Pilot study of oilfield wastewater treatment by micro-flocculation filtration process

Shaoxiong Si, Zhong Yan, Zhaobo Gong, Pengfei Liu, Yumin Zhang and Yu Xiang

ABSTRACT

In order to meet the latest *Environmental Protection Law* of China on wastewater discharge standards, this paper studied a pilot-scale micro-flocculation filtration pretreatment process for the treatment of oilfield wastewater. The experiment showed that the removal rate of oil and suspended solids (SS) respectively increased from 91.52% to 95.38% and from 66.42% to 97.19%. After the treatment by the micro-flocculation filtration device, the relevant characteristics of the discharge wastewater satisfied the latest standards continuously. Moreover, the polyaluminum chloride (PAC) dosage was reduced from 200 mg/L to 100 mg/L (50 mg/L in micro-flocculation device and 50 mg/L in the cyclone reactor) at the same time. In order to decrease the degree of scaling in the filter, ceramsite was chosen as the filter material instead of quartz sand that is widely applied in the oilfields. The scaling experiment showed that the HCO_3^-, Ca^{2+} and Mg^{2+} contents in the extract from quartz sand after the scaling study were increased by 38.05, 35.91 and 0.28 mg/L, respectively. Meanwhile, the HCO_3^-, Ca^{2+} and Mg^{2+} contents in the extract from ceramsite were only increased by 13.14, 6.26 and 0.27 mg/L, respectively. Therefore, the ceramsite is not so prone to scaling as compared to quartz sand under identical test conditions, which avoided a hardened and impervious filter after operating for some time. These results suggest that the micro-flocculation filtration with the ceramsite as filter media is a suitable pretreatment process for the oilfield wastewater treatment.

Key words | dynamic pilot-scale study, micro-flocculation filtration, oilfield wastewater, scaling, wastewater treatment

Shaoxiong Si (corresponding author)
Zhong Yan
Zhaobo Gong
Pengfei Liu
Yumin Zhang
Experimental Detection Research Institute,
Xinjiang Oilfield Company,
PetroChina, Karamay, Xinjiang 834000,
China
E-mail: *sishaoxiong@126.com*

Yu Xiang
Chemical Engineering Specialty of Science College,
China University of Petroleum,
Beijing 102249,
China

INTRODUCTION

With the progress of oil production in Xinjiang Oilfield, the water content of crude oil has been gradually increasing. This requires some new processes for the treatment of wastewater thus produced. On the other hand, the new *Environmental Protection Law* of China executed in 2015 increased the standards for wastewater discharge (Zhang *et al.* 2016). Previous studies found that the effluent of Xinjiang Oilfield was sometimes heavily contaminated, and it hardly met the standards of water for re-use in oilfields or for direct discharge continuously (Yan *et al.* 2014). The main reason is that the oil and suspended solids (SS) content of the raw water from crude oil exhibited a considerable variation. Therefore, it is imperative to add some appropriate pretreatment processes before the raw water is introduced into the present processes. This could guarantee that the wastewater discharge from Xinjiang Oilfield continuously meets the new national standards of China.

The general processes used for wastewater pretreatment include precipitation (Mbamba *et al.* 2015), membrane filtration (Pugh *et al.* 2014) and redox treatment (Huang *et al.* 2011) The micro-flocculation filtration technique can be realized by adding chemical coagulants to the water stream before filters. Micro-pollutants form small and dense flocs in the water stream, and the flocs are precipitated and are removed in the filter bed (Wu *et al.* 2016). This technique has a couple of advantages such as the small volume of the equipment, the low coagulant dose (Zhang *et al.* 2017), and the good quality of effluent (Babu & Chaudhuri 2005). Currently, the micro-flocculation filtration is mainly applied in the field of urban sewage and

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drinking water treatment. Despite that the micro-flocculation filtration is a very promising technique for sewage treatment (Logsdon *et al.* 1993; Wu *et al.* 2016), there is no report about the application of this technique in oilfield wastewater treatment.

Furthermore, the sewage of oilfield often contains high concentrations of calcium ions, magnesium ions and carbonate ions, which result in a strong scaling tendency (Floquet *et al.* 2016; Liu *et al.* 2016). It would significantly decrease the filtration permeability and eventually affect the whole water treatment process after filter fouling. Therefore, the scaling not only affects the normal oil production but also poses some security risks (Chen *et al.* 2012). On the other hand, ceramsite has been widely applied in industrial wastewater treatment as filtration media in the light of its large specific surface area and a lower frequency of necessary backwashing in filtration (Zou *et al.* 2012; Lu *et al.* 2013). Based on these characteristics, a micro-flocculation filtration device with ceramsite as media was designed as the pretreatment process in this study.

In this paper, an integrated device for dynamic treatment was assembled. The effect of chemical coagulant, polyaluminum chloride (PAC), dosage on the performance of the micro-flocculation filtration was studied. Also continuous operation evaluated the capability of the micro-flocculation experiments to remove oil and SS from raw water. Finally, the scaling properties of quartz sand and ceramsite were compared to evaluate the feasibility of the micro-flocculation filtration technique for the treatment of wastewater in Xinjiang Oilfield (Fakhrul-Razi *et al.* 2009; Chen *et al.* 2011).

MATERIALS AND METHODS

Materials

PAC was prepared by the Experimental Detection Research Institute. Poly(acryl amide) (PAM) was purchased from Mangyongdae Co. Ltd (China). Ceramsite was supplied by Tianyuan Corundum Abrasive Co., Ltd (China). Quartz sand was obtained from Qingdao Capitaland Ltd (China). All other reagents used were of analytic grade.

Properties of the raw water

The raw water was sampled from a process station of Xinjiang Oilfield 2# oil production plant, which is from the light oil wastewater. The wastewater was treated between 14 °C and 25 °C (outdoor temperature). The properties of the raw water are analyzed based on SY/T 5523-2016 and the results are shown in Table 1.

Table 1 | Properties of the raw water samples

Items	Results	Items	Results
Na^+-K^+ (mg/L)	2,556.43 to 2,698.51	Water type	Na_2SO_4
Ca^{2+} (mg/L)	263.82 to 298.39	Total dissolved solid (mg/L)	7,341 to 8,289
Mg^{2+} (mg/L)	20.94 to 38.38	Suspended solids (mg/L)	59.2 to 97.9
Cl^- (mg/L)	4,052.69 to 4,153.61	Oil (mg/L)	22.9 to 47.5
SO_4^{2-} (mg/L)	41.10 to 82.9	Zeta potential (mV)	−8.15 to −9.43
CO_3^{2-} (mg/L)	0	Polymer (mg/L)	0.00
HCO_3^- (mg/L)	998.65 to 1,059.30	Surfactant (mg/L)	0.00
pH	7.09 to 7.31		

Flow diagram and equipment of the process

In the pilot study, dynamic simulation technology was employed. Compared with static laboratory experiments, the dynamic simulation technology has higher authenticity for simulating on-site operation. A schematic flow diagram of the experimental process is illustrated in Figure 1(a), and a view of the pilot equipment is shown in Figure 1(b).

The process of production plant is integrated into a single device (as shown in Figure 1(b)) for the dynamic wastewater treatment. This integrated device was designed and made by the Experimental Detection Research Institute, Xinjiang Oilfield Company. The experiment consists of two parts, the micro-flocculation filtration and the process of production plant. In the process of production plant (Figure 1(a)), only the micro-flocculation process was added to the existing wastewater treatment process. The raw water stream was passed through the micro-flocculation filtration device, which ensured afterwards low concentration of the oil and SS in the water. Then the water stream was introduced into the cyclone reactor, the settling tank and the two-stage filter in series.

The specific parameters are as follows: the capacity of the distribution reservoir was 1 m^3, the influent was mixed with PAC solution by mechanical agitation (50 r/min). The micro-flocculation filter column had an inner diameter of 0.12 m, and it was 1.2 m high. The micro-flocculation filter material was ceramsite whose diameter was 2–3 mm.

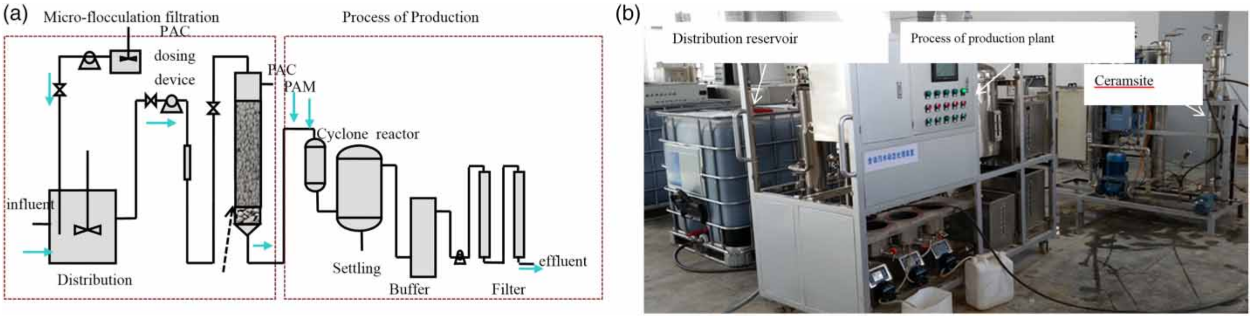

Figure 1 | Schematic flow diagram (a) and field picture of pilot equipment (b).

The cyclone reactor was 15 L, of which the hydraulic retention time (HRT) was 8 min. Prior to the reactor, PAC and PAM solutions were added by peristaltic pump and mixed by the hydrocyclone. The volume of the settling tank was 70 L, of which the HRT was 40 min. The buffer tank was 30 L, of which the HRT was 17 min. The two-stage filter on the right was filled with quartz sand whose diameter was 0.5 mm–1 mm. The inner diameter of the filter was 0.15 m, the height 0.7 m. In addition, there was an oil recovery port at the top of the distribution reservoir.

Micro-flocculation experiments

PAC solution at a concentration of 50 mg/L was added into the distribution reservoir. The sewage from the distribution reservoir was pumped into the ceramic filter column at a flow velocity of 120 L/h, and afterwards it was passed through the cyclone reactor where again a certain amount of PAC and 10 mg/L PAM were added. Finally the water stream was passed through the settling tank, the buffer tank and the two-stage filter in sequence. The removal rates of oil and SS in wastewater were measured at the outlet of the ceramic filter column, and at the two-stage filter outlet respectively.

Analysis methods

The SS and oil contents of the water were analyzed according to the procedure of standard methods (SY/T 5523-2016). The floc size was measured by a laser diffraction instrument (Malvern Mastersizer 2000, UK). In this study, the value of floc size was represented by the median volumetric diameter ($d_{0.5}$). Zeta potential was determined by a Malvern Zetasizer (Malvern Zeta Nano ZS, UK).

RESULTS AND DISCUSSION

The removal rate of oil and SS

Without the micro-flocculation process, the removal rates of oil and SS were 91.52% and 66.42%, respectively, after adding 250 mg/L PAC (the present on-site operation dosage). This indicates that the present on-site operation process is already effective for the removal of waste oil; however, it is not effective enough in removing SS. Figure 2 shows the effect of PAC concentration on the removal rate of oil and SS with the micro-flocculation process. When the PAC dosage was 200 mg/L, the removal rate of oil was increased from 91.52% to 96.38% (Figure 2(a)) and the removal rate of SS was increased from 66.42% to 97.19% (Figure 2(b)), which means the micro-flocculation process could improve the removal rate of SS significantly. Even when the dosage of PAC was as low as 50 mg/L (one-quarter of the original dosage), the removal rate of SS was 91.47% (Figure 2(b)). These findings proved that the integration of the micro-flocculation process could improve the removal rate of SS and reduce PAC dose at the same time.

Continuous operation

The micro-flocculation experiment was performed with the PAC dosage of 100 mg/L for 30 days, to investigate the (long-term) stability of the treatment processes. As illustrated in Figure 3, the oil and SS concentrations of the effluent were all less than 2 mg/L during the study. The oil removal rate was higher than 94%, and the SS removal rate was higher than 97%. The effluent in these experiments meets the SY/T 5329-2012 (China) standards about reinjection in low permeability reservoirs, and also meets the SY/T 0097-2016 (China) standards about the generator water treatment. It suggested that the PAC dose decrease

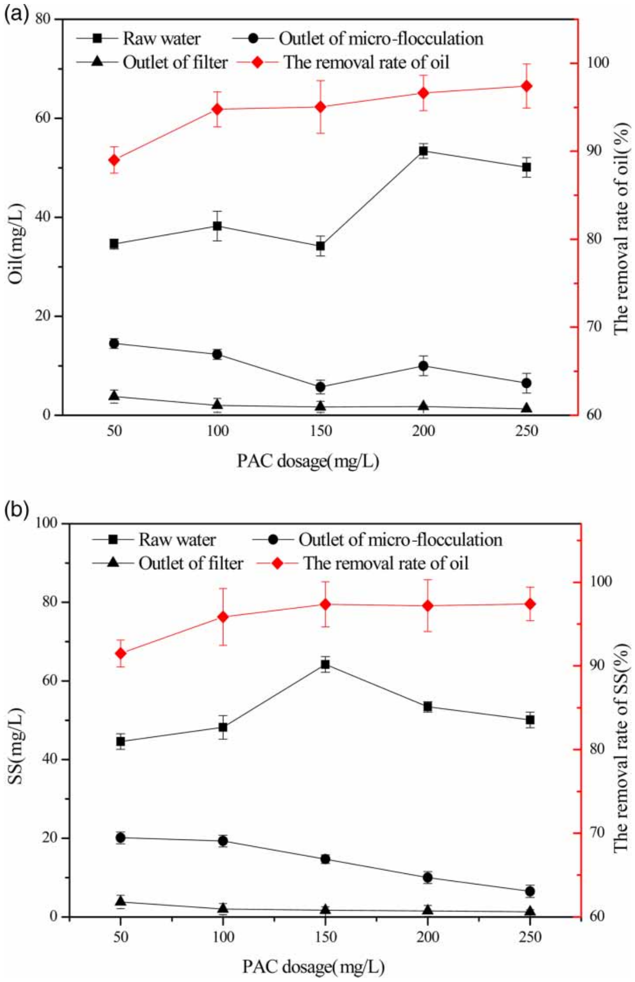

Figure 2 | Effect of PAC dosage on oil (a) and suspended solids (b) removal.

from 200 mg/L to 100 mg/L could still result in treated water that meets the national standards of China, after adding the micro-flocculation filtration process. The price of PAC is about 2200 RMB per ton, equivalent to 323.53 US dollars per ton. Usually the volume of treated wastewater in Xinjiang Oilfield Company is around 7.81×10^7 m^3/year. This technique could therefore save 2.53 million US dollars annually in reagent cost. Meanwhile, if the micro-flocculation filtration process is applied in a wastewater treatment plant, the energy demand of the micro-flocculation filtration processes is only the electricity consumed by the peristaltic pump. Based on our data, the calculated electricity cost is about 357,000 US dollars a year. Therefore, the micro-flocculation filtration process has benefits for the update of existing wastewater treatment processes, since these experiments have displayed excellent stability of the process with regard to the fluctuation of raw water properties, and have also showed significant ability of

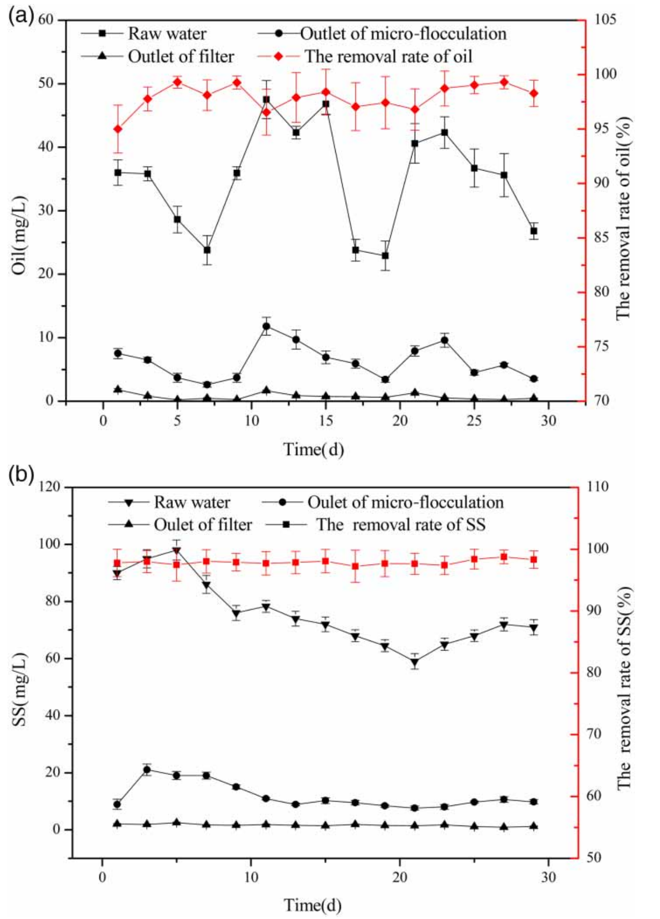

Figure 3 | Effect of operation time on oil (a) and suspended solids (b) removal.

cost-savings. Furthermore, the micro-flocculation filtration process is applicable to the treatment of oilfield water containing the wellhead measures' fluids (the slushing fluids, workover fluids, fracturing flowback fluid, etc.), which are harmful for the growth of activated sludge.

The change of floc size

The sewage floc size changed in the course of treatment steps, as is shown in Figure 4. The floc in the raw water had a median size ($d_{0.5}$) of 11.48 μm, while the median floc size of the effluent at the micro-flocculation outlets grew to 20.64 μm. It indicated that the median diameter of floc in the wastewater increased obviously during the micro-flocculation filtration process. The mechanism of such a phenomenon could be the re-stabilization of the colloidal particles (Yan *et al.* 2008; Zhan *et al.* 2010). Firstly, the aluminum ions of PAC interacted with the flocs bearing negative surface charges in the raw water; this interaction

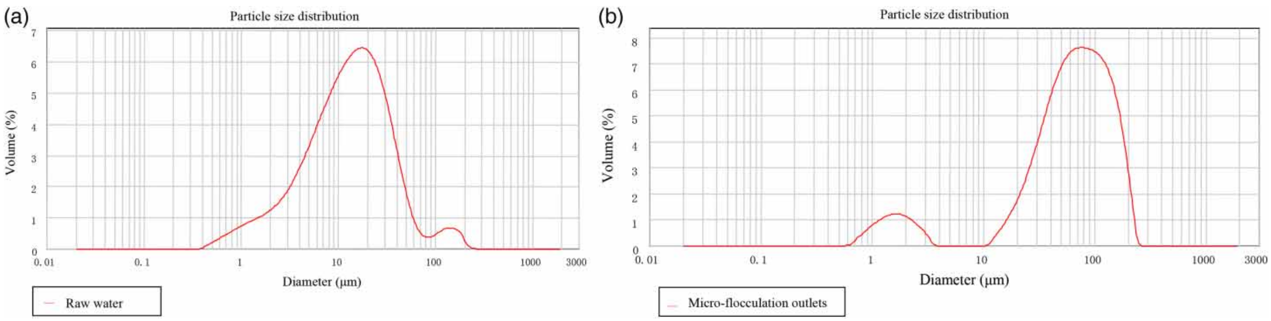

Figure 4 | Size distribution of floc in raw water (a) and in the effluent at the micro-flocculation outlets (b).

results in insoluble products that are charge-neutral (Shon *et al.* 2005; Jeong *et al.* 2014). Then, the small flocs flocculated into larger aggregates by surface adsorption with the increase of PAC concentration (Huang *et al.* 2015). Furthermore, some precipitate formation was ascribed to the complexion reaction with aluminum ions (Zhan *et al.* 2010). Thus, the retention capacity of the ceramsite filter and following process was enhanced significantly.

Scaling study

The raw water has a strong tendency towards scaling, owing to the high concentrations of calcium ions, magnesium ions and bicarbonate ions, as shown in Table 1. Also, through vast on-site observations, we found that quartz sand widely applied in the oilfield is prone to scaling and compaction, leading to the failure of filters. In a separate scaling test, two filters filled with the quartz sand and ceramsite respectively were arranged in parallel. The raw water was passed through the filters at a flow rate of 120 L/h and the processes were operated for 30 days continuously, to investigate the oil deposition and scale formation on these filter media.

Figure 5 depicts that the quartz sand had a deposition amount of 8.04 mg oil per gram quartz sand after the scaling test, higher than the amount of 1.83 mg oil per gram ceramsite. This proved that quartz sand had a stronger affinity towards oil than ceramsite did. Furthermore, the oil deposition amount on quartz sand reduced to 0.48 mg and 0.07 mg after water washing and surfactant washing, respectively. However, the oil deposition amount on ceramsite reduced to 0.14 mg and 0.01 mg after identical treatments. The amount of adsorbed oil on ceramsite remained lower compared with that on the quartz sand, which indicated that it was easier for quartz sand to aggregate after the oil deposition, which led to an inferior filter function and a higher frequency of necessary backwashing.

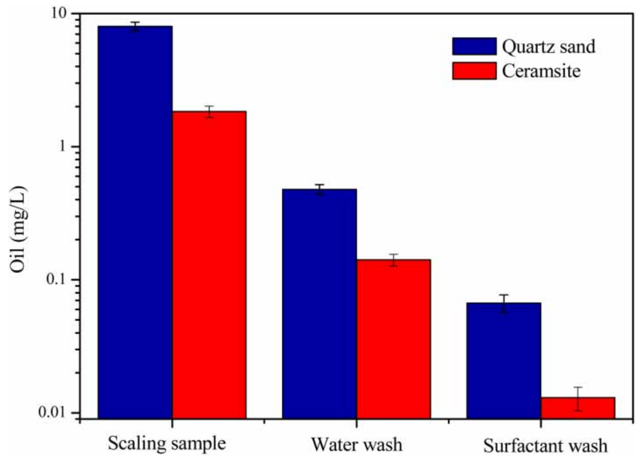

Figure 5 | Oil content of ceramsite and quartz sand.

The extract from the quartz sand and ceramsite scale both contained HCO_3^-, Ca^{2+} and Mg^{2+}, while the elements Ba, Si, Al, Fe, Mn and Ba were not detected in the extract. Thus, the main components in these two kinds of scale are $CaCO_3$ and $MgCO_3$. Figure 6 shows that the HCO_3^-, Ca^{2+}

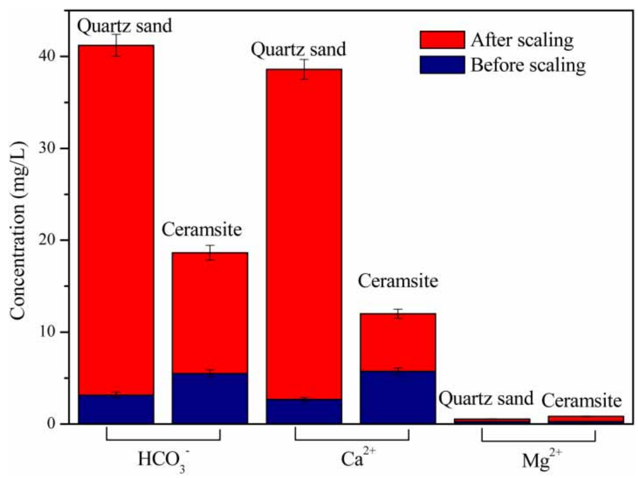

Figure 6 | Composition of the scale formed on ceramsite and quartz sand.

Table 2 | Zeta potential and initial composition of ceramsite and quartz sand

		Component (%)		
Sample	**Zeta potential (−mV)**	**Al_2O_3**	**SiO_2**	**K_2O**
Ceramsite	−19.23 (±0.21)	27.07 (±0.38)	68.75 (±5.24)	1.77 (±0.06)
Quartz sand	3.84 (±0.05)	3.84 (±0.34)	95.07 (±8.64)	1.09 (±0.03)

and Mg^{2+} contents in the extract from quartz sand after the scaling study were increased by 38.05, 35.91 and 0.28 mg/L, respectively. Meanwhile, the HCO_3^-, Ca^{2+} and Mg^{2+} contents in the extract from ceramsite were increased by 13.14, 6.26 and 0.27 mg/L, respectively. The results showed that the ceramsite was not so prone to scaling as compared to quartz sand under identical test conditions.

The quartz sand and ceramsite have also been examined with zeta potential determination and energy spectrum analysis. As shown in Table 2, the Al_2O_3 component ratio of the ceramsite was larger than that of quartz sand. Because the electronegativity of Al_2O_3 is stronger than SiO_2, the zeta potential value of the ceramic filter material containing higher contents of Al_2O_3 is lower than that of the quartz sand (Jiang *et al.* 2014). It is consistent with the measured zeta potential of these filters. The zeta potential of quartz sand was 3.84 mV, and the zeta potential of the ceramsite was −19.23 mV. Meanwhile, the most naturally occurring species in the raw water from Xinjiang Oilfield showed a net negative surface charge. Because of the repelling interaction between similarly charged surfaces, the probability of scaling for ceramsite with a net negative surface charge is much lower than that of the quartz sand with a net positive surface charge. In addition, the water head loss (hydraulic resistance) of the ceramsite filter is smaller and the surface sediment of ceramsite is easier to be removed by backwashing due to the regular shape of the ceramsite.

CONCLUSIONS

In summary, the pilot study of oilfield wastewater treatment in a dynamic operation mode showed that the micro-flocculation filtration technique led to a better performance with regard to the removal of oil and SS in wastewater. The removal rates of oil and SS were significantly improved by adding the micro-flocculation device. Continuous operation tests for 30 days showed that the effluent could meet the standards of SY/T 5329-2012 and SY/T 0097-2016 even with PAC (coagulant chemical) dose as low as 100 mg/L. Importantly, the ceramsite fillers used in the micro-flocculation filtration process, compared with the quartz sand widely applied in oilfield sewage treatment currently, had a smaller adsorption capacity towards sewage oil and smaller scaling tendency. These unique results prove that the micro-flocculation filtration process is an environmentally benign and cost-effective technique for oilfield wastewater treatment with the existing filtration processes.

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