Advanced treatment of heavy oil wastewater for reuse by the combination of microwave enhanced coagulation and iron/carbon micro-electrolysis

Yong-Ming He, Ke-Yong Chen and Tian-Yu Zhang

ABSTRACT

A combination process was developed in laboratory scale including microwave (MW) coagulation and iron/carbon micro-electrolysis (Fe/C ME) in series for treatment of heavy oil produced water (HOPW) with high concentrations of oil and chemical oxygen demand and high corrosion rates. The effects of coagulant dosage, MW irradiation time, settling time, and Fe:C mass ratio on the actual treatment results were investigated. The use of MW irradiation brought some benefits including enhancing oil removal, reducing coagulation consumption, shortening settling time and lowering corrosion rate. During the 30-day continuous treatment period, the Fe-based metallic glasses/activated carbon (MGs/AC) ME system exhibited high performance stability, whereas the iron shavings/AC ME system had good performance for only 8 days. The total reduction percentages of oil, suspended solids and corrosion rate were 95.5%, 98.3% and 96.5%, respectively, in the combined MW coagulation-MGs/AC ME system, and the corrosion rate of the treated HOPW was only 0.025 mm/year. The quality parameters of the treated heavy oil produced water (HOPW) could completely meet the requirements of the C1 grade in the SY/T 5329-1994 standard for wastewater reinjection in oilfields. Moreover, the biodegradability of the HOPW was greatly improved after treatment, creating favorable conditions for subsequent biological treatment if not reinjection.

Key words | corrosion, metallic glasses, passivation, produced water, reinjection

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INTRODUCTION

During oil exploitation, a large amount of wastewater is produced in oilfields. This kind of wastewater, generally called oilfield produced water, is designated as the wastewater generated after separation from oil using three-phase separators (Lu & Wei 2011). In China, some oilfields such as the Liaohe Oilfield are abundant in heavy oil resources. Polymers, surfactants and some other chemicals are injected into heavy oil reservoirs to enhance crude oil recovery (Jiang *et al.* 2011). Thus, heavy oil produced water (HOPW) is more difficult to treat than conventional produced water due to the presence of high concentrations of polymers, surfactants and heavy mineral oil (Ji *et al.* 2009).

Traditionally, coagulation, sedimentation, filtration and their combinations are widely used to treat produced

water in many Chinese oilfields. However, these primary processing technologies have a low capability to remove soluble chemical oxygen demand (COD) and sterilize microorganisms from the wastewater, making the effluent quality not satisfy the reuse requirement for reinjection in oilfields (Wu & Wang 2009).

In general, conventional produced water could be efficiently treated by biological processes alone (Dong *et al.* 2011; Lu *et al.* 2011). However, it will be difficult to remediate HOPW through biological methods alone to meet the discharge or oilfield reinjection standards, because this wastewater generally contains polymers, surfactants, high concentrations of emulsified oil (100–200 mg/L) and COD (800–2,000 mg/L) (Zou *et al.* 2013). Ji *et al.* (2009) applied
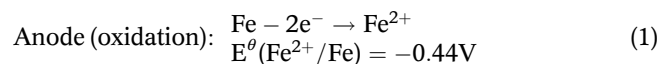
an anaerobic baffled reactor to treat HOPW, but the start-up stage was as long as 164 days and the effluent COD concentration was still up to 200–300 mg/L. More recently, Liu et al. (2013) used the combination of upflow anaerobic sludge blanket and immobilized biological aerated filter (BAF) to treat heavy oil wastewater in a pilot-scale experiment. Tong et al. (2013) conducted research on the treatment of heavy oil wastewater by a conventional activated sludge process coupled with an immobilized BAF. However, the wastewater used in these studies was a mixture of produced water and several other wastewaters, and thus the COD was reduced to around 200 mg/L. Therefore, more effective treatment is necessary for such wastewater before release into the environment or reinjection into the stratum.

Coagulation is an applicable and effective method for demulsification of oily wastewater (Ma et al. 2013). As a typical inorganic coagulant, polyaluminium chloride (PACl) was widely used as pre-treatment or post-treatment for oily wastewater due to its rapid reaction and lower price (Van Le et al. 2012; Yang et al. 2014; Hoseini et al. 2015). However, PACl also has some disadvantages such as producing small, loose and light floc, leading to increased difficulty in separation. Thus, some strengthening measures, such as preparation and application of PACl-containing composites, have been studied to improve the treatment performance (Ng et al. 2012; De Feo et al. 2013; Lu et al. 2014; Yeap et al. 2014; Tolkou & Zouboulis 2015). Nevertheless, the preparation processes for these coagulant composites are somewhat complex and involve high-cost reagents.
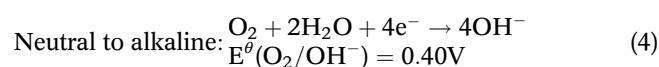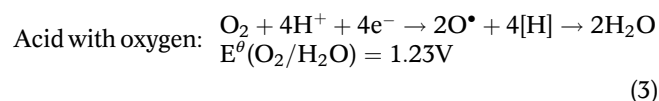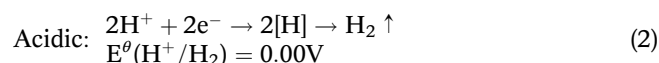
A number of studies have been performed on the microwave (MW) enhancement of demulsification of petroleum emulsions (Kuo & Lee 2010; Ferreira et al. 2013; Kang et al. 2015). MW heating offers a faster processing rate than traditional heating methods. The increase in temperature causes a reduction of viscosity and coalescence velocity of water settling, and accelerates the separation of the emulsion. A higher temperature and a lower viscosity facilitate the coagulation process, resulting in a larger droplet diameter and a more rapid separation.

Recently, the iron/carbon (Fe/C) micro-electrolysis (ME) process has become a cost-effective and operationally simple technology for treating recalcitrant wastewater including oilfield produced water (Zhu et al. 2014; Zhang

2015). Iron chips (Fe^0) and granular activated carbon (GAC) are commonly used as electrolytic materials of the Fe/C ME system. In the Fe/C ME system, GAC was added as cathode to increase the current efficiency of the Fe/C ME system because of its conductance and high adsorption capacity. When a mixture of Fe^0 and GAC is in contact with wastewater, numerous macroscopic galvanic cells are formed between Fe^0 and GAC, and also in the interior of Fe^0. The electrons are supplied from the galvanic corrosion of Fe^0 (anode), and the half-cell reactions can be represented as (Lai et al. 2013):

Anode (oxidation):
$$\text{Fe} - 2e^- \rightarrow \text{Fe}^{2+} \\ E^\theta(\text{Fe}^{2+}/\text{Fe}) = -0.44\text{V} \tag{1}$$

Cathode (reduction):

Acidic:
$$2\text{H}^+ + 2e^- \rightarrow 2[\text{H}] \rightarrow \text{H}_2 \uparrow \\ E^\theta(\text{H}^+/\text{H}_2) = 0.00\text{V} \tag{2}$$

Acid with oxygen:
$$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{O}^\bullet + 4[\text{H}] \rightarrow 2\text{H}_2\text{O} \\ E^\theta(\text{O}_2/\text{H}_2\text{O}) = 1.23\text{V} \tag{3}$$

Neutral to alkaline:
$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \\ E^\theta(\text{O}_2/\text{OH}^-) = 0.40\text{V} \tag{4}$$

Obviously, organic pollutants can be oxidized or reduced by radicals and oxidants such as free hydrogen [H] and O$^\bullet$ formed from the above electrode actions. Nevertheless, there also exist some disadvantages for the practical application of Fe/C ME, for example, easy plugging of ME materials and decreasing reactivity of iron with time because of the accumulation of corrosion products.

Over the past several decades, a large number of studies on Fe-based metallic glasses (MGs) (also called Fe-based amorphous alloys) have been developed for wastewater treatment (Lin et al. 2012; Yang et al. 2012; Kong et al. 2014; Wang et al. 2014). The Fe-based MGs are a special zero-valent iron with an amorphous structure. Unlike crystalline metals, MGs are formed by a far-from-equilibrium process and the constituent atoms do not reside at the thermodynamic equilibrium positions. The metastable nature imparts many excellent properties to amorphous alloys

that are unachievable for crystalline alloys, such as good catalytic and chemical properties, low-cost, high corrosion resistance, and excellent soft magnetic properties (Lin et al. 2012; Wang et al. 2014). Thus, the use of MGs shows great potential for application in Fe/C ME treatment of wastewater. To the authors' knowledge, however, there have been no reports on the application of MGs in ME processes.

In this work, to meet the reuse standards for reinjection water in oilfields, an actual HOPW sample was treated sequentially by MW-enhanced coagulation and Fe/C ME processes. A series of batch coagulation tests were conducted to evaluate the relevant influencing factors involved. In addition, $Fe_{78}Si_9B_{13}$ MGs and activated carbon (AC) were used as the electrode materials for ME treatment, and batch experiments were performed to optimize their mass ratio.

MATERIALS AND METHODS

Chemicals and materials

Polyacrylamide (PAM) was purchased from the Dongyi Chemical Company (Shanghai, China), with an average molecular weight of 1.86×10^6 g/mol. AC was supplied by the Jieli Activated Carbon Company (Huaibei, China). The AC had a diameter of about 2 mm and a length of 5 mm, with a columnar shape. PACl (purity: 30 wt% Al2O3) was provided by the Sinopharm Chemical Reagent Co., Ltd (China). Iron shavings obtained from a metal processing factory nearby were cut to a diameter of about 2 mm and a length of 5 mm, with an irregular shape. The composition of iron shavings was (mass basis): Fe 96.3%, O 2.4%, C 1.1%, others 0.2%. The iron shavings were degreased in 10% hot alkaline solution and then soaked in 2% H_2SO_4 solution to remove surface rusts; finally they were washed three times with deionized water and the cleaned iron was dried naturally. The $Fe_{78}Si_9B_{13}$ MGs (Fe-based MGs) ribbons used in this work were bought from the Ruihua New Materials Co., Ltd (Changsha, China). The MGs were cut to be 5 mm wide and 50 ± 10 μm thick. All other reagents used in the experiments were of analytical-reagent grade or higher purity and were used without further purification.

Wastewater sample

The HOPW in this study was obtained from the Liaohe Oilfield located in Liaoning Province, China. This oilfield is rich in heavy and ultra-heavy oil resources. After transporation to the laboratory, the wastewater was settled for 2 days at room temperature to skim off the floating oil. The main pollutants in this wastewater were mineral oil and partially hydrolyzed polyacrylamide (HPAM) (Table 1). As measured, heavy oil in this wastewater had a density of 1.02 g/cm^3, a freezing point of 36 °C, a wax content of 2.5%, and a viscosity of 50,620 mPa s. The wastewater parameters measured are shown in Table 1. As shown, this oil-in-water emulsified wastewater was characterized by poor nutrient levels with a 5-day biological oxygen demand (BOD$_5$): COD ratio of 0.09–0.11, and a COD:TN:TP ratio of 3,790:122:1 after primary oil floatation.

Coagulation tests

All coagulation experiments were conducted in 1.0 L glass beakers using a programmable jar-test apparatus (Model DC-506, Shanghai Waterworks Company, Shanghai,

Table 1 | Characteristics of the HOPW used in this study

Parameter	Range	Average
pH	7.2–7.4	7.3
COD (mg/L)	1,530–1,887	1,688
BOD$_5$ (mg/L)	156–215	190
BOD$_5$/COD	0.09–0.11	0.11
Oil (mg/L)	135–186	159
NH$_3$-N (mg/L)	38–48	45
TN (mg/L)	54–65	57
TP (mg/L)	0.36–0.50	0.46
SO$_4^{2-}$ (mg/L)	55–68	61
TDS (mg/L)	6,540–7,620	6,750
SS (mg/L)	135–178	155
HPAM (mg/L)	18–26	22
SRB (cells/mL)	3,200–3,700	3,400
SB (cells/mL)	7,400–9,600	8,700
Corrosion rate (mm/year)	0.692–0.735	0.716

TN, total nitrogen; TP, total phosphorus; TDS, total dissolved solids; SS, suspended solids; SRB, sulfate reducing bacteria; SB, saprophytic bacteria.

China). In each case, 0.5 L wastewater was dosed with the desired amounts of PACl. The pH was not adjusted and was maintained at the original value of 7.2–7.4. After rapid stirring at 200 rpm for 2 min, an appropriate amount of PAM was added to the solution, followed by a 15 min period of slow stirring (40 rpm) and settling. Supernatant after settling was taken from a point 3 cm below the surface.

MW enhanced coagulation experiments were conducted using a domestic MW oven (frequency 2.45 GHz, the Guangdong Galanz Group Co., Ltd, Foshan, China). A hole was drilled in the oven top to allow the stirrer to pass through it. The sample beaker (containing 0.5 L wastewater) was placed in the middle of the oven tray, using 500 W of irradiation power. MW irradiation coagulation tests were conducted for specific times, with variation in PACl dosage, PAM dosage, MW irradiation time, and settling time. The effect of each factor was studied by fixing the values of other factors. The stirring step was identical to that without MW irradiation. After irradiation, a thermometer was immediately inserted into each sample to measure instantaneous temperature in the solutions. The oil floating on the water surface was skimmed out using filter paper.

The reproducibility of coagulation tests was evaluated through the repetition of experiments. One sample within each set of coagulation tests was repeated three times in order to assess the reproducibility of the test method. The maximum fluctuation in the results, for a given set of experimental conditions, was found to be below 10%. For a high proportion of MW enhanced coagulation, a variation of only ±2.7% was found.

Fe/C ME tests

After the MW coagulation treatment under optimum conditions, the wastewater was subjected to the ME process.

To investigate the optimum Fe:C mass ratio, batch tests were first conducted in beakers containing 100 mL wastewater. The dosage sum of iron shavings (or MGs) and AC was fixed at 10 g/L while varying the Fe:C mass ratio as 1:6, 1:5, 1:4, 1:3, 1:2, 1:1, 2:1, 3:1, 4:1, 5:1, and 6:1, respectively. The mixture was stirred at 200 rpm for 3 h, and then was analyzed. To eliminate the adsorption effect, the AC was saturated with the wastewater for 24 h prior to use.

Based on the optimum Fe:C mass ratio, the subsequent experiments were carried out using an ME reactor in a continuous flow mode. The cylindrical reactor was made of plexiglass with a height of 25 cm, diameter of 8 cm and effective volume of 0.96 L. The MGs (or iron shavings) and AC were mixed together with the optimum mass ratio by sufficient spiral mechanical agitation to guarantee the high mixing uniformity of the fillers, and then packed in the reactor as a fixed bed with a bed height of 18 cm. In the experiments, influent pH was not adjusted. The systems were operated continuously 30 days with a constant hydraulic retention time (HRT) of 2 h.

Analytical methods

All analytical procedures were performed according to standard methods (China EPA 2002). COD was determined using the potassium dichromate oxidation method. BOD_5 were measured through the oxygen consumption of bacteria breaking down organics in the sample over a 5-day period under standardized conditions. The oil content was determined by an infrared spectrometer oil content analyzer (model CY2000, Laoshan Electronic Instrument Factory, Qingdao, China). The suspended solids (SS) concentration was measured using the drying and weighing method. Sulfate reducing bacteria (SRB) and saprophytic bacteria (SB) were enumerated by the vanish dilution method. In addition, the corrosion rate was determined using the carbon steel Q235 through the weight-loss method according to standard methods (ASTM 1994).

RESULTS AND DISCUSSION

Effect of PACl dosage

Oil content is one of the most important water quality parameters for reinjection water in oilfields, and there is no requirement for the COD concentration. Thus, oil concentration was selected as a primary evaluation index for the present study.

To study the effect of PACl dosage on oil removal, jar tests were conducted with PACl dosages of 0, 50, 100, 150, 200, 250, 300, 350 and 400 mg/L. The results obtained are
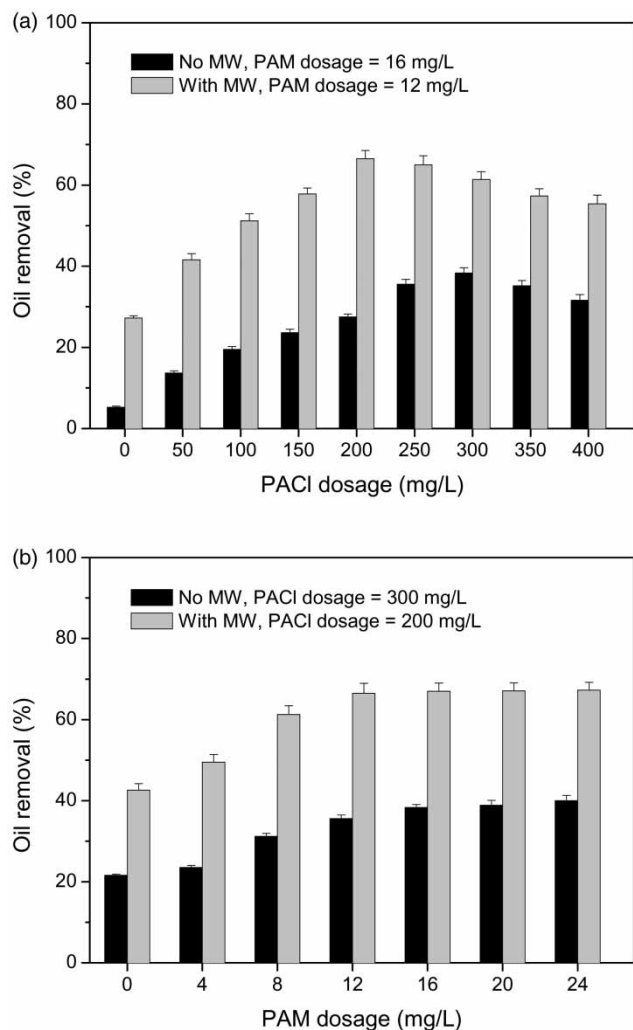
Figure 1 | Effect of PACl dosage (a) and PAM dosage (b) on oil removal of the HOPW with or without MW irradiation. Experimental conditions: 500 mL wastewater, irradiation power 600 W, irradiation time 150 s, settling time 30 min. Error bars represent the standard error of the mean ($n = 3$).

presented in Figure 1(a). As shown, the oil removal efficiency increased with an increase in coagulant dosage till it reached its highest value, after which the removal efficiency began to decrease. The zeta potential of oil droplets is associated with the stability of oil-in-water emulsions, and the zeta potential is negative for oilfield produced water (Ma et al. 2013). At less than critical coagulant concentration, there are not enough oppositely charged ions present to adequately neutralize the negative charges of the emulsion. Thus, the demulsification efficiency increases with an increasing coagulant concentration. However, the restabilization of the system occurs at over the critical

coagulant concentration due to a reversal of the charges caused by the presence of excess counter ions (Santander et al. 2011). It seems that such a phenomenon caused a reduction in treatment efficiency at higher coagulant concentrations.

Aluminum salts are widely used as coagulants in water and wastewater treatment. Their mode of action generally involves two mechanisms: charge neutralization of negatively charged colloids by cationic hydrolysis products, and the incorporation of impurities in an amorphous hydroxide precipitate, so-called sweep flocculation (Ahmad et al. 2008). In this study, the pH range of 7.2–7.4 (Table 1) was favorable for the formation of amorphous solid-state $Al(OH)_3$, because the aluminum ions could get sufficient alkalinity to form it.

The maximum oil removal was 38.3% and 66.5% in the absence and presence of MW irradiation, respectively, which was obtained at 300 mg/L and 200 mg/L of PACl, respectively (Figure 1(a)). Without the addition of PACl, only 5.2% oil removal was achieved by stirring alone in the absence of MW irradiation; however, 27.2% oil removal was achieved with the use of MW irradiation. Obviously, MW irradiation could not only remarkably enhance the demulsification of the emulsion, but also reduce the coagulant consumption. MW heating can quickly raise water temperature, and promote and accelerate the formation of flocs. This is because the hydrolysis reactions of coagulants are generally endothermic, and when the water temperature is lower, the rate of hydrolysis is slow and incomplete. In addition, a rapid increase in temperature reduces the emulsion viscosity and breaks the outer film of droplets (Kuo & Lee 2010). As non-ionizing radiation, MW energy causes molecular motion by migration of ions and dipole rotations, leading to neutralization of the zeta potential of the emulsified oil droplets (Fang et al. 1989). A synthesis of these mechanisms results in separation of an emulsion without the addition of any chemical agent.

Recently, Kang et al. (2015) reported a 63.4% removal of oil from oilfield produced water through MW application, which was apparently higher than that obtained in the present study (27.2%, Figure 1(a)). This could be due to the presence of HPAM residue in the HOPW in this study. The HPAM residue can significantly enhance the stability of oil-in-water emulsions (Ma et al. 2013).

Effect of PAM dosage

In this study, PAM was chosen as the coagulant aid added to the solution, because it can enhance the formation of larger flocs and increase the sedimentation rate (Ahmad *et al.* 2008). The effect of PAM addition on the removal of oil was investigated. PAM dosage was increased from 4 to 24 mg/L, while fixing the dosage of PACl at the respective optimum values.

Figure 1(b) plots the effect of PAM addition on oil removal, pointing to the substantially increased performance for PAM as the PAM dosage increased. The oil removal efficiency increased rapidly with the increasing dosage of PAM up to 16 mg/L and 12 mg/L, without or with MW irradiation, respectively. However, when the PAM dosage was raised further, the removal efficiency increased little. Moreover, the solution turbidity quickly increased when the PAM dosage was more than 20 mg/L. Considering this, the best PAM dosage was determined to 16 mg/L and 12 mg/L for the case without or with MW irradiation, respectively. The aforementioned results demonstrate that MW heating can not only enhance treatment efficiency, but also reduce the dosage of PACl and PAM by 33.3% and 25.0%, respectively.

Effect of MW irradiation time

In general, an increase in irradiation time can raise emulsion temperature and may improve separation efficiency. To investigate the effect of MW radiation time on oil removal of the HOPW, batch experiments were conducted at a radiation time of 0–200 s, while fixing MW power was at 600 W and the dosages of PACl and PAM at the respective optimum values.

As shown in Figure 2, the oil removal increased continuously with irradiation time to 150 s, and then increased little with time. With increasing radiation time, the interfacial film of the emulsions was gradually destroyed and the zeta potential of the oil droplets decreased (Kang *et al.* 2015). However, there existed limiting values for the destruction of the interfacial film and the zeta potential of oil droplets. In addition, if the irradiation time was too long, the water temperature would become very high and even reach boiling point. Therefore, the optimum operating conditions for MW irradiation were 600 W of power and 150 s of irradiation.
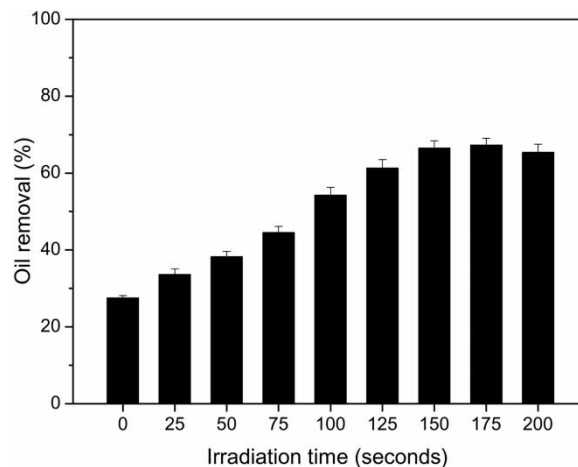

Figure 2 │ Effect of MW radiation time on oil removal from the HOPW. Experimental conditions: 500 mL wastewater, PACl dosage 200 mg/L, PAM dosage 12 mg/L, irradiation power 600 W, settling time 30 min. Error bars represent the standard error of the mean ($n = 3$).

Effect of settling time

In general, an increase in settling time may enhance separation efficiency. To investigate the effect of settling time on oil removal of the HOPW, batch experiments were conducted at settling times of 0–60 min, while fixing the MW power at 600 W and the dosages of PACl and PAM at the respective optimum values.

It is seen from Figure 3 that the removal efficiency of oil increased continuously with increasing settling time up to
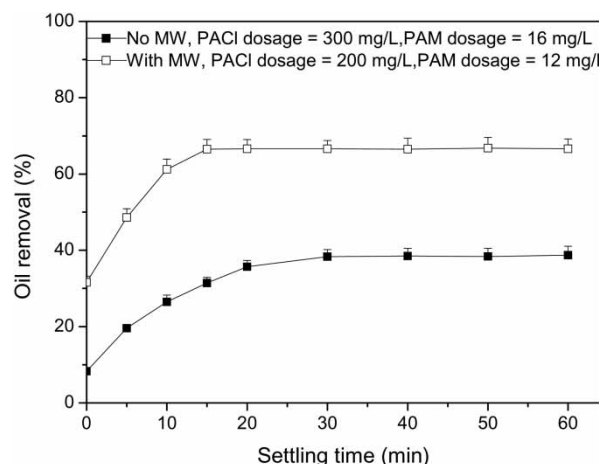

Figure 3 │ Effect of settling time on oil removal from the HOPW. Experimental conditions: 500 mL wastewater, irradiation power 600 W, irradiation time 150 s. The dosages of PACl and PAM were fixed at the respective optimum values. Error bars represent the standard error of the mean ($n = 3$).

15 min and 30 min with or without MW, respectively. Separation levels improved little if settling time was further increased, and we concluded that a settling time of 15 min and 30 min was optimal with or without MW, respectively. Thus, it can be found that MW irradiation could shorten settling time and enhance separation efficiency.

Over treatment performance of coagulation process

Based on the aforementioned results, the optimum conditions for MW coagulation were: 500 mL wastewater, irradiation power 600 W, irradiation time 150 s, settling time 15 min, PACl dosage 200 mg/L, and PAM dosage 12 mg/L. Under these conditions, the COD concentration decreased from an average of 1,688 mg/L (Table 1) to 952 mg/L (Table 2), corresponding to 43.6% removal. This value was lower than the oil removal (66.5%, Figure 1(a)), which was attributed to the fact that some dissolved pollutants were not removed by MW irradiation and coagulation. In addition, a high removal of SS (more than 90%) was achieved (Table 2), whereas there was no significant difference between conventional coagulation and MW coagulation. The removal efficiency for BOD_5 (42.1%) was close to that of COD, thus the biodegradability of the wastewater (BOD_5/COD) was not improved. More importantly, MW irradiation removed more than 90% of SRB and SB (Table 2), compared with about 40% removal without MW. Remarkable removal of these corrosion bacteria by MW caused a substantial reduction in the corrosion rate

of the solution. SRB and SB are abundant in natural environments including oilfield produced water, and are known to be two of the key microbes in the microbiologically influenced corrosion process (You & Wang 2011).

Chemical coagulation alone can only remove a small portion of the corrosion bacteria by flocculation/precipitation. MW is used in the sterilization of medical waste and the inactivation of micro-organisms in foods, animal manure, and soil (Oliveira et al. 2010). MW can affect the mortality rate, cell structure, cell inclusion and DNA of micro-organisms. Besides the thermal effect of MW exposure, one of the more important killing mechanisms of micro-organisms by MW is that the application of MW fields can cause polarized side chains of macromolecules to align with the direction of the electric field, leading to the possible breakage of hydrogen bonds and alteration of the hydration zone (Hong et al. 2004). Actually, in the present study, the water temperature was no more than 70 °C under 150 s of irradiation. Thus, non-thermal MW effects are the major reason for sterilization in this study.

Effect of Fe:C mass ratio

To investigate the optimum Fe:C mass ratio, batch ME experiments were performed on the HOPW treated under the optimum process conditions of MW coagulation found above. Figure 4 illustrates the oil removal efficiencies of the wastewater by iron shavings/AC ME and MGs/AC ME systems at different mass ratios. The results suggest that oil removal was highest with an iron shavings:AC mass ratio

Table 2 | Water quality parameters for the HOPW after treatment. The various treatments were performed under their respective optimum conditions

Parameter	After coagulation	After MW coagulation	After MGs/C ME process	Reinjection Standard[a]
COD (mg/L)	1,208	952	457	NR
BOD_5 (mg/L)	136	110	192	NR
BOD_5/COD	0.11	0.12	0.42	NR
Oil (mg/L)	98	53	7.2	≤ 15
SS (mg/L)	18	14	2.6	≤ 5.0
SRB (cells/mL)	2,100	120	9	≤ 100
SB (cells/mL)	5,200	170	16	≤ 100
Corrosion rate (mm/year)	0.526	0.073	0.025	≤ 0.076

[a]SY/T 5329-1994 standard (a criterion of China Petroleum Industry). NR: no requirement.
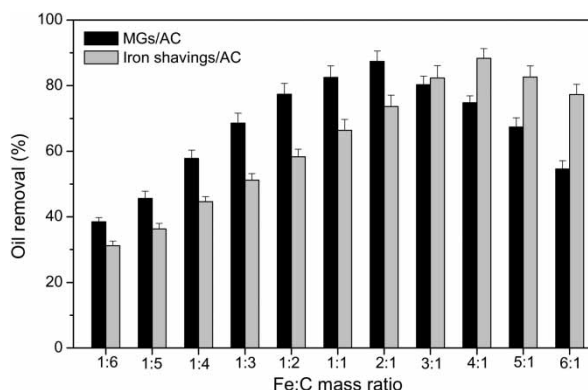

Figure 4 | Effect of Fe:C mass ratio on oil removal. The dosage sum of iron shavings (or MGs) and AC was 10 g/L. Error bars represent the standard error of the mean ($n = 3$).

of 4:1 and an MGs:AC mass ratio of 2:1, respectively. Higher or lower Fe:C mass ratios would result in decreasing removal efficiency. In addition, no significant difference was observed in oil removal efficiency between the two systems. In an Fe/C ME system, iron particles serve as an anodic metal, providing electrons for organic destruction, while AC particles act as cathodes to form macroscopic galvanic cells by contacting iron particles (Zhang 2015). When the Fe:C mass ratio reaches a certain value, the total surface area of iron and carbon particles is similar, which is helpful for the formation of macroscopic galvanic cells. Fewer carbon particles cannot exert the best internal electrolysis efficiency, whereas more carbon particles can inhabit much more space of iron particles and hinder the reactions (Zhang 2015). Therefore, mass ratios of 4:1 for iron shavings/AC and 2:1 for MGs/AC were selected in the following studies.

Performance of ME reactors

Figure 5 shows the oil concentrations in the influent and effluent of the two ME reactors during the 30-day study period. In the initial 8 days of continuous running, the effluent oil concentration was lower than 15 mg/L in the iron shavings/AC ME system. Afterwards, the effluent oil concentration in this system continuously went up and reached about 30 mg/L at day 30. In the MGs/AC ME
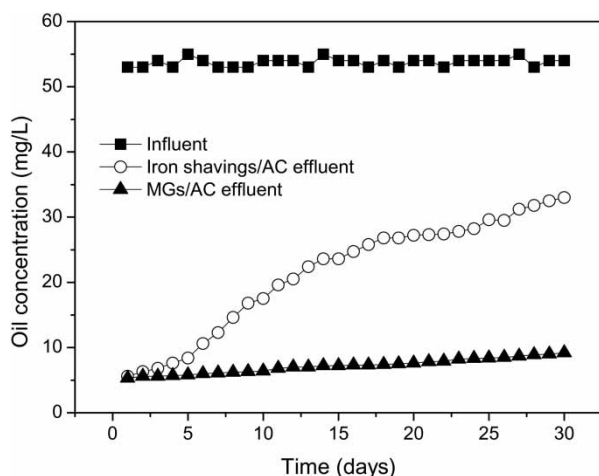
system, by contrast, the effluent oil concentration only increased a little and was maintained below 10 mg/L until the end of the experiments (Table 2). The average value of effluent oil concentration was 7.2 mg/L in the MGs/AC ME system, and other indexes also decreased obviously (Table 2). Especially, the BOD_5/COD ratio was remarkably improved after the ME treatment, indicating that this effluent could easily be further treated by biological methods. The total removal efficiencies for oil, SS and corrosion rate were 95.5%, 98.3% and 96.5%, respectively, in the combined MW coagulation-MGs/AC ME system.

Passivation of iron is inevitable for Fe/C ME reactions (Cheng *et al.* 2007). As the ME reactions proceed, more and more ferrous and ferric hydroxides are produced and precipitate on the surface of the iron. This passivation layer would become thick with time in long-term operation, block the electron transfer between the iron and the wastewater, and eventually lead to deactivation of the iron surface and termination of ME reactions. It is well known that the atomic configuration of Fe-based MGs is in a metastable state (Lin *et al.* 2012; Wang *et al.* 2014). For the metastable Fe-based MGs, amorphous matrix atoms have higher potential energy than crystalline atoms, which results in the easy passivation of the MGs. The link between the amorphous matrix atoms of the MGs and the orderly atoms of the passivation layer is not compact. Thus, the passivation layer of MGs is easily detached by water impact, leading to the stable reaction activity.

CONCLUSIONS

This study was performed to investigate the performance of combined MW enhanced coagulation and Fe-based MGs/AC ME processes on treating HOPW. The results demonstrated that the hybrid system was highly efficient in removing oil, SS, COD and corrosion bacteria. The application of MW irradiation could reduce the consumption of PACl and PAM, and could remarkably sterilize corrosion bacteria during coagulation treatment. The MGs/AC ME system showed high performance stability during the 30-day treatment period. The indexes of the treated HOPW could completely meet the requirements for the C1 grade in the SY/T 5329-1994 standard for wastewater

Figure 5 │ Oil concentrations in the influent and effluent of the ME reactors during the 30-day study period. The iron shavings/AC mass ratio = 4:1, MGs/AC mass ratio = 2:1, and HRT = 2 h.

reinjection in oilfields. The corrosive rate of the treated HOPW was only 0.025 mm/year. Therefore, the hybrid system is a promising solution for treating HOPW.

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