types of wastewater supplied from different two production wells were studied during experiments: Vakıflar (oil and gas production well) and Devecatagi (only oil production well). Produced water characteristics of these wells are given in Table 2. COD, conductivity, sodium and chloride values of Vakıflar produced water were very high in July 2006. The highest

Table 2
Raw produced water characteristics of Vakıflar and Devecatagi well

Parameters	Vakıflar				Devecatagi	Standard values in TWPCR for petroleum industry [10]
	June 2005 [11]	July 2006 ITU (in this research)	June 2005 [12]	June 2005 [13]	July 2006 ITU (in this research)	
		–	Unmixed sample	Settled sample		
BOD, mg/L	7000	–	–	–	–	
COD, mg/L	24,500	1681	3480	–	588	250
SS, mg/L	35,830	–	606	132	–	100
NH_4-N, mg/L	2.4	–	14.5	–	–	10
Phenol, mg/L	10	–	0.59	–	–	1
CN^-, mg/L	<0.01	–	0.005	–	–	0.5
Oil and grease, mg/L	1565	–	472	–	–	10
Total salinity, ‰	–	7.2	8.2	–	7.13	
Free chlorine, mg/L	<0.02	–	–	–	–	
pH	7.85	7.8	7.87	–	7.1	6–9
Conductivity, µS/cm	–	18,770	14,322	–	47,600	
Na^+, mg/L	3165	4480	4096	–	18,900	200
Cl^-, mg/L	–	3199	4004	–	16,745	
SO_4^{-2}, mg/L	355	–	390		–	1700
Cd, mg/L	<0.15	–	0.001	0.001	–	0.1
Co, mg/L	–	–	–	–	–	
Cr, mg/L	1.75	–	–	–	–	0.2
Cu, mg/L	0.98	–	0.01	0.002	–	0.5
Fe, mg/L	30	–	1.63	0.25	–	8
Ni, mg/L	–	–	0.004	0.004	–	
Zn, mg/L	2.22	–	0.001	0.001	0.225	0.5
Pb, mg/L	0.52	–	0.006	0.003	–	0.5
Alkalinity, mg/L $CaCO_3$	–	–	–	–	–	
Total sulphate, mg/L	1.7	–	13.6	–	–	

salinity was measured at the Devecatagi well and the conductivity of this well was measured as 47,600 μS/cm. Conductivity of produced water in Vakıflar varied between 14,000 and 18,700 μS/cm. The biggest contribution to conductivity was coming from sodium and chloride ions. Besides, the highest COD values were measured at the Vakıflar well and it varied between 1681 and 24,500 mg/L.

2.5. Membrane treatment strategies

Summary of membrane treatment strategies applied in experimental studies are given in Table 3. Firstly, water was passed through the 5 and 1 μm filters to remove larger particles. Then, MF and UF membranes were used as a pre-treatment before RO and NF membranes. Acid cracking (AC) was applied to crack the organic materials as another pre-treatment method. After that, dissolved organics coagulated with lime and coagulated wastewater was then applied to MF and then RO membranes. Dissolved air flotation (DAF) + coagulation were used to separate oil.

3. Results and discussion

3.1. Treatability studies on Vakıflar produced water

A series of treatability studies were performed with Vakıflar produced water. Studies were concentrated on the best pre-treatment methods before the reverse osmosis and nanofiltration units. 5 and 1 μm cartridge filters, 0.2 μm MF and ultrafiltration membranes were used as pre-treatment units. Additionally, acid cracking + coagulation with lime, flotation + coagulation with lime and only flotation were studied as a pre-treatment before 0.2 μm MF membranes.

Fluxes versus time graph at 20 bar pressure for RO and 10 bar pressure for NF membranes which is obtained after different pre-treatment combinations are shown in Fig. 2. Besides, permeate water quality parameters are given in Table 4. In all experiments, raw wastewater was passed through the 1 μm cartridge filter.

RO1 membrane was more dense membrane than RO2 membrane. For this reason, low flux values were obtained with RO1 membrane at 20 bar pressure. UF + RO1 combination gave very high flux values compared to MF + RO1 and only RO1 membranes. Flux values of UF + RO2 and MF + RO2 membranes were almost the same. However, very low flux values were obtained after acid cracking + precipitation pre-treatment. This was probably due to the changes on organic matter characteristics after acid cracking. After an addition of acid, high molecular weight organic matters were dissolved to low molecular weight organic matters and they passed easily through the RO2 membrane. Dissolved air flotation

Table 3
Membrane treatment strategies of produced water

Vakıflar	Devecatagi
5 μm + 1 μm + RO1	5 μm + 1 μm + RO2
0.2 μm MF + RO1	0.2 μm MF + RO2
UF + RO1	UF + RO2
0.2 μm MF + RO2	AC + CA + 0.2 μm MF + RO2
UF + RO2	0.2 μm MF + NF
AC + CA + 0.2 μm MF + RO2	
DAF + 0.2 μm MF + RO2	
DAF + CA + 0.2 μm MF + RO2	
0.2 μm MF + NF	

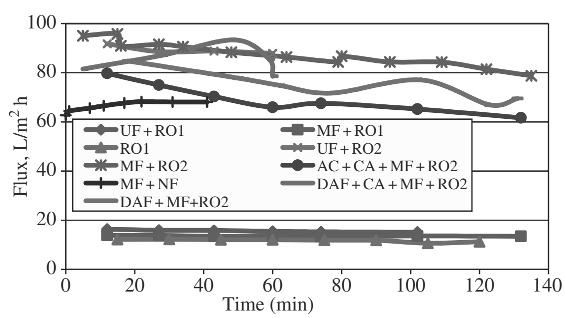

Fig. 2. Flux versus time graph for Vakıflar produced water.

Table 4
Treatment effluents of Vakıflar produced water

Parameter	RO1	MF + RO1		UF + RO1		MF + RO2		UF + RO2		AC + CA + 0.2 µm MF + RO2	MF + NF		DAF + 0.2 µm MF + RO2		DAF + CA with lime + 0.2 µm MF + RO2		
		0.2 µm MF	RO1	UF	RO1	0.2 µm MF	RO2	UF	RO2	RO2	MF	NF	DAF + 0.2 µm MF	RO2	DAF + CA with lime	0.2 µm MF	RO2
COD, mg/L	180	1483	201	1446	485	1483	34	1446	53	145	1483	137	1532	<30	1740	1663	<30
Conductivity, µS/cm	11,130	11,130	1164	9970	1094	11,130	373	9970	621	340	11,130	4320	12,680	363	12,680	12,470	516
TDS, mg/L	554	6510	573	6670	573	6510	196	6670	299	162	6510	2240	6830	170.1	6940	6800	249
Sodium, mg/L	492	5169	416	5277	416	5169	184	5277	123	156	5169	1059	4280	156	4850	4650	201
Chlorine, mg/L	300	2949	325	3074	325	2949	100	3074	150	75	2949	1200	3199	200	–	3124	125
Salinity, ‰	0.5	6.7	0.6	6.9	0.6	6.7	0.2	6.9	0.3	0.2	6.7	2.3	7.1	0.2	7.2	7.0	0.2
pH	7.4	8.0	7.4	8.0	7.4	8.0	7.6	8.0	7.9	8.8	8.0	7.6	8.35	8.93	8.59	8.56	9.02
Zn, mg/L	–	–	–	–	–	0.304	–	–	–	–	–	–	–	–	–	–	–
Cr, mg/L	–	–	–	–	–	0.236	–	–	–	–	–	–	–	–	–	–	–
Cu, mg/L	–	–	–	–	–	2.458	–	–	–	–	–	–	–	–	–	–	–

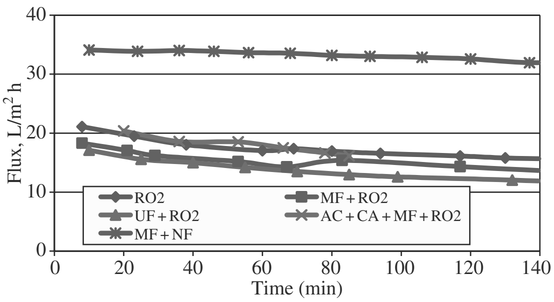

Fig. 3. Flux versus time graph for Devecatagi produced water.

and precipitation with lime before RO2 membrane did not affect the flux values. Fluxes of NF membrane at 10 bar pressure were lower compared to fluxes of RO2 membrane at 20 bar pressure. However, there was no flux decline during NF run.

Permeate water qualities of RO2 membrane supplied the discharge standards of TWPCR. DAF + 0.2 μm MF + RO2 membrane combination gave the best permeate water quality especially by means of COD parameter. NF permeate also supplied the COD parameter. However, salt content was very high in NF permeate due to the monovalent ions and did not supply the sodium standard in TWPCR. According to these permeate qualities, RO2 permeate can be used for irrigation.

3.2. Treatability studies on Devecatagi produced water

A series of treatability studies were performed for Devecatagi produced water. Reverse osmosis and nanofiltration were used as final treatment units. Permeate flux versus time graph for Devecatagi produced water is shown in Fig. 3. The highest flux values were obtained with NF membrane while there were almost no differences on RO flux values with different pre-treatment combinations. NF membrane fluxes did not decrease with time while flux decline was observed for RO2 membrane.

The results of permeate qualities are given in Table 5. Permeate COD value supplied the discharge standards after RO2 membrane. However, salt concentration was high due to the high feed salt content although 87% of removal efficiency was achieved for sodium. Two pass-RO systems can be applied or the treated water should be recycled to the influent of RO2 in order to dilute the feed and cover TWPCR limit values for sodium. MF + NF system did not supply the TWPCR limit values of COD and sodium.

Table 5
Treatment effluents of Devecatagi oil well produced water

Parameters	RO2	MF + RO2		UF + RO2		AC + CA + 0.2 μm MF + RO2	MF + NF	
		0.2 μm MF	RO2	UF	RO2		MF	NF
COD, mg/L	208	781	108	710	131	175	781	316
Conductivity, μS/cm	7480	45,700	3340	44,700	5110	5230	45,700	32,500
TDS, mg/L	4040	28,400	1726	27,500	2690	2730	28,400	19,750
Sodium, mg/L	2500	19,700	1640	19,300	1890	1800	19,700	7620
Chlorine, mg/L	2299	15,745	1000	15,895	1829	1500	15,745	11,147
Salinity, ‰	4.2	29.5	1.8	28.6	2.7	2.8	29.5	20.5
pH	6.7	7.2	7	7.4	7.2	8.3	7.2	7.2
Zn, mg/L	–	–	–	–	–	0.200	–	–
Cr, mg/L	–	–	–	–	–	–	–	–
Cu, mg/L	–	–	0.299	–	–	0.201	–	–

4. Management of produced water at oil production fields

4.1. Proposed treatment method

According to the experimental results, schematic diagram of the proposed treatment method is given in Fig. 4. After primary sedimentation, oil separated from water. Then, DAF system is applied to remove smaller oil particles. After that, 1 µm ceramic or metallic cartridge filter and 0.2 µm ceramic or metallic microfiltration is used to remove very small particles. Finally, activated carbon adsorption is applied to remove any organic matter before RO membrane.

4.2. Management of produced water and cost analysis

There are about 40 oil and gas production wells in Trakya region. All of them produce very small amounts of produced water. The daily total average is about 100 m^3/day. For this reason, different management options were investigated for the region in this study. Schematic flow diagram of the proposed management options are shown in Fig. 5.

Four alternatives were evaluated for collection and treatment of oil production wastewaters. Firstly, wastewater wells, which have low flowrate, may be collected at four intermediate stations and treated by one mobile membrane treatment unit. Mobile membrane plant consists of 1 µm cartridge filter, 0.2 µm MF, activated carbon adsorption and RO units. Other pre-treatments which are proposed are constructed in four different intermediate stations. Secondly, wastewater of well which have low flowrate may be collected at three intermediate stations and treated by one mobile treatment unit. Thirdly, production wastewaters may be collected at one place and treated in place. There is no mobile membrane plant in this option. Fourth option is collecting the wastewater at three main stations and treating in site by different three membrane plants. There is also no mobile plant in this option.

Cost analysis of alternatives is summarized in Table 6. According to cost analysis, third option which consists of only one membrane plant gave the cheapest solution. The unit costs of other alternatives were almost the same. Third option can be constructed if the company guarantees the transportation of wastewater between intermediate stations. The distance is about 100 km. For this reason, there may be some problems on collecting the wastewaters at one place and establishing only one membrane plant. There may be transportation problem. For this reason, fourth alternative may be a best solution by means of flexibility of three membrane plants. If one membrane plant damaged, the other ones can be used for treatment.

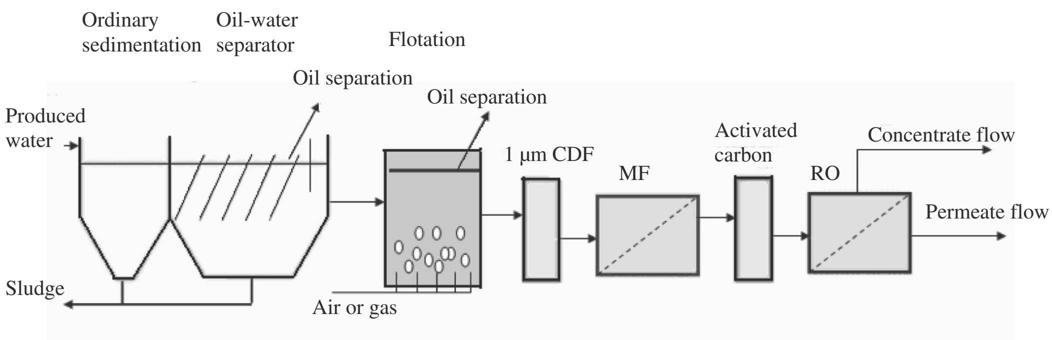

Fig. 4. Proposed treatment alternative for oil production wastewater.

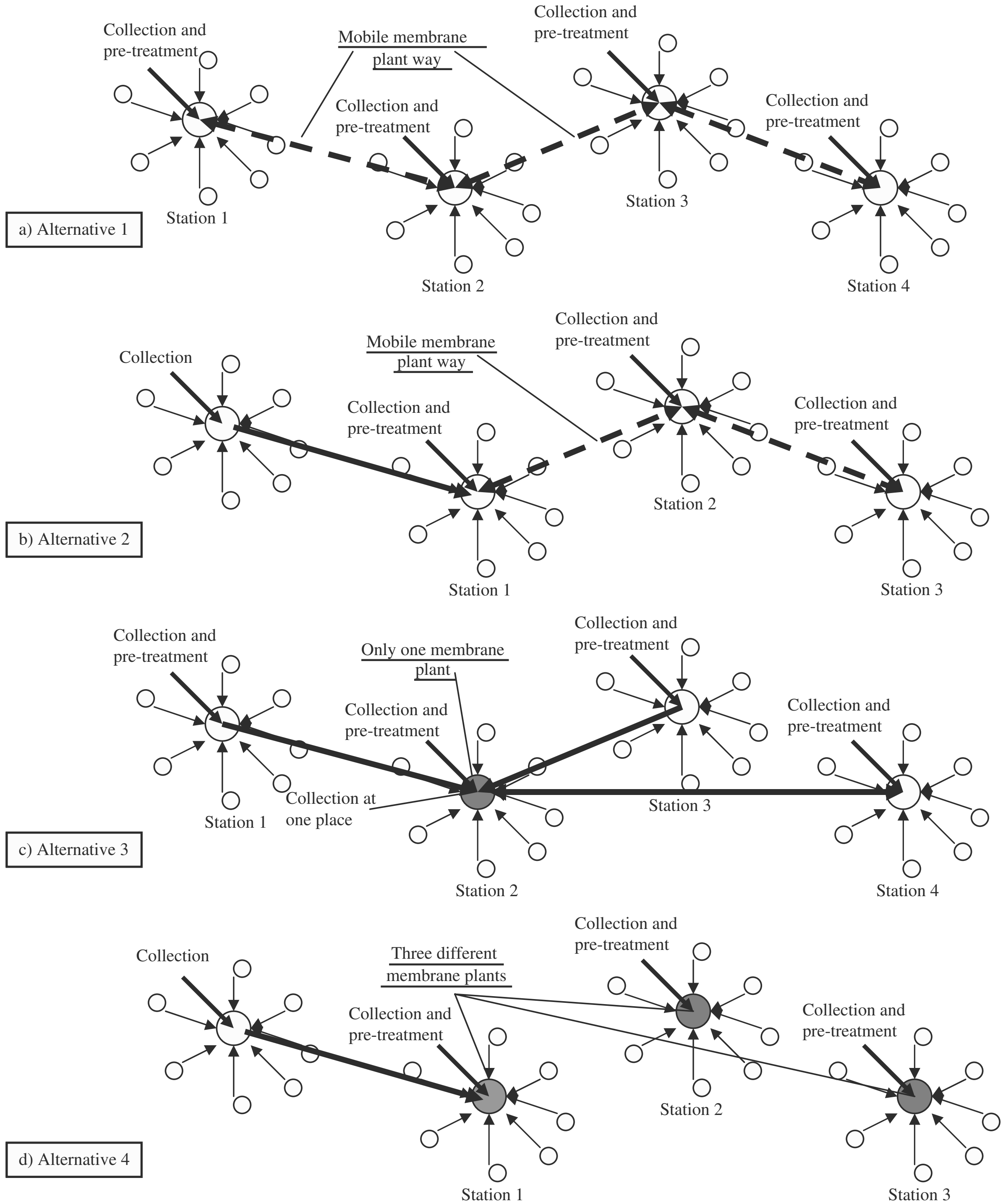

Fig. 5. Management alternatives for produced water from oil production fields.

Table 6
Cost of collection and treatment alternatives for oil produced water

Alternatives	Capital cost ($)	Operation cost ($/year)	Capital cost ($/m³)	Unit operation costs						Total unit cost ($/m³)
				Fuel needs of tankers for transportation of waters to intermediate stations ($/m³)	Cost of pre-treatment established at intermediate stations ($/m³)	Fuel cost of mobile plant ($/m³)	Cost of pre-treatment with membrane ($/m³)	Cost of RO system ($/m³)	Cost of workmanship ($/m³)	
1	218,000	140,500	1.57	1.00	0.60	0.58	0.72	1.15	0.35	5.97
2	215,000	141,500	1.55	1.05	0.58	0.58	0.72	1.15	0.35	5.98
3	172,000	125,000	1.24	1.30	0.43	0	0.72	1.15	0.35	5.19
4	200,000	121,500	1.44	1.05	0.58	0	0.72	1.15	1.04	5.98

5. Conclusions

Although NF membrane supplied the COD discharge standards, salt concentration was high in permeate. Thus, RO membrane can be effectively applied for the treatment of produced water after appropriate pre-treatment. The experimental results showed that primary sedimentation + oil/water separator + DAF system + 1 μm ceramic or metallic cartridge filte + 0.2 μm ceramic or metallic MF gave the best pre-treatment option by means of permeate flux and water quality before RO membrane. Activated carbon adsorption can also be used which we could not investigate between 0.2 μm MF and RO membranes. According to cost analysis, collecting wastewater and establishing only one membrane plant at one place gave the cheapest solution. However, fourth alternative which is collecting the wastewater at three main stations and treating in site by different three membrane plants may be a best solution by means of flexibility of three membrane plants. Additionally, pilot scale experiments should be carried out for final decision.

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