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Combined effect of ozone and PTFE membrane on treating shale gas produced wastewater in Fuling Shale Gas Field

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ABSTRACT

Shale gas produced wastewater (SGPW) is difficult to be treated by conventional treatment processes due to its high total dissolved solids, chemical oxygen demand (COD), salinity (SAL), bacteria, and complex physicochemical composition. In this study, a new combined process of ozonation and polytetrafluoroethylene (PTFE) membrane was developed to treat SGPW in Fuling Shale Gas Field, China, for the first time. Polyaluminum chloride (PAC) was selected as flocculant for the pretreatment, and the ozonation was used to control sulfate-reducing bacteria (SRB), iron bacteria (FEB), total growth bactericide (TGB), and degrade macromolecule organic matter. The PTFE microfiltrate membrane was applied to treat COD and SAL. The results demonstrated that the removal of SRB, FEB, TGB, and COD was 55.6%, 78.6%, 77.3%, and 67.0%, respectively, with the conditions of PAC dosing quantity 400 mg/L, Ozone dosing quantity 3 g/h, and residence time 20 min. The combined process exhibited effective removal performance and is potential to be applied for treating SGPW in China.

Keywords: Shale gas produced wastewater (SGPW); Microfiltration; Ozonation; PTFE membrane; Combined effect

1. Introduction

As an unconventional natural gas resource with both economic and environmental values, shale gas mining has gradually become a research hotspot for global resource exploration [1]. According to research and evaluation by the Ministry of Land and Resources of the United States and the U.S. Department of Energy, China's shale gas reserves are high and the total recoverable amount is about (25.08–36.00) $\times 10^{12}$ m^3 [2]. In December 2015, a shale gas demonstration area with annual production of 5 billion square meters was established in the Fuling shale gas field in Chongqing, China, which meant that the Chinese shale gas industry was in the early stage of large-scale commercial development [3]. However, the environmental impacts caused by shale gas mining cannot be underestimated. The exploitation of shale gas requires a large amount of water resources, and the water consumption is generally (0.8–10) $\times 10^4$ m^3/well, which is 50–100 times that of traditional petrochemical resources explorations [4–6].

The wastewater generated during the mining of shale gas mainly comes from the horizontal fracturing process. The wastewater produced by this process (shale gas produced wastewater [SGPW]) is very special in water quality, and its composition is very complex and has potential ecological risks [7,8]. The study found that the concentration of benzene and xylene in the water resources of the U.S. shale gas development zone became higher, and the concentration of trihalomethane in drinking water increased. In addition, sewage from SGPW wastewater treatment plants will increase the

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concentration of bromide and total dissolved solids (TDS) in surface water [9]. In the process of wastewater treatment, sulfate-reducing bacteria (SRB), total growth bactericide (TGB), and iron bacteria (FEB) will have a serious negative impact on the treatment effect [10,11]. Due to the high content of TDS, chemical oxygen demand (COD), salinity (SAL), bacteria, heavy metal elements, and radioactive elements in SGPW, the composition is complex, so SGPW is difficult to process by conventional processing [12,13]. An EPA investigation showed that SGPW is recognized as one of the most intractable wastewater at present [14]. In summary, SGPW can cause serious pollution problems, so it is imperative to choose the appropriate processing technology to deal with [15].

Flocculation is one of the most widely used solid–liquid separation methods in traditional industrial wastewater treatment. This process is often used to remove suspended and dissolved solids, colloids, and organic matter in industrial wastewater [16,17]. It is a simple and efficient wastewater treatment method and has been widely used to treat various types of wastewater, such as dyeing wastewater, landfill leachate, papermaking wastewater, and oily wastewater [18–21]. In the flocculation method, the flocculant is added to the wastewater, and the finely divided or dispersed particles are attracted to each other, aggregated into larger-sized particles, and then precipitated to purify the water.

As a highly effective oxidant, ozone has been widely used in the treatment of refractory organics in municipal wastewater and industrial wastewater [22,23]. Chandrasekara Pillai et al. [24] showed that the ozone oxidation process can remove 40% of COD in wastewater with a COD content of 35,000 mg/L in 100 min. Ozone has strong oxidizing properties and can destroy the cell wall and cell membrane of microorganisms. Therefore, ozone oxidation technology can obviously inactivate all microorganisms including bacteria, viruses, molds, and fungi [25,26]. In addition, membrane separation technology which is simple to operate and can be oil repellent is currently being applied to the treatment of industrial wastewater [25,27]. Recently, ultrafiltration and microfiltration technologies have been applied in some practical projects [28,29]. Some studies had modified the polytetrafluoroethylene (PTFE) membrane to achieve solar desalination [30], which showed that 3.5% NaCl solution can be purified into purified water by modified PTFE membrane technology. The main reason is that the hydrophobic PTFE membrane inhibits the natural penetration of raw water into the membrane to prevent the treated water from being contaminated.

In summary, in view of the difficulty of SGPW purification, we have designed a combination of flocculation, ozone oxidation, and membrane separation technology to deal with SGPW, providing a reference for practical applications.

2. Material and methods

The SGPW used in this study was from Fuling Shale Gas Field, Chongqing, China. The average water quality is listed in Table 1.

The testing apparatus is shown in Fig. 1. The apparatus was made up of coagulating sedimentation tank, ozone oxidation and microfiltrate membrane module. The ozone generator (no. SW-002-3g) used in the experiment was produced by Qingdao West Electronic Purification Equipment Co., Ltd. (Jiaodong Industrial Park, Qingdao, Shandong, China). The ozone production was 3 g/h, and the power was 80 W. The material of microfiltration membrane (PTFE) was hollow fiber with oxidation resistance, with the average pore diameter 0.45 μm, inner diameter 0.8 mm, outside

Table 1
The parameters of shale gas produced wastewater

Indicators	Average water quality	Emissions standard[a]
COD	4,575 ± 386 mg/L	<1,000 mg/L
SS	685 ± 12 mg/L	50 mg/L
SAL	20.3 ± 2 mg/L	–
SRB	$4.5 \times 10^5 \pm 343$ cuf/mL	–
FEB	$1.5 \times 10^6 \pm 176$ cuf/mL	–
TGB	$1.1 \times 10^6 \pm 426$ cuf/mL	–
pH	7.6 ± 0.5	6.5–9.0

[a]Emission standard of pollutants for petroleum chemistry industry (GB 31571-2015).

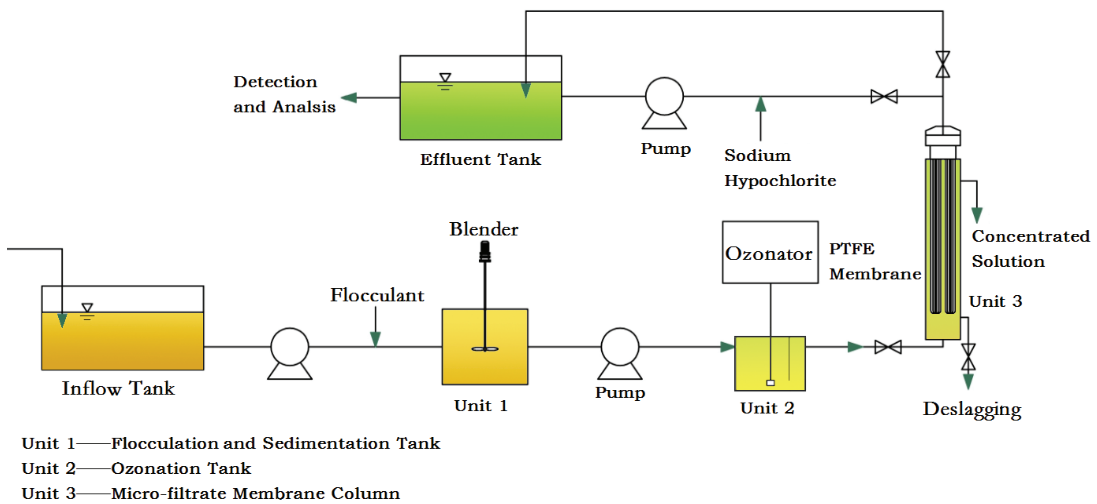

Fig. 1. Test apparatus used in the experiment.

diameter 1.6–1.7 mm, membrane area 0.1 m^2, and pore rate 85%. The membrane column is 0.6 m high and has a radius of 30 mm, and the membrane flux could be increased from 0 to 100 L/(m^2·h) without affecting normal use.

The wastewater was injected into the coagulating sedimentation (Unit 1) by a pump to remove the tiny suspended solid (SS) and the colloidal impurities through flocculation sedimentation. The effluent flowed into ozone oxidation unit (Unit 2) to remove SRB, TGB, FEB, and macromolecule organics. Then the effluent of Unit 2 was put into the column of microfiltrate membrane (Unit 3), and the discharged was tested and analyzed.

The testing parameters included COD, SAL, SS, membrane permeate flux, SRB, FEB, TGB, and pH. COD was tested by COD detector (HACH DR1010 COD Tester, USA). SAL and pH were determined by precise pH/conductivity-measuring instrument. MPN method was used to test the amount of SRB, FEB, and TGB.

3. Results and discussion

3.1. Flocculation process

The purpose of the flocculation process is to remove the SS from the SGPW. SS is an important carrier of bacteria and viruses. High concentration of SS affects the processing efficiency of subsequent processing units of the system, so it is necessary to reduce the SS concentration by flocculation precipitation. According to the characteristics of wastewater, the purification effect of different kinds and dosage of flocculant on SGPW was studied.

In this section, four common flocculants (polyaluminum chloride [PAC], PAS, PFS, and $AlCl_3$) were selected for SS and COD removal experiments. The amount of flocculant and SGPW used in the experiment was 400 mg and 1 L, respectively. The wastewater was first stirred at 300 rpm for 5 min, then at 50 rpm for 8 min, and finally at rest for 5 min. The supernatant was taken for testing, and the removal rates of SS and COD by the four flocculants were analyzed.

The result is shown in Fig. 2(a). The optimal removal rates of SS by PAC, PAS, PFS, and $AlCl_3$ were 40.91%, 38.96%, 35.93%, and 28.38%, respectively. The COD removal rates of each flocculant were 25.36%, 21.41%, 20.09%, and 13.41%, respectively. According to the result, PAC was chosen as the flocculant in Unit 1.

The effect of different PAC dosages on the removal of SS and COD is shown in Fig. 2(b). It can be seen from the figure that as the dosage of PAC increased, the removal rate of COD and turbidity increased under the same conditions. In the flocculation process, negatively charged colloidal particles in SGPW and metal cations in PAC generated electric scavenging neutralization effect, which promoted agglomeration of colloidal particles. However, when the dosage of PAC was higher than 400 mg/L, the increase of COD removal rate was not obvious, and the SS removal rate even showed a downward trend. The reason was that by gradually adding a strong electrolyte to the wastewater, the charge balance in the wastewater was gradually destroyed, and the suspended matter gradually aggregates to form alum, resulting in a decrease in SS in the wastewater. As the charge in the wastewater gradually reaches equilibrium, the flocculation effect reached the best. However, if the PAC dosage increased, the positive metal ions in SGPW would increase, resulting in electrostatic repulsion between the colloidal particles, so the particles would be difficult to aggregation, and removal effect would decrease.

3.2. Ozone oxidation process

Fig. 3(a) shows the COD removal effect of the hydraulic retention time in Unit 2. As shown in Fig. 3(a), with the residence time increased, the COD removal effect was very noticeable in the first 20 min. However, as the residence time increased further, the improvement in COD removal effect was gradually reduced.

SRB is the main harmful bacteria in the SGPW, which may cause metal equipment corrosion, pipeline blockage, and water quality worsening, producing many problems to the reuse of SGPW [31]. With the propagation of FEB, a large amount of iron hydroxide is produced, which is wrapped around the metal surface to form a sheath, which reduces heat transfer efficiency. The resulting electrical corrosion provides favorable conditions for the growth of SRB bacteria. In addition, the formation of oxygen concentration cell

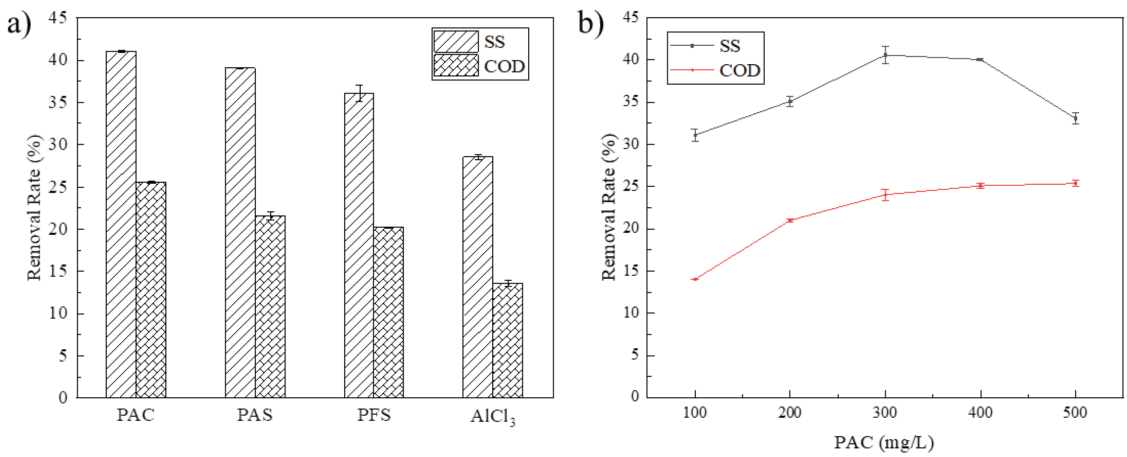

Fig. 2. The performance of flocculation sedimentation process: (a) removal rate of SS and COD with different flocculants and (b) removal rate of COD and turbidity of PAC dosing quantity.

corrosion will result in an anaerobic environment where SRB grows well and exacerbates corrosion. Therefore, SRB, FEB, and TGB are three important harmful microorganisms in SGPW.

Fig. 3(b) shows the influence of residence time on SRB, FEB, and TGB in Unit 2. According to Fig. 3(b), under the condition of ozone at 3 g/h, as the residence time increased, the number of three microorganisms decreased rapidly. Take comprehensive consider of COD removal rate and sterilization effect, the appropriate retention time of was 20 min in Unit 2.

3.3. Microfiltrate membrane process

3.3.1. Influence of membrane pore size

Two kinds of PTFE membrane with pore sizes 0.45 and 0.80 μm were used to investigate the removal rate of COD and SAL. The result is shown in Fig. 4(a). As shown in Fig. 4(a), COD removal rate was 34.38% and 22.73%, respectively. SAL removal rate of the pore size 0.45 and 0.80 μm was 21.11% and 19.90%, respectively. Thus, it could be seen that the both removal rates of COD and SAL were higher with the use of the membrane with average pore size 0.45 μm.

3.3.2. Effect of the membrane flux

Fig. 4(b) shows the removal rates COD and SAL according to different membrane flux tested by meter pumps with the pore size of 0.45 μm. According to Fig. 4(b), the removal rates of COD and SAL showed no obvious change with the increase of membrane flux. The removal rate of COD and SAL was about 34% and 21%, respectively.

3.3.3. Influence of serial columns

Fig. 4(c) shows the experiment results of the combining form of serial columns for further study on the influence on the removal rates of COD and SAL. COD removal rate was 34.38% when a single reaction column was used and increased to 35.56% as another column was added. Furthermore, SAL removal rate was 21.11% with a single column and increased to 25.38% with two columns. Thus, SAL removal rate could be increased by serial columns obviously.

3.4. Combined process

The optimal technological conditions using a single-membrane reaction column were listed as follows:

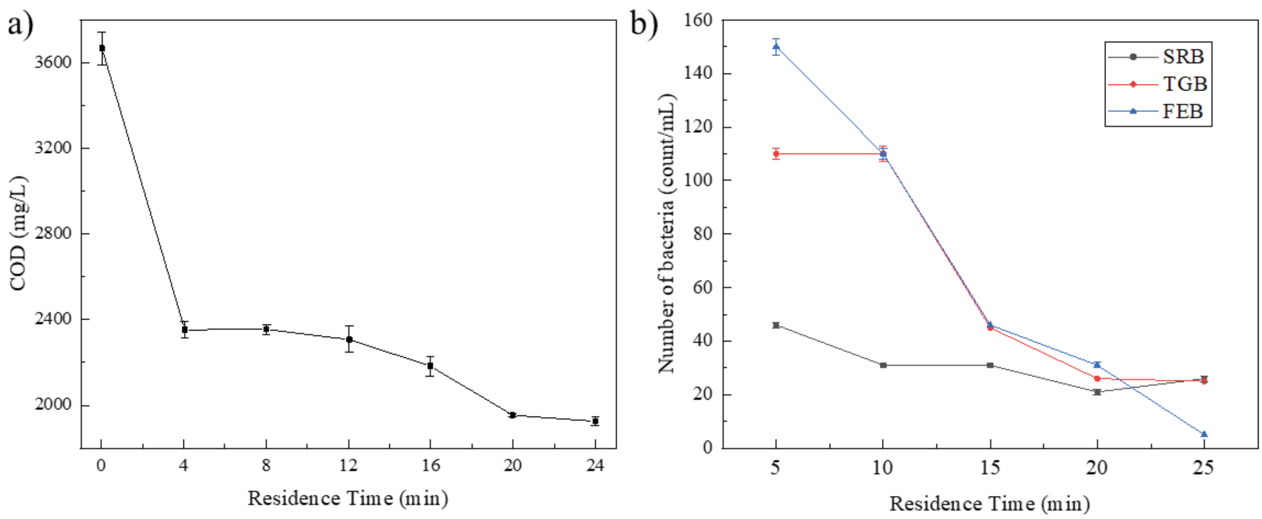

Fig. 3. The performance of ozone oxidation process: (a) the effect of oxidation and (b) influence of oxidation time on the bacteria removal.

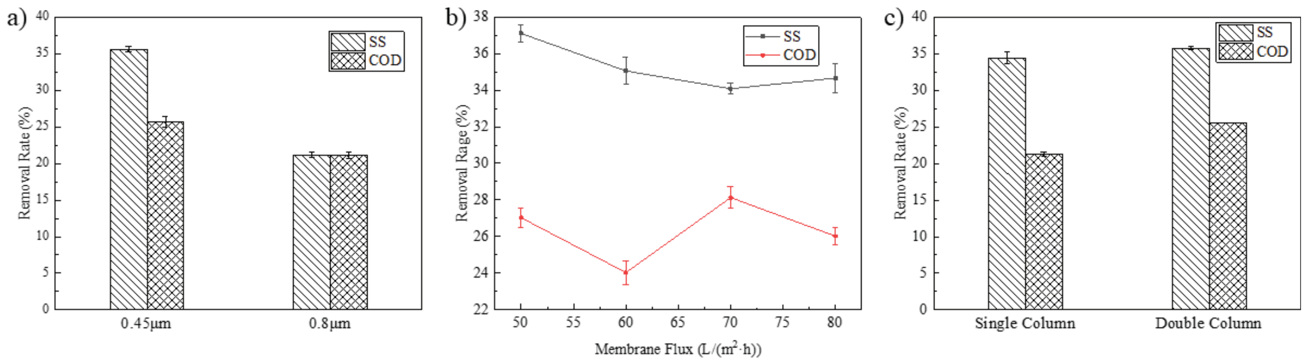

Fig. 4. The performance microfiltrate membrane process: (a) removal rate of COD and SAL with different pore size, (b) COD and SAL removal rates with different membrane flux, and (c) COD and SAL removal rates of single column and serial columns.

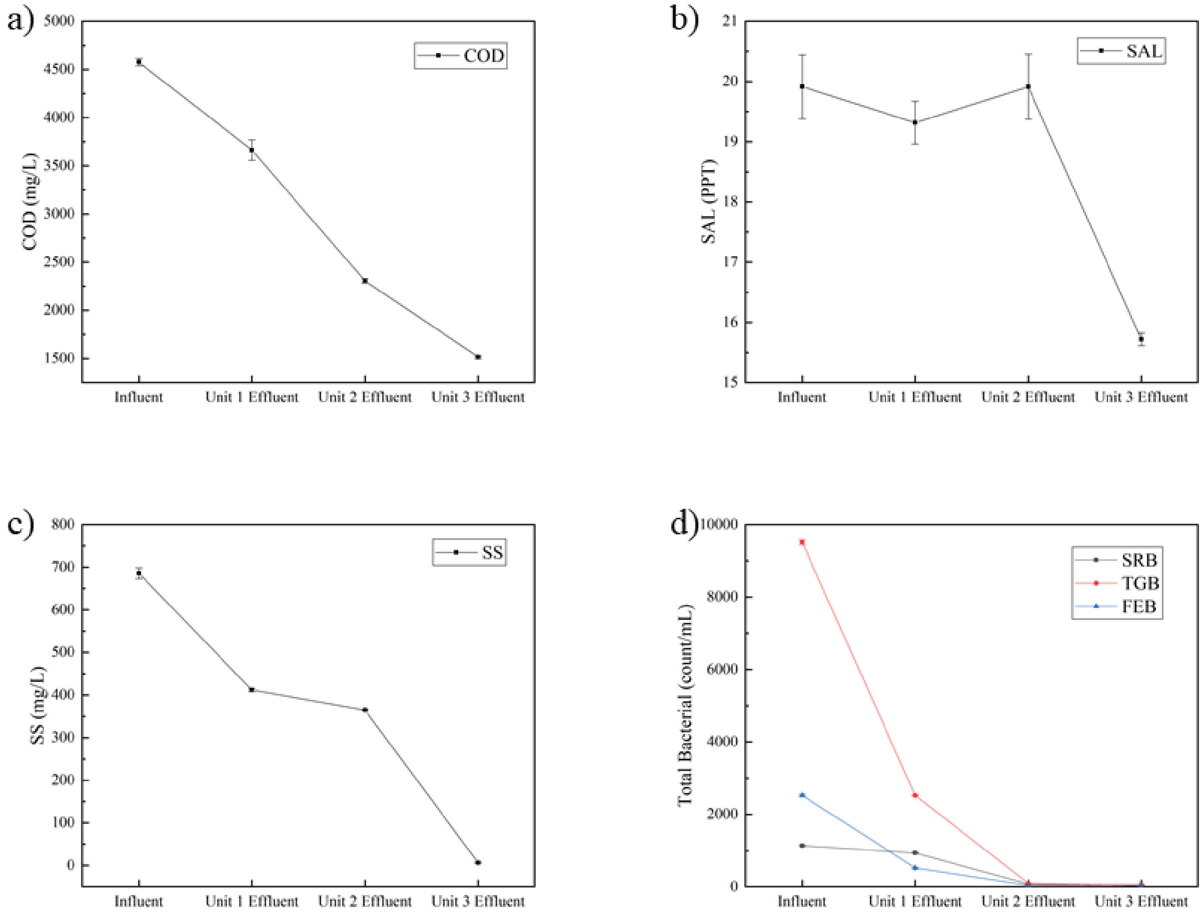

Fig. 5. The removal efficiency of each unit on each indicator: (a) COD removal, (b) SAL removal, (c) SS removal, and (d) total bacterial removal.

PAC dosing quantity in Unit 1 was 400 mg/L; ozone dosing quantity in Unit 2 was 3 g/h, and the residence time was 20 min; the average pore diameter of PTFE membrane used in Unit 3 was 0.45 µm. Under these conditions, purifying water effects are shown in Fig. 5.

As shown in Fig. 5(a), COD decreased from 4,575 to 1,510 mg/L through three units. Based on the result and analysis, we could find that the constituent of COD in the wastewater could be removed effectively by the flocculation and sedimentation effect of PAC. In Unit 2, part of refractory organic compounds was removed by strip, ozone direct oxidation, and hydroxyl indirect oxidation. At last, SSs, bacteria, and large molecule colloidal substances were intercepted by PTFE microfiltration membrane in Unit 3, so COD of the effluent was further declined.

As shown in Fig. 5(b), SAL could not be effectively declined in units 1 and 2, but it fell by 21.11% after PTFE microfiltration membrane filtration in Unit 3, which indicated that SAL could be declined in a certain degree through PTFE microfiltration membrane in this process.

As to Fig. 5(c), SS decreased from 685 to 411 mg/L through Unit 1, and Unit 2 was the only unit that cannot remove SS in the wastewater effectively. Effluent was decreased to 5 mg/L.

As shown in Fig. 5(d), bacteria could be removed by Unit 1 in a certain degree, because SS was important carrier of bacteria, which indicated that the removal of SS also had certain antibacterial function. Through ozone oxidation unit, a large number of bacteria and microbes were killed by strong oxidizing of ozone, and PTFE microfiltration membrane itself also had the function of intercept bacteria.

4. Conclusion

1. Through the process test, PAC was chosen as flocculants in coagulating sedimentation unit, and the mass doping concentration was 400 mg/L. In ozone oxidation unit, production of ozone was 3 g/h, and residence time was 20 min. In microfiltrate membrane unit, serial PTFE columns were used.
2. Fracturing fluid contains high SS and bacteria with complicate compositions. This study provided a new process that combines coagulating sedimentation, ozone oxidation, and microfiltrate membrane, achieved efficient removal effect: SS decreased from 685 to 5 mg/L (removal rate was 99.15%); COD decreased from 4,575 to 1,510 mg/L (removal rate was 66.99%); SAL decreased from 19.9 to 15.7 ppt (removal rate was 22.1%); and bacteria was less than the detection limit. The combined process exhibited effective removal performance and is potential to be applied for treating SGPW.

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