Study on cooperative treatment of natural gas pipeline cleaning wastewater and membrane module

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Abstract—Membrane module and pigging wastewater are common pollutants in natural gas transmission process. The treatment of these pollutants is difficult. In this paper, ultrasonic (US), persulfate (PS) and ultrasonic coupled persulfate were used to degrade organic matter in natural gas cleaning wastewater. The effects of pH, initial PS concentration, ultrasonic power, PS dosing batch and other factors on chemical oxygen demand (COD) degradation efficiency of pigging wastewater were investigated. The experimental results show that the optimal treatment effect can be obtained when the dosage of sodium PS is 80g/L, pH=4, the dosing number is 5, and the ultrasonic power is 840 W. After 6 h of reaction, the removal rate of COD can reach 80.08 %. Considering the synergistic treatment of the ultrasonic coupling PS on the solid-liquid pollutant, we adjust the ultrasonic power to 55W (frequency is 40kHz), pH=4.5, dosing twice (total dosage 150mg/L), and the final COD concentration below 100mg/L. However, when pre-ultrasonic activated persulfate in clear water, COD removal rate can reach 95.35 %, which can meet the effluent requirements.

1. Introduction

Natural gas transmission pipelines often form scaling, hydrate and liquid accumulation\textsuperscript{[1]}, which affect the normal operation of pipelines. Regular cleaning of pipes will flush out substances such as scaling, hydrate and liquid accumulation. Polyester fiber membrane is widely used to remove impurities in natural gas\textsuperscript{[2]}. After the treatment, the surface material composition of the membrane would be complex since the concentration of COD (Chemical Oxygen Demand), petroleum, and Fe is almost up to 1575.84 mg/L, 129.32 mg/L, 122.29 mg/L, respectively. There is no effective solution to the industry's treatment with respect to the disposal of pipeline cleaning wastewater and membrane components. The natural gas pipeline cleaning wastewater has low pH, complex composition (COD up to 7966 mg/L, manganese and iron content is high), and small water volume, so how to choose the appropriate treatment method and equipment is an urgent problem to be solved. The current membrane components processing method is focused on centralized delivery processing, while the annual cost is very high.

The treatment of membrane module and pigging wastewater is difficult. there is little literature on separate treatment, while the method of collaborative treatment of pigging wastewater and membrane module has not been reported in detail for the time being. Theoretically, chemical cleaning can be used to remove COD, but chemical cleaning itself will also provide a large amount of COD, but makes the cleaning greatly increased difficulty. Using ultrasonic activation PS (persulfate) to obtain sulfate radical to degrade organic pollutants has the advantages of simple equipment, low energy consumption, long service cycle, simple operation, safety, cleanliness and no secondary pollution\textsuperscript{[3, 4]}. Manganese, iron, and other transition metals in the raw water also have a certain activation effect on the added PS\textsuperscript{[5, 6]}. In the cleaning process of membrane components, the US (ultrasound) can also strengthen the transfer of
pollutants from the solid phase surface to the liquid phase, and then PS can be added to carry out collaborative treatment of pigging sewage and membrane components. This study focuses on the influence of pH value, PS concentration, ultrasonic power (frequency: 40kHZ) and PS dosage batch on the COD degradation efficiency of pigging sewage, and follows up and detects the changes in the concentration of $\text{S}_2\text{O}_8^{2-}$ and $\text{SO}_4^{2-}$ ions in the reaction process. The change of COD and its components in pigging sewage was further investigated to reveal the degradation process of various pollutants in pigging sewage, providing certain data and theoretical support to solve the problems of cleaning sewage and waste membrane components in natural gas pipelines.

2. Materials and Methods

2.1. Experimental materials

The membrane components and test water samples were taken from the cleaning sewage of a natural gas pipeline of a natural gas operation company limited. Dichloromethane ($\text{CH}_2\text{Cl}_2$) organic solvent was used as the extraction agent to extract organic substances in the membrane assembly of the natural gas pipeline. Various analytical methods were used to analyze the membrane leaching solution and determine the main substances. The main indexes of the membrane leaching solution and the main indexes of the tested water sample are shown in Table 1.

| COD (mg/L) | SS (mg/L) | pH | petroleum pollutant (mg/L) | Mn (mg/L) | Fe (mg/L) |
|------------|-----------|----|---------------------------|-----------|-----------|
| 1574.84    | 12.33     | 6.5 | 129.316                   | 12.535    | 122.287   |

Table 2 Main indicators of pigging sewage

| COD (mg/L) | SS (mg/L) | pH | petroleum pollutant (mg/L) | Mn (mg/L) | Fe (mg/L) |
|------------|-----------|----|---------------------------|-----------|-----------|
| 7966       | 603       | 4.5 | 11.15                     | 17.248    | 164.621   |

2.2. Materials

PS (Na2S2O8, AR), Sodium thiosulfate pentahydrate (Na2S2O3·5H2O, AR), ferrous ammonium sulfate (Fe(NH4)2·(SO4)2·6H2O, AR), anhydrous sodium sulfate (Na2SO4, AR), etc. were purchased from Kelong Chemical Reagent Factory of Chengdu, China. all chemicals used were analytically pure.

2.3. Methods

When pigging sewage is treated separately, a 500mL water sample is taken and placed in an ultrasonic pot. The water sample is adjusted to a certain pH with H2SO4 or NaOH, and quantitative PS is added to react under different ultrasonic powers. Sampling is carried out at fixed time intervals to measure COD value and examine the treatment effect. In the collaborative treatment of membrane assembly and pigging wastewater, 500mL and 10g membrane assembly placed in the ultrasonic pot and react to a certain time. Samples are taken at fixed time intervals to measure water sample COD, membrane leaching liquid COD and PS residue.

COD is measured by the improved sealing method of high chlorine wastewater in the oil and gas fields. Among them, the determination of residual persulfate content by iodimetry (DZ/T 0064.66-2021). According to the "solid waste leaching toxicity method - horizontal oscillation method (HJ 557-2010)", the extraction agent was added at the ratio of liquid to solid of 10 : 1 (L/kg). The bottle was sealed, shook at room temperature for 8h. Then the extraction bottle was removed and stood for 16h. The filter membrane is installed in the pressure filter, and the leaching solution is filtered and collected, and the COD of the leaching solution is measured.
3. Results and Discussion

3.1. Study on pigging wastewater treatment by activated PS

3.1.1. Effect of PS dosage

The effects of US/PS reaction system on pigging wastewater treatment were investigated and compared with those of US and PS reaction systems alone. The pH of the water sample was 4.5, the ultrasonic power was 900W, and the reaction time was 180min. Sodium PS dosage was 25g/L, 50 g/L and 75 g/L, and samples were taken every 30min for dilution and determination of COD. Two parallel samples were taken to determine COD, and PS residual amount was determined. The COD removal rate of pigging wastewater is shown in Fig.1.

![Fig.1 Effect of PS dosage](image)

It can be seen from Fig.1, with the increase of PS dosage, the COD removal rate gradually increases. When the PS dosage is 25g/L, 50g/L and 75g/L, respectively, the COD removal rates are 34.61%, 51.89% and 72.09% at 180min. With the increase of PS dosage, the COD removal rate also increases. Na2S2O8 dosage is positively correlated with COD removal rate in the range of 25-75g/L. This result shows that the increase of Na2S2O8 dosage can effectively improve the COD removal rate of pigging wastewater, which is consistent with the conclusion of ultrasonic activated PS degradation of dinitrotoluene in wastewater obtained by Chen et al.[7].

![Fig.2 Change of COD removal rate with time](image)

![Fig.3 PS consumption rate over time](image)

It can be seen from Fig.2 that, on the whole, the COD removal rate increases with time in the first 2 hours and then decreases greatly. According to Fig.3, PS consumption also increases sharply in the first
2 hours and then decreases sharply and tends to be flat. This tendency indicates that the increase of PS dosage will activate and generate more SO4·-, thus accelerating the removal rate of COD.

3.1.2. Effect of pH

The dosage of PS was 75g/L, the ultrasonic power was 900W, and the reaction time was 180min. PH values were 4.5, 7 and 9, and samples were taken every 30 minutes for dilution and determination of COD. Two parallel samples were taken to determine COD and PS residue. The COD removal rate of pigging wastewater is shown in Fig.4.

As can be seen from Fig.4, the COD removal rate decreases with the increase of pH. When pH=4.5, the removal effect is the best, and the removal rate can reach 72.09%. It can be seen that sulfate radical is more easily generated under acidic conditions[8], as shown in equation (1). However, according to equation (2), the excess sulfate radical generated under alkaline conditions will react with OH- to generate hydroxyl radical (-OH), which also affects the removal of organic matter[9], and the COD removal rate can reach more than 60% after the reaction. Therefore, PS has a good degradation effect in a wide range of pH, but the best in acid.

\[
\begin{align*}
S_2O_8^{2-} + H^+ &\rightarrow HSO_4^- + SO_4^{2-} \quad (1) \\
SO_4^{2-} \bullet + OH^- &\rightarrow \bullet OH + SO_4^{2-} \quad (2)
\end{align*}
\]

3.1.3. Effect of ultrasonic power

The control water sample pH is 4.5, and PS dosage is 75 g/L. Ultrasonic power was set at 600W, 900W and 1200W, and samples were diluted at intervals to determine COD. Two parallel samples were taken for COD determination, and PS residue was measured. Fig.5 shows the COD removal rate of pigging wastewater.
As can be seen from Fig.5, as the ultrasonic power increases from 600W to 1200W, the COD removal rate increases from 54.2% to 73.67%, but when the ultrasonic power increases from 900W to 1200W, the COD removal rate only increases by 1.58%. Within 60min, the degradation ability is significantly enhanced, and the COD removal rate is high, while the curve tends to be flat after 60min. The reason for increase in power is that the ultrasonic cavitation effect cause the collapse of cavitation bubbles and the growth of energy. The formation of local high temperature and high-pressure environment generates more energy for PS activated into sulfate radical[10], at the same time, this process leads to more severe mechanical action to strengthen mass transfer effect, improve the removal rate of COD[11].

3.1.4. Effect of batch feeding

The pH of the water sample was 4.5, the total dosage of PS was 75g/L, the ultrasonic power was 900W, and the reaction time was controlled. The dosage times were 1, 3 (2h/ time) and 5 (1.2h/ time), respectively. Samples were diluted every 30min for COD determination, and two parallel samples were taken for COD determination, and the residual PS content was determined. The COD removal rate of pigging wastewater is shown in Fig.6.

It can be seen from Fig.6 that the COD removal rate of each batch is higher than 70%. However, in the case of five dosages, the COD removal amount is 607.2mg/L more than that of one dosage, and the removal rate increases by 7.62%. Due to the sufficient PS, the number of sulfate radicals generated instantly is large, and the COD removal rate is fast. It can be seen from Fig.7 that PS consumption is particularly fast within 2h after one addition because excessive PS will produce a large amount of
SO$_4$-$^·$ in a short time, and these SO$_4$-$^·$ will self-quench[12], reducing the total amount of SO$_4$-$^·$ generated in the system, thus affecting the COD removal rate. However, the reaction system inhibits the formation of SO$_4$-$^·$ due to the small amount of PS added each time. In general, adding batch has a certain influence on the removal of COD in pigging wastewater.

3.1.5. Condition optimization

Four factors that may affect the COD removal effect of pigging wastewater by ultrasonic activation of PS were selected for investigation, including PS dosage, pH value, the batch of PS dosage and ultrasonic power. Three levels of each factor were selected for investigation. After optimization by orthogonal test, the order of experimental influencing factors is as follows: PS dosage > pH > ultrasonic power > batch. The optimal condition is that PS dosage is 80g/L, pH=4, dosage times is 5, ultrasonic power is 840W.

The optimal combination was verified by two parallel experiments and one blank experiment. Finally, the optimal removal rate of ultrasonic activated PS treatment was 80.08%.

3.1.6. Comparison of treatment methods

The single factor experiment or orthogonal experiment of single ultrasonic treatment, single PS treatment and ultrasonic activated PS treatment were respectively selected to compare the best experimental results. The experimental results are shown in Fig.8.

![Fig.8. Comparison of COD removal effect between three treatment methods](image)

As can be seen from FIG.8, when the reaction reaches 6h, the optimal removal efficiency of the three treatment methods is 13.89%, 26.35% and 80.08%, respectively. Among the three treatment methods, ultrasonic activated PS has the highest COD removal rate for pigging wastewater, followed by PS only, and ultrasonic only has the lowest removal rate. The ultrasonic activation system increased by 66.19% and 53.73% compared with that of the PS system. It can be seen from the figure that the removal of COD by ultrasound and PS alone is not obvious, and only a small part of organic matter can be removed. However, ultrasound activated persulfate generates sulfate radical by activating persulfate to carry out hydrogen abstraction electron transfer and other reactions on organic matter[13], which is better than the simple addition of the two.

3.1.7. Quenching experiment

To further explore the mechanism of generating sulfate radical by ultrasonic activation of PS and the reduction of COD in pigging wastewater the reaction rate difference among different alcohols and SO$_4$-$^·$ and ·OH was determined under the optimal conditions generated by orthogonal test According to the literature, the reaction rates of methanol and sulfate radical are $1.1 \times 10^7$~$9.7 \times 10^7$ (mol·s)$^{-1}$, and that of tert-butanol and hydroxyl radical are $4.0 \times 10^5$~$6.0 \times 10^5$ (mol·s)$^{-1}$. The free radical formation was identified by adding excess methanol and tert-butanol[14, 15].
As shown in Fig.9, the inhibition effect is more evident after methanol is added, and the COD removal rate decreases from 80.08% to 18.74%. The COD removal rate of the reaction system with tert-butanol is 59.64%. The inhibition effect of adding the tert-butanol to COD removal is not obvious. The removal rate is significantly reduced after adding methanol because methanol can capture SO$_4$· and ·OH in the system simultaneously[16], and the inhibition effect of methanol is significantly stronger than that of tert-butanol. It also shows that the reduction of COD in pigging wastewater is mainly the result of ultrasonic activation of PS to generate SO$_4$·.

3.2. US activated PS co-processing membrane modules for pigging wastewater

3.2.1. The release law of pollutants

Ultrasound the membrane module directly in clean water, control the pH to 7.4, the ultrasonic frequency of 40 kHz, and the power to be 55 W. Without adding PS, cut the membrane module directly into the reactor for joint treatment (20 kg/m$^3$).

It can be seen from Fig.10 that the COD release rate of the water sample is slower within 2h, and the COD release rate is significantly accelerated within 2~4h, after which the COD concentration tends to be flat, reaching the highest COD concentration on 4.5h, with a concentration value of 404.16 mg/L, that is, the COD released per kilogram of the membrane module is 20.2g. At the same time, the filter membrane was intercepted, and the COD concentration of the material leachate was measured. The
results showed that the COD concentration of the leachate increased first and then decreased, reaching the highest value in 4 hours. As shown in Fig. 10, the highest value was 6.2gCOD/kg membrane material.

3.2.2. US activated PS synergistic treatment membrane module for pigging sewage

Based on controlling the ultrasonic frequency of 40kHz, power of 55W, pH=4.5 and dosing twice (total dosage of 150g/L), the membrane module was cut and directly put into the reactor for joint treatment (20 kg/m3).

![Fig.11. Ultrasonic activated PS membrane treatment](image)

The results after treatment are shown in Fig.11. The COD can reach the effluent standard after 6h of reaction. The experimental results show that the effluent COD is basically not affected when the membrane assembly and the cleaning wastewater are treated together under these conditions.

3.3. Collaborative processing mechanism

3.3.1. Pigging wastewater treatment mechanism

When COD is determined by potassium dichromate, although most organic substances in water can be oxidized, some stubborn organic substances (such as pyridine and aromatics) are not easy to be oxidized and recognized, and cannot fully represent the total amount of organic substances[17]. Therefore, it is necessary to use other indicators to express. Total organic carbon (TOC) is expressed by carbon content, which can be used as another basis for treating pigging wastewater by ultrasonic activated persulfate treatment. The optimal conditions obtained from the orthogonal experiment of ultrasonic activation were selected for this experiment.

![Fig.12. TOC removal under optimal conditions](image)

It can be seen from Fig.12 that the TOC content shows a downward trend as a whole. In addition, the TOC mineralization is relatively slow in the first 3 hours of the reaction, and the mineralization rate
becomes faster in the last 3 hours. The TOC decreased from 3065 g/L to 863.2 g/L, and the TOC mineralization rate reached 71.84%, clarifying that the ultrasonic activation of PS has a good effect on the treatment of the organic matter in pigging wastewater.

Dichloromethane (CH$_2$Cl$_2$) organic solvent was used as the extractant to extract the organic substances in the original water sample and the water sample after ultrasonic activation of PS treatment, and the changes in the organic components of the sewage were measured by gas chromatography-mass spectrometry. Ultrasonic activated PS treatment pigging sewage GC-MS test conditions are the best conditions under the orthogonal experiment: PS dosage is 80 g/L, pH value is 4, ultrasonic power is 900 W, PS dosage is added The batch is 5 times, and samples are taken for extraction every 3h. The extraction is carried out according to the ratio of water sample and extractant 1:2, and gas chromatography-mass spectrometry analysis is carried out according to relevant conditions to determine the organic components in the water sample. The GC-MS spectrum is shown in Fig.13.

![Fig.13. GC-MS diagrams of water samples at different time periods](image)

Through GC-MS, the chromatograms of the water samples of the original treatment, the 3h and the 6h of the treatment were obtained. The total number of peaks in the original water was 22, which consisted of more substances and complex components. As shown in Fig.13, there are more alkanes, including linear alkanes such as heptadecane, hexadecane, tetradecane, and branched alkanes 8-
hexylpentadecane, halogenated hydrocarbons such as 1-iodooctadecane; aromatic benzyl alcohol; cyclic substance cyclohexylbarbital. Only one kind of substance is detected after the treatment, indicating that alkanes, aromatics and other substances in the raw water have been degraded, mainly through hydrogen abstraction and electron transfer to break the chain and ring into small molecular substances with less carbon or CO2.

3.3.2. **Cooperative processing mechanism**

The organic substances in the original sample and the membrane module after cleaning for 6h were extracted and analyzed by gas chromatography-mass spectrometry (Fig.14). It can be seen from the figure that the content of organic substances in the cleaned membrane module is significantly reduced compared to the original.

![Fig.14. GC-MS component analysis of membrane extracts before and after treatment](image)

After cleaning the membrane module according to Solid Waste Leaching Toxicity Method-Horizontal Oscillation Method(HJ557-2010), the COD of the leachate was measured. The results are shown in Fig.15.

![Fig.15. COD of membrane module leachate after cleaning](image)
As shown in Fig. 10, the release rate of COD increases from slow to fast and then tends to be gentle. The release rate of COD in the rapid release stage is greater than that of ultrasonic degradation, so COD increases sharply and then decreases slowly in 1-2h.

4. Conclusion

Based on the results and discussions presented above, the conclusions are obtained as below:

(1) Ultrasonic activation of PS has a good effect on the treatment of natural gas pipeline cleaning sewage. First, through single-factor experiments and then orthogonal experiments, it is concluded that the effects of various factors on the degradation of sewage COD from large to small are: PS addition, pH, ultrasound Power, dosing batches. The best conditions are that the dosage of PS is 80g/L, the initial pH is 4, the ultrasonic power is 840W, the number of times of PS is added 5 times, and the COD removal rate after the reaction is 80.08%. Through molecular probe competition experiments, it is shown that the process of ultrasurally activating PS to degrade the COD of pig sewage is mainly SO4−·oxidation.

(2) Through the GC-MS spectrum analysis of the ultrasonic activation of PS to degrade COD, the sulfate radicals generated by the activation have a significant effect on the degradation of the organic matter of the pigging sewage. The alkane and aromatic substances are more thoroughly degraded.

(3) Ultrasonic activation of PS has a good effect on synergistic treatment of membrane modules and pigging wastewater. The final COD concentration can reach 48.82mg/L, and the residual PS is 99.03%. When pigging wastewater is treated separately, the final COD concentration can reach 37.65. mg/L, the residual amount of PS is 97.35%. Experiments show that when the membrane module and cleaning wastewater are treated together, the COD of the effluent is basically unaffected.

(4) Ultrasonic activation of PS with clean water has a poor effect on membrane components. The residual amount of PS is about 84%, the reaction rate of PS is about 0.309 kg/h, and the treatment effect is 1.4g COD/(kg PS-h). The results show that the final residual amount of sodium persulfate is 16.63%, the reaction rate of sodium persulfate is about 1.61 kg/h, the treatment effect is 5.25 g COD/(kg persulfuric acid Sodium-h), and the COD removal rate reaches 95.35%.

(5) A coupled treatment method was come up to treat solid wastes and waste water at the same time. Natural gas and related industries can draw a lesson from this treatment method. This study raises a likelihood towards onsite treatment of membrane module and pigging wastewater in natural gas industry as well.

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