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Use of flocculated magnetic separation technology to treat Iraqi oilfield co-produced water for injection purpose

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ABSTRACT

Bench-scale simulation of flocculated magnetic separation (FMS) technology was performed using a jar-tester to treat produced water from four Iraqi oilfields. The results revealed that effluent water with low oil content and suspended solid can be achieved. Settling time for FMS is several times less than that of conventional process. These features make FMS, followed by a polishing oil removal step, such as nutshell filters, attractive to treat Iraqi produced water for injection purpose.

Keywords: Flocculated magnetic separation; Oil removal; Produced water

1. Introduction

Produced water is water trapped in underground formations that is brought to the surface along with oil and gas. It may include water from the reservoir, water injected into the formation, and any chemicals added during production and treatment processes. Produced water is not a single commodity. The major constituents of concern in produced water are salt content, oil and grease, various natural inorganic and organic compounds or chemical additive used in drilling and operating the well, natural occurring radioactive material. These produce water constituents are in general is harmful to the environment. Produced water is by far the largest volume by-product or waste stream associated with oil and gas exploration and production [1–3].

Iraqi oilfields are dispersed over vast areas. The water-to-oil may reach 20% in some mature oil fields especially in southern and northern parts of Iraq. This ratio may reach the world average in the near future [4]. There is a growing need to water flooding process in some Iraqi oilfields to sustain the productivity of these fields. In year 2010, Exxon Mobil oil company has been picked to lead a “multibillion-dollar” water-injection project on behalf of international oil companies that won contracts in southern Iraqi oilfields in the two auctions Iraq held year 2009 [5]. Produced water is a possible source for water injection operations. For the re-injection of produced water residual oil and suspended solids (SSs) should be removed.

The first step of the oil production process involves separating the oil, gas, and water into different streams where they can be managed appropriately. In Iraq, this is typically accomplished by gravity separation system. This system includes four step gas separators. Between the second and the third gas separation steps, the produced water separation process is accomplished by a dehydrator unit and then desalter unit in which the crude-oil washing with fresh water is accomplished. A typical dehydration/desalting operation usually comprises the following

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six major steps: water-in-oil emulsion breaker injection, separation by electrical coalescing and gravity settling, addition of fresh (less salty) water, electrical coalescing and gravity settling. The treatment involves allocating time till water drops settled out and be drained off [1,6]. Produced water separated by this process contains residual oil and SSs. For the re-injection of produced water, residual oil and SSs should be removed.

Conventional treatment of PWs includes gravity separation and skimming, dissolved air flotation, de-emulsification, coagulation, and flocculation [7]. Coagulation plays a vital role in enhancing air flotation process to remove high level of oil, SS, reductive substances, bacteria in the oilfield wastewater [8]. Coagulation sedimentation may be used to remove a large portion of oil and SS from produced water. Settling time is a governing factor for equipment sizing of this technology. It can be reduced and consequently reduce the size of the separation equipment by using magnetic separation process.

Magnetic separation of pollutants from water is not a new process, as it has already been widely used to remove kaolin, to treat magnetic mineral ores and for the removal of ferromagnetic impurities from mixtures [9]. Moreover, there are studies about removal of heavy metals, turbidity using this technology [10–13]. This technique involves the adsorption of pollutants on the surface of iron oxide power. On the other hand, flocculated magnetic separation (FMS) technology involves the encapsulation of the ferromagnetic particles with the flocculated pollutant resulting in a heavier floc which can be settled faster with the aid of permanent magnet.

The FMS is one of the advance technologies in removing oil emulsion from wastewater, including SSs. In this process, a flocculation agent and ferromagnetic powder is added to the produced water. The flocs formed can be separated by a magnetic separator with a settling velocity many times higher than settling velocity by gravity alone resulting in efficient small footprint separation equipment [14,15]. The aim of this research is to characterize and to investigate the efficiency of FMS technology to remove the residual oil and SS content from produced water of four oilfields in the southern parts of Iraq.

2. Materials and methods

Bench-scale simulations of conventional and FMS mode have been performed using a jar-tester to treat synthetic oily water as well as produced water from four Iraqi oilfields, hyper-saline water. The jar was capable for testing 8 L water. Based on a previous analysis of total dissolved solid and oil content of produced water from Missan Iraqi oil fields, synthetic water was prepared in stirred tank through mixing 3 mL crude oil with 8 L water containing 100,000 mg/L dissolved NaCl by using high-speed mixer with 10,000 rpm. After mixing for about 30 min, the water was left in the jar for about 24 h to clarify and to remove floating free oil. The resultant oily water was analyzed for oil content.

Using synthetic oily water, different chemical coagulant doses of 100, 50, 20, 10 mg/L ($FeCl_3$), and 5 mg/L polyacrylamide polyelectrolyte were tested for conventional coagulation mode and along with 100, 200, 400 mg/L ferromagnetic particles (88–74, 37–25 μm) for FMS mode while stirred with 300 rpm for 1 min. Then, two slow mixing periods with 50 and 25 rpm, respectively, for 1.5 min each. FMS mode settling was done by placing the jar on a disc magnet of 5,000 gauss to attract the magnetic flocs containing oil particulates and ferromagnetic particles.

The applicability of FMS technology to treat the oilfields produced water has been tested. The total Fe in three of these produced waters was relatively high. In these cases, the pH of the water is adjusted to 8 to enhance the oxidation of ferrous ion by using NaOH solution. The oxidation of Fe^{2+} ions was done by the addition of 8 mL of 5% free chlorine solution to 8 L of the produced water resulting in 50 mg/L free chlorine in the produced water. All the Fe^{2+} ion have been oxidized to ferric ion and the final pH was being 7.0. Precipitated ferric ions will act as a coagulant and no additional dose of $FeCl_3$ is needed. Only 2 mg/L of cationic polyelectrolyte is used as flocculent along with 200 mg/L ferromagnetic particles (88–74 μm) for FMS mode while stirred with 300 rpm for 1 min. Then, as mentioned previously, two slow mixing periods with 50 and 25 rpm, respectively, for 1.5 min each. FMS mode settling was done by placing the jar on a disc magnet of 5,000 gauss for 2 min to attract the magnetic flocs containing oil particulates and ferromagnetic particles.

Nutshell filtration of the treated water has been performed using a glass column of 7.5 mm ID and 1.5 m height. The column was filled with 1 m bed depth of nutshell particles. The nutshell bed had particle size ranged from 2 to 4 mm. The filtration of the 8 L treated water was done by flowing through the nutshell by gravity. Recovery of the ferromagnetic particles was investigated by washing the flocs collected from all the experiments, twice, with kerosene with stirring with 300 rpm for 15 min then flushing with water and drying them at 250˚C for 1 h.

Raw and treated water oil content was measured. CCl_4 was used as an extractor. The analysis of oil in water was done using oil in water analyzer based on IR spectrophotometry (OCMA-350, Horiba). Total organic carbon (TOC) and chemical oxygen demand (COD) (with correction for Cl^-) were measured using spectrophotometer (DR-5000, Hach). Turbidity is measured using turbidity analyzer (TurbiDirect, Lovibond). pH was measured using portable meter (pH3110, WTW). Electrical conductivity was measured using conductivity analyzer (Cond 315i, WTW). TDS, SS, and inorganic ions concentrations were measured using standard methods [16]. Micrographs of the flocs were done using optical microscope connected to a camera.

3. Results and discussion

About 50 L produced water samples, each, were supplied from four Iraqi oil fields in the southern region of Iraq. These fields are Rumaila North, Rumaila South, Al-Zubair, and Qurna West. Produced water characteristics of the samples are given in Table 1. It is clear that the oil content of the produced water is relatively low in comparison with produced water oil content shown in literature [2,10–12]. The total dissolved solid is high; about eight times that of seawater. The chloride and sodium are the dominant ions. Such water is characterized as a hyper-saline water chloride type. Total hardness is relatively high. Total Fe concentration is high. This may be a piping and equipments corrosion product attributed to the low pH and very high TDS of the produced water.

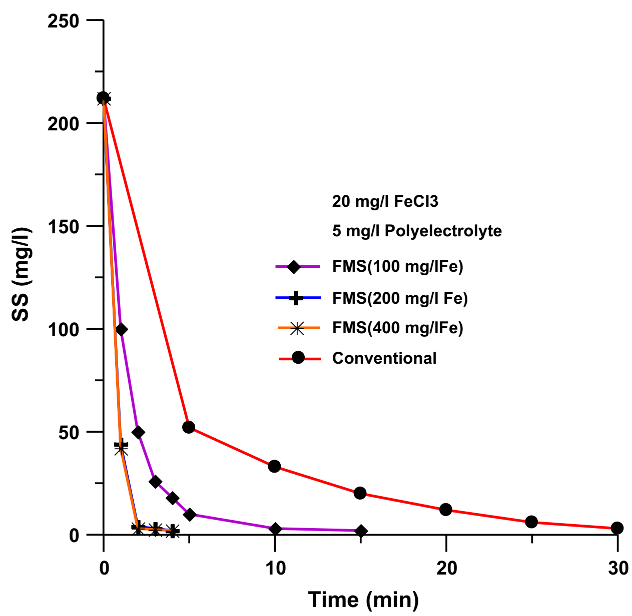

Fig. 1. SS variation during settling for synthetic oily water using different ferromagnetic particles doses.

Table 1
Characteristics of the produced water of the four oilfields

Analysis	Rumaila North	Rumaila South	Al-Zubair	Qurna West
pH	4.8	4.1	6.62	4.9
Conductivity, μS/cm	280,000	278,000	268,000	300,000
TDS, mg/L	247,000	246,000	238,000	264,000
TSS, mg/L	141	260	110	75
TH, mg/L as $CaCO_3$	54,000	40,000	50,000	43,000
Alkalinity, mg/L as HCO_3^-	238	110	262	347
Oil content, mg/L	36	53	66	57
Oil content$_{filtrated}$, mg/L	4	5	16	10
COD, mg/L	800	1,400	1,800	1,500
COD$_{filtrated}$, mg/L	108	150	380	260
TOC, mg/L	300	500	610	520
TOC$_{filtrated}$, mg/L	12	20	125	80
S^{2-}, mg/L	0.156	0.165	0.625	0.133
SO_4^{2-}, mg/L	108	116	104	94
Fe^{2+}, mg/L	18	10	0.6	0.61
Total Fe, mg/L	98	110	50	2.4
Mn^{2+}, mg/L	2.5	1	2.2	1.5
Ca^{2+}, mg/L	17,234	12,826	14,028	12,024
Mg^{2+}, mg/L	2,655	1,930	3,632	3,148
Na^+, mg/L	89,000	91,000	87,000	98,000
Cl^-, mg/L	138,000	141,000	134,000	151,000

High COD concentration may be attributed to the high particulate organic matter content in addition to fatty acids content in the produced water.

Fig. 1 shows a profile of SS of the treated synthetic wastewater during settling using different ferromagnetic particles doses along with 20 mg/L ($FeCl_3$) and 5 mg/L polyelectrolyte. It is clear that 200 mg/L is the optimum dose. The ferromagnetic particle size 88–74 μm gave similar results as 37–25 μm. Different chemical coagulant doses of 100, 50, 20, 10 mg/L ($FeCl_3$), and 5 mg/L polyelectrolyte were tested for conventional coagulation mode and along with 200 mg/L ferromagnetic particles (88–74, 37–25 μm). Best coagulant dose was 20 mg/L ($FeCl_3$) and 5 mg/L polyelectrolyte as shown in Fig. 2. The turbidity of the treated wastewater was high when using doses of 100 and 50 mg/L ($FeCl_3$) due to coagulant residue in the wastewater. Figs. 3 and 4 shows the profile of oil content and TOC of the treated wastewater using optimum coagulant and ferromagnetic particles doses, respectively. The results show the high removal efficiency of oil and SS of conventional and FMS process. A final oil concentration and SS of about 5 and 2 mg/L, respectively, can be achieved. Taking into consideration short settling time for FMS, 4 min, compared to conventional process, 30 min, a plant based on FMS has about one seventh the size and footprint of that based on conventional process.

Fig. 5 shows a typical flocs micrograph. Differs from Pickering-emulsion in which solid particles with diameter much lower than the diameter of oil colloidal

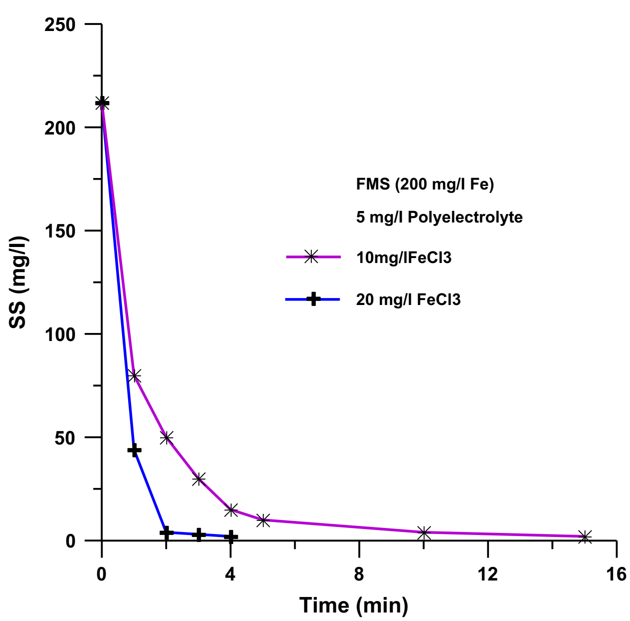

Fig. 2. SS variation during settling for synthetic oily water using two different coagulant doses.

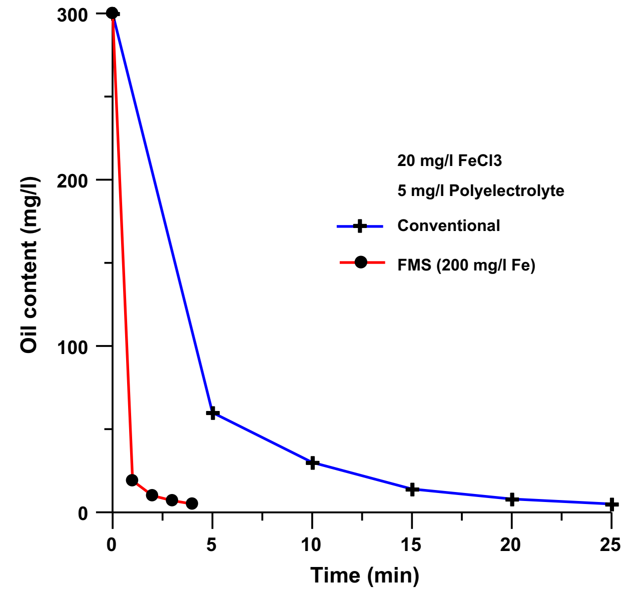

Fig. 3. Oil content variation during settling for synthetic oily water.

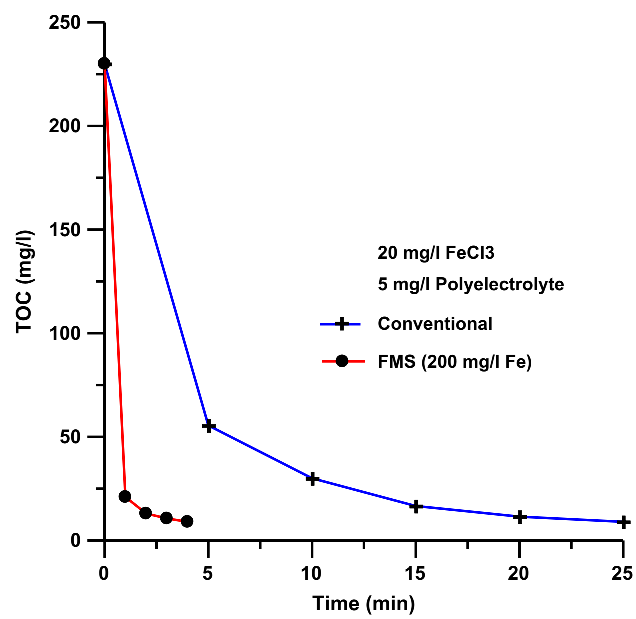

Fig. 4. TOC variation during settling for synthetic oily water.

adsorb onto interface between oil and water [17], the possible mechanism of FMS is the flocculation of oil colloidal together with the ferromagnetic particles and the formation of ferromagnetic particles containing flocs that can be separated easily by a magnetic field.

Table 2 presents the treated water characteristics for the four Iraqi oilfields produced water using FMS.

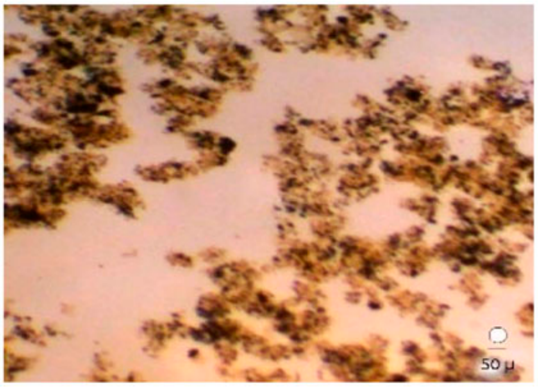

Fig. 5. Micrograph of flocs for synthetic oily water.

Table 2
Treated water characteristics for the four oilfields by FMS

Analysis	Rumaila North	Rumaila South	Al-Zubair	Qurna West
Coagulant dose				
$FeCl_3$, mg/L	*	*	*	20
Polyelectrolyte, mg/L	2	2	2	2
Ferromagnetic particles (88–74 μm), mg/L	200	200	200	200
Effluent analysis				
Oil content, mg/L	5	6.8	17	11.5
TSS, mg/L	15	30	20	20
COD, mg/L	108	180	400	250
TOC, mg/L	15	25	65	40
pH	7.0	7.5	7.5	7.2
Total Fe, mg/L	0.30	2.4	4	2.6
Fe^{2+}, mg/L	0.22	0.6	0.6	0.6
After nutshell filter				
Oil content, mg/L	4	5	16	11
TSS, mg/L	Non	Non	Non	Non
Turbidity, NTU	2.2	2.4	2.1	1.1

*Precipitated ferric ions act as coagulant and no additional dose of $FeCl_3$ is needed.

The settling time was 2 min. In comparison with data in Table 1, it is clear that oil contents in the treated water are approximately equal to the filtrated oil content in the raw water samples. TSS is relatively high after treatment by FMS only. After nutshell filter, it is clear that all treated water samples have very low TSS, turbidity, and dissolved oil content oil which may be suitable for reinjection. About 85% recovery of the ferromagnetic particles was achieved. These features make FMS, followed a polishing oil removal step, such as nutshell filters, suitable to treat Iraqi produced water for injection purpose.

4. Conclusions

In this study, the characterization of produced water from four Iraqi oil fields, and the treatability to remove oil content and SSs using FMS technology, to be suitable for injection purpose, was investigated. The water quality characterization showed that these produced waters were hyper-saline water chloride type with relatively low oil content. Injection is the most suitable practice to manage these waters. The results of FMS experiments revealed that effluent water with low oil content and SS can be achieved. Settling time for FMS is several times less than that of conventional process. These features make FMS, followed by a polishing oil removal step, such as nutshell filters, attractive to treat Iraqi produced water from the above-mentioned oilfields for injection purpose. A pilot plant with continuous FMS process mode to test the treatability of the produced water under consideration is needed.

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