Pilot-scale study of forward osmosis for treating desulfurization wastewater

Cong Ma, Qianqian Li, Chang Dai, Liang Wang, Bin Zhao, Zhaohui Zhang, Siguo Xue and Wende Tian

ABSTRACT

Forward osmosis (FO) treatment of desulfurization wastewater shows great potential in laboratory scale tests. To explore the adaptability of the forward osmosis system in the practical treatment of desulfurization wastewater, we carried out a pilot test on desulfurization wastewater treated by the traditional method under the conditions of adding soda ash (SA) and adding FO scale inhibitor (FOSI). The results showed that the FO system could concentrate desulfurization wastewater with an average TDS of 15,816–32,820 mg/L in the influent water to an average TDS of more than 120,000 mg/L, which was concentrated 3.8–7.8 times. The removal rates of Ca^{2+}, Mg^{2+} and Cl^{-} were more than 99% and the system could operate stably for a long time. Under the condition of adding SA and FOSI, the system recovery rate was 85.38% and 73.02%, respectively. The operating cost was 25 RMB/ton and 21.77 RMB/ton, respectively. The results showed that the application of forward osmosis in desulfurization wastewater treatment was technically feasible and economically effective.

Key words | desulfurization wastewater, forward osmosis, pilot-scale

Cong Ma
Qianqian Li
Chang Dai
Liang Wang (corresponding author)
Bin Zhao
Zhaohui Zhang
State Key Laboratory of Separation Membranes and Membrane Processes, School of Environmental Science and Engineering,
Tiangong University,
Tianjin 300387,
China
E-mail: *mashi7822@163.com*

Cong Ma
Tianjin Haiyuanhui Technology Co., Ltd,
Tianjin 300457,
China

Siguo Xue
Fluid Technology Solutions (FTS), Inc.,
Beijing Office, Beijing 101101,
China

Wende Tian
Shenzhen Demark Environmental Technology Co., Ltd,
Shenzhen 518000,
China

HIGHLIGHTS

- Desulfurization wastewater could be directly concentrated in the forward osmosis system.
- OsmoBC™ could adapt to the complex characteristics of desulfurization wastewater.
- The system recovery rate was between 70% and 90%, and the system energy consumption was low.

INTRODUCTION

In the short term, China will not change the energy structure dominated by coal (Shuangchen *et al.* 2016), and the SO_2 produced by coal combustion in coal-fired power plants is the main pollutant of the air (Zhu *et al.* 2017). If you do not control emissions, it will cause great environmental pollution. Due to high efficiency, wide applicability and high reliability, lime-gypsum desulfurization technology is widely used in flue gas desulfurization (Lee *et al.* 2018; Ma *et al.* 2019).

In the flue gas desulfurization process, not only sulfur dioxide will enter the limestone circulating slurry, but a large amount of Cl^{-} and F^{-} plasma generated by coal combustion will also be absorbed into the washing liquid, and a large amount of accumulation will corrode the desulfurization equipment. Therefore, in the circulation process, the concentration of Cl^{-} needs to be controlled. When the concentration of Cl^{-} reaches the set range, a certain amount of desulfurized wastewater will usually be discharged from the system to supplement the fresh absorption liquid to reduce the Cl^{-} concentration in the system (Ma *et al.* 2019). Desulfurization wastewater has the characteristics of complex composition, high Cl^{-} ion content, large hardness, and high salt content. If the desulfurization wastewater is discharged without sufficient treatment, it will pose a huge

doi: 10.2166/wst.2020.533

threat to the water environment and may also cause soil salinization (Xia *et al.* 2017). Therefore, removing various pollutants in the desulfurization wastewater to low concentrations is still one of the important problems in the water treatment industry (Huang *et al.* 2013).

At present, the main methods used for advanced treatment of desulfurization wastewater include chemical precipitation, the membrane concentration method and the evaporation concentration method. The chemical precipitation method is the most widely used desulfurization wastewater treatment method in the world. However, the chemical precipitation method has the disadvantages of requiring large investment and difficult recovery (Shuangchen *et al.* 2016). Evaporation concentration can effectively remove impurity ions in desulfurization wastewater (Zheng *et al.* 2019), but the high concentration of Cl^- in the concentrated liquid puts forward higher requirements on the corrosion resistance of the equipment (Zhang *et al.* 2019). In addition, the research on the evaporation control and chemical mechanism of desulfurization wastewater is not yet mature, which also restricts the industrial application of the method (Shuangchen *et al.* 2016).

The membrane method is relatively mature and has been widely used in wastewater treatment, gas separation and microalgae dewatering (Wang *et al.* 2019; Ma *et al.* 2020a, 2020b). Membrane methods such as ultrafiltration (UF) and microfiltration (MF) can improve the treatment efficiency, but the TDS of effluent is high and can not meet the requirements of the discharge of desulfurization wastewater (Yin *et al.* 2013). FO and reverse osmosis (RO) have high desalination rates (Altaee *et al.* 2017). Since FO uses the osmotic pressure gradient as the driving force for water penetration, it has the advantages of low energy consumption and high fouling reversibility. FO can replace RO to become a process of concentrated desulfurization wastewater with development potential (Lee *et al.* 2010).

FO treatment desulfurization wastewater has achieved great results on the laboratory scale (Lee *et al.* 2018). However, due to the limitations of laboratory conditions, there was still a certain gap with practical applications. The pilot of forward osmosis combined with other processes (such as RO) to treat desulfurization wastewater has achieved good results (Choi *et al.* 2017), but the pilot of commercial FO system for desulfurization wastewater treatment has received little attention.

Therefore, we conducted this research used the OsmoBC™ (Figure 1) process from FTS (Fluid Technology Solution) to apply the FO membrane technology to treat desulfurization wastewater. In order to reduce membrane pollution, the desulfurization wastewater treated by the traditional method (three-headed tank system) was tested in two different working conditions with the addition of SA and FOSI. The purpose of this experiment was to evaluate the practical feasibility of FO treatment of desulfurization wastewater. By analyzing water quality, treatment volume, system recovery rate, and operating costs, the adaptability of a commercial FO system in the actual treatment of desulfurized wastewater was investigated to provide solutions for problems such as long process line, unstable operation, low water recovery, etc.

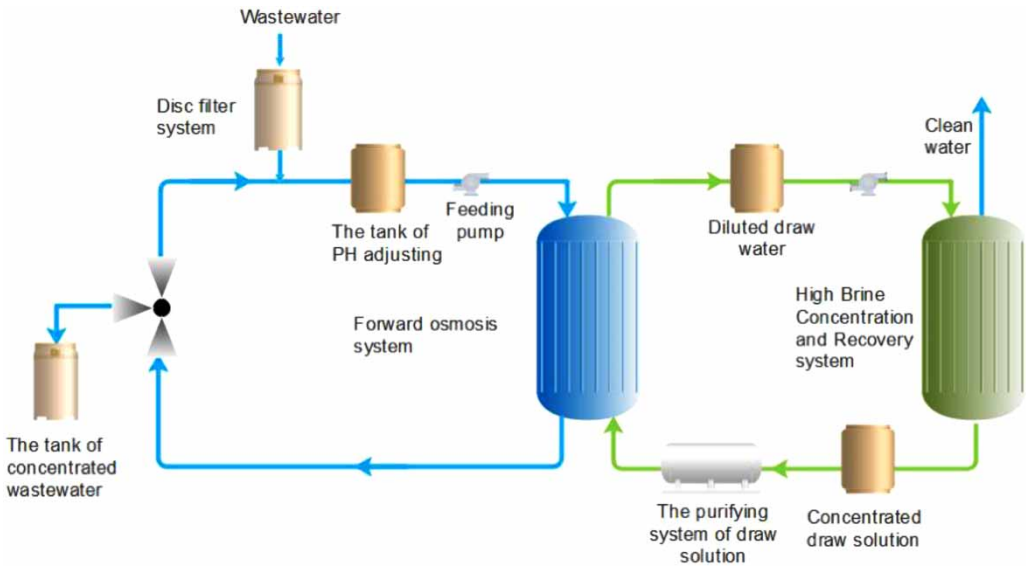

Figure 1 | Schematic representation of the OsmoBC™ treatment system.

MATERIAL AND METHOD

The quality of sampling

The desulfurization wastewater came from a power plant in a city in China, where a wet limestone-gypsum flu gas desulfurization progress was applied for flu gas purification. The component parameters of the desulfurization wastewater treated by the triple tank are listed in Table 1. The concentrations of calcium ions, magnesium ions and sulfate ions in the raw water were very high, which might cause severe scaling. Large changes in water quality had caused difficulties in wastewater treatment. The influent water pH was high, and the pH of system influent water needed to be controlled between 5 and 6.5 to control the deposition of organic matter and Ca^{2+} on the membrane surface, so HCl was used to adjust the pH of the feed water.

FO membranes

The FO membrane utilized low fouling cellulose acetate (CTA) membranes. The FO-8040 membrane element provided by FTS had an open chevron feed spacer for providing stable FO fluxes and a standard draw solution spacer for low-viscous draw solutions. The membrane element had a length of 1.016 m and a diameter of 0.201 m. FTS H_2O^{TM} membranes were used in an FO-8040 membrane element. The pure water permeability coefficient (A), salt permeability coefficient (B) and structural parameter (S) of the FO membrane (Xiao *et al.* 2017) are shown in Table 2.

Table 1 | Concentrations of major contaminants in the desulfurization feed wastewater in two different systems

Index	Add SA system	Add FOSI system
pH value	8.5 ± 1.14	8.0 ± 0.38
Ca^{2+} (mg/L)	908 ± 636.14	628 ± 63.10
Mg^{2+} (mg/L)	851 ± 319.14	2,882 ± 241.86
SO_4^{2-} (mg/L)	2,350 ± 192.22	8,148 ± 1,632.55
Cl^- (mg/L)	5,598 ± 1,292.04	4,654 ± 825.53
TDS (mg/L)	15,816 ± 5,670.81	32,820 ± 1,088.85

Table 2 | Characteristics of FO membrane

Membrane	A (L/m²·h·bar)	B (L/m²·h)	S (μm)
CTA	0.38 ± 0.01	0.09 ± 0.01	170 ± 10

Chemical reagents

Soda ash (SA) and NaCl (all with >98% purity) were purchased from Shanghai Fuqi Industry and Trade Co., Ltd. FO scale inhibitor (FOSI) was provided by FTS. The pH was adjusted with HCl from Shanghai Yuna Chemical Co., Ltd.

Experimental setup

The pilot plant technology used in this experiment came from Shanghai Yuanmai Environmental Technology and American FTS Company. The whole device was divided into two parts: FO concentration and High Brine Concentration and Recovery (HBCR) (Figures 2 and 3). The core of the forward osmosis membrane system was a three-stage total of 12-piece FO membrane modules. The feed water entered the FO system after adjusting pH. NaCl solution with a concentration of 230 g/L was used as the draw solution. The feed water and the draw solution were separated on either side of the membrane. The water naturally permeated from the low-salt side to the high-salt side. Both the treated water and the draw solution were in circulation. FO concentrated water was discharged when it was concentrated to the set concentration. The draw solution entered the FO system continuously. After being diluted, the draw solution was discharged to the HBCR system for concentration.

The core of the HBCR was a three-stage 36-piece high-salt concentration RO membrane module. The diluted draw solution discharged from the forward osmosis system entered the HBCR for concentration, and the concentrated brine regenerated was returned to the FO system as the draw solution. The organic and inorganic contamination of the permeable membrane generated during the concentration of wastewater could be removed by simple washing to recover membrane performance. The system effluent could be discharged into natural water bodies or used for industrial water and farmland irrigation.

Analytical method

The experiment ran continuously for 24 hours, and the whole process was automatically controlled. A water sample was taken once a day to test the water quality of each section. The concentrations of anions and cations were analyzed using ion chromatograph (IC, ICS1000, DIONEX, USA) and inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP6300, Thermo Scientific, USA). The pH was measured by pH meter (PHST-6, LINESA, China). TDS was measured by steam method.

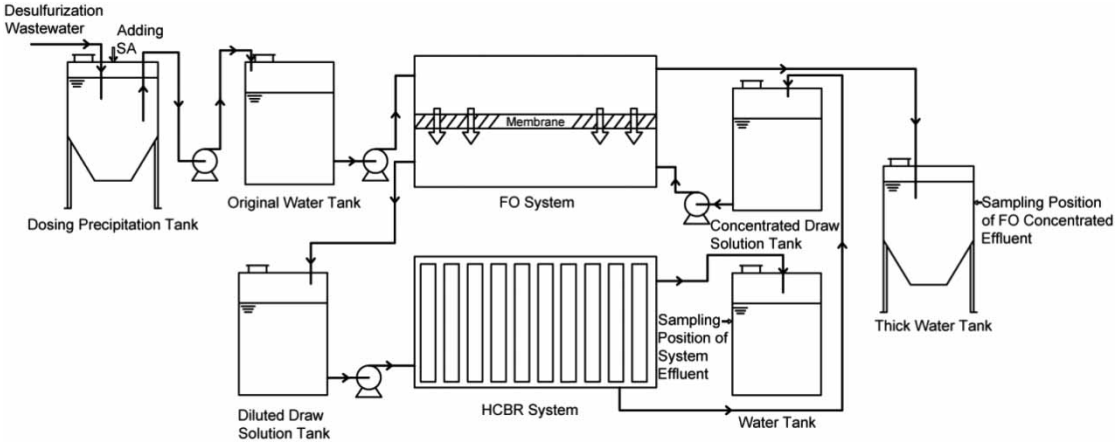

Figure 2 | Simplified flow chart of the process of adding SA.

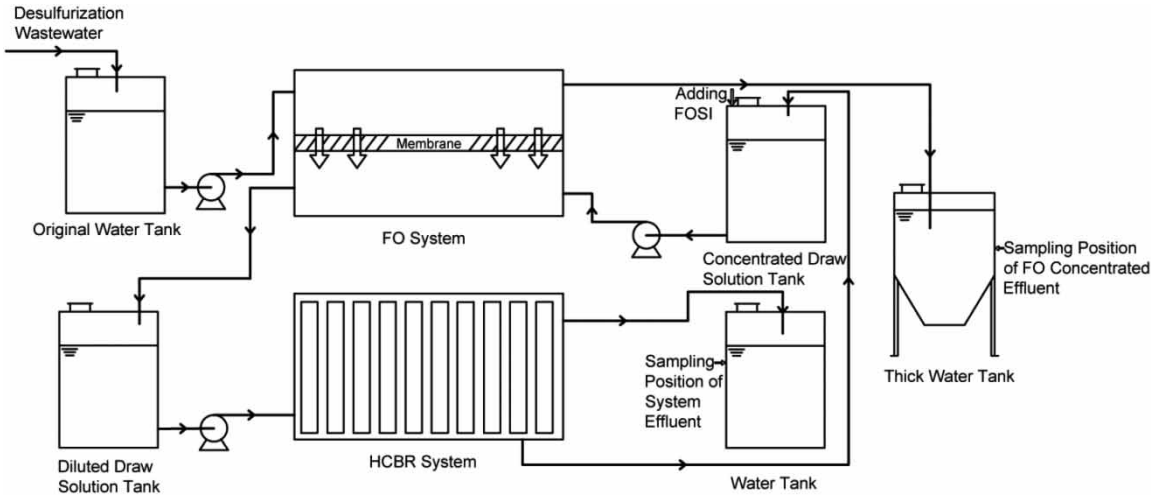

Figure 3 | Simplified flow chart of the process of adding FO scale inhibiter.

The power consumption of the device was monitored through the electric meters installed in the FO system and HBCR system.

RESULTS AND DISCUSSION

Water quality analysis

After the system was stable, a pilot test of 15 consecutive days was conducted. The quality of concentrated water produced by the raw water passing through the FO concentration system and the effluent quality of the system are shown in Table 3. In the condition of adding SA, the TDS of raw water was 15,816 mg/L, and the average TDS of the FO concentrated water discharged was 124,858 mg/L, which was about 7.9 times concentrated. Under the condition of adding the FOSI, the TDS of raw water was 32,820 mg/L, the intermittent discharged FO concentrated water TDS average value was 123,600 mg/L, and the concentration was about 3.8 times.

Both working conditions showed a good concentration effect. Due to the increased degree of hydrolysis of non-alkaline metals at high concentrations (Zheng *et al.* 2019), the pH of the FO-concentrated water with FOSI added was lower than the system influent pH. There was little difference in the Cl^- concentration of the raw water between the two working conditions, but the larger difference in the Cl^- concentration in the FO concentrated water might be caused by the adjustment of the influent pH (Kowalczyk *et al.* 2008). The high concentration of Cl^- in FO concentrated water had strong penetration and corrosiveness, so it put forward

Table 3 | The quality of effluent from FO and the system

	Add SA system		Add FOSI system	
Index	**FO concentrated water**	**System effluent**	**FO concentrated water**	**System effluent**
pH value	7.0 ± 0.24	5.7 ± 0.22	4.5 ± 0.46	6.6 ± 0.77
Ca^{2+} (mg/L)	368 ± 304	1.03 ± 0.95	1,816 ± 124	0.93 ± 0.43
Mg^{2+} (mg/L)	5,348 ± 1,109	0.02 ± 0.02	9,766 ± 758	0.8 ± 0.74
SO_4^{2-} (mg/L)	17,633 ± 3,460	0.24 ± 0.15	27,360 ± 4,492	2.63 ± 2.09
Cl^- (mg/L)	51,800 ± 4,363	4.67 ± 3.55	18,980 ± 4,102	12.03 ± 9.34
TDS (mg/L)	124,858 ± 26,157	552.5 ± 328.75	123,600 ± 11,723	280.2 ± 196.11

higher requirements for the corrosion resistance of concentrated water tanks and related equipment (Riedel *et al.* 1999).

It can be seen from Tables 1 and 3 that the removal rates of Ca^{2+}, Mg^{2+} and Cl^- in the two conditions were above 99%. The average TDS of the effluent under the adding SA condition was 552 mg/L, and the TDS removal rate reached 96.5%. Under the condition of adding FOSI, the average TDS of produced water was 280 mg/L, and the TDS removal rate was 99.15%. The quality of the system effluent was good. The various index met the 'Industrial Circulation Cooling Water Treatment Design Specification'. The effluent of the system could be used as reuse water after adjusting pH.

Throughput and system recovery

Figures 4(a) and 5(a) show the curves of the influent and effluent and the recovery of clean water under the two operating conditions. The water treatment capacity of the system with SA and FOSI was 0.62–0.76 m^3/h and 0.63–0.98 m^3/h. The average recovery rate of the system with SA was more than 85.38% (Figure 4(b)), and the average recovery rate of the system with FOSI was about 73.02% (Figure 5(b)). The difference in system water intake was one of the reasons for the difference in system recovery rate. The reason why the recovery rates of the two operating systems were different might also be that the two operating conditions prevent the membrane from fouling by different mechanisms, resulting in different membrane fouling conditions.

From the picture, both operating conditions were stable and the membrane flux did not decrease significantly. Since the diluted draw solution in the forward osmosis system was concentrated by the HBCR system and then returned to the forward osmosis system, the effective osmotic pressure gradient of the forward osmosis system was ensured. After desulfurization wastewater was treated with SA, the concentration of calcium ion in the wastewater was reduced, and the higher the calcium ion concentration in the feed solution, the more the membrane flux decreases (Kim *et al.* 2014). For the condition of adding FOSI, the scale inhibitor in the draw solution changed the gypsum crystal morphology on the scale surface by reverse transportation to inhibit membrane scaling (Lee *et al.* 2018), so the water flux of the membrane was not significantly reduced.

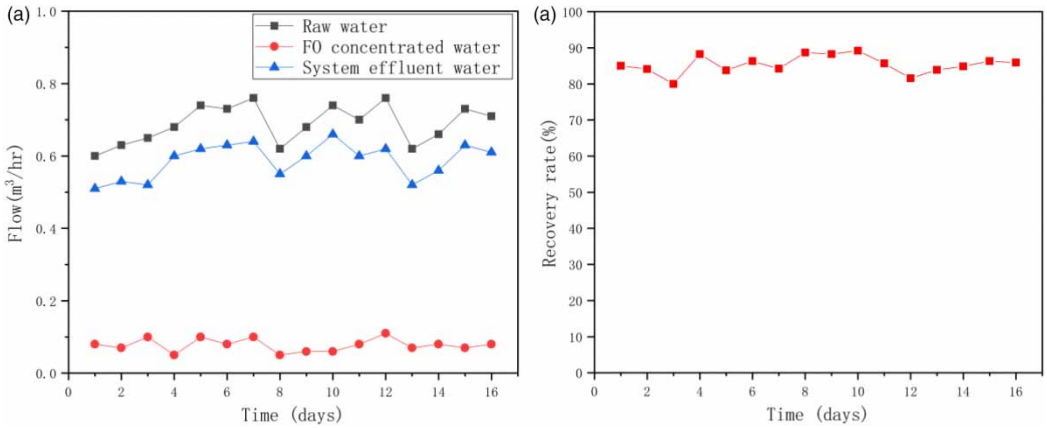

Figure 4 | The discharge of the influent and effluent of the system (a) and the recovery rate of the system (b) with SA.

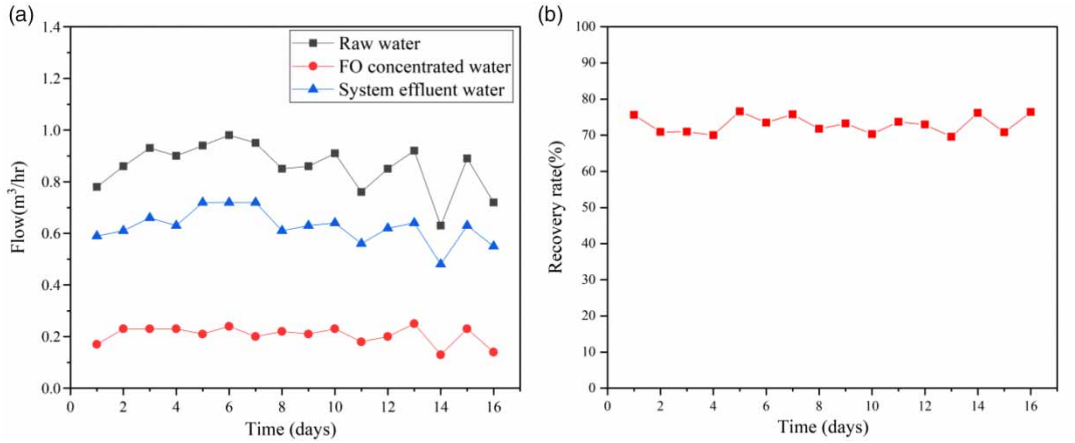

Figure 5 | The discharge of the influent and effluent of the system (a) and the recovery rate of the system (b) with FOSI.

Operating costs

The running cost of the pilot test mainly included power consumption and chemical consumption. The power consumption was mainly electricity consumption. The power consumption in the conditions of adding SA and FOSI was 21.8 kW·h/ton and 19.2 kW·h/ton, respectively. The electricity price was estimated at 0.5 RMB/kW·h. The power consumption cost under operating conditions was 10.9 RMB/ton and 9.6 RMB/ton, respectively. It can be seen from Table 4 that the total chemical cost of the two working conditions was 14.1 RMB/ton and 12.17 RMB/ton, respectively. After being calculated, the operating costs of adding SA and FOSI were 25 RMB/ton and 21.77 RMB/ton.

CONCLUSIONS

(1) The forward osmosis system could concentrate the desulfurization wastewater with an average TDS of 15,816–32,820 mg/L in the influent water to an average TDS of more than 120,000 mg/L, which was concentrated 3.8–7.8 times. The removal rates of Ca^{2+}, $Mg^{2+}$and Cl^{-} were more than 99%. Under the condition of adding SA and FOSI, the system recovery rate was 85.38% and 73.02%, respectively. The effluent of the system was stable.

(2) The operating cost was 25 RMB/ton and 21.77 RMB/ton with the condition of adding SA and FOSI, respectively. The application of forward osmosis in desulfurization wastewater treatment was economically effective.

(3) Compared with the traditional membrane technology, the front of the complete osmosis system did not require complex pre-processing technology, and the equipment process path was simple, and could adapt to the characteristics of complex and fluctuating quality of the desulfurized wastewater.

(4) This successful pilot project of forward osmosis treatment of desulfurization wastewater provides useful insights for forward osmosis treatment of landfill leachate and seawater desalination.

Table 4 | The price and consumption of chemicals

		Add SA system		Add FOSI system	
Item	**Unit price (RMB/ton)**	**Consumption**	**Cost (RMB/ton)**	**Consumption**	**Cost (RMB/ton)**
Hydrochloric acid (L/ton)	700	2.5	2	0.24	0.07
Sodium chloride (kg/ton)	1,200	0.083	0.1	0.083	0.1
Sodium carbonate (kg/ton)	2,000	6	12		
FOSI (kg/ton)	60,000			0.2	12
Total chemicals cost			14.1		12.17

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation of China (51508383, 51978465, and 51638011), the Natural Science Foundation of Tianjin Province (18JCQNJC09000 and 19JCZDJC39800).

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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First received 27 June 2020; accepted in revised form 23 October 2020. Available online 5 November 2020