

Treatment of hydraulic fracturing wastewater by wet air oxidation

Wei Wang, Xiuyi Yan, Jinghui Zhou and Jiuli Ma

ABSTRACT

Wastewater produced by hydraulic fracturing for oil and gas production is characterized by high salinity and high chemical oxygen demand (COD). We applied a combination of flocculation and wet air oxidation technology to optimize the reduction of COD in the treatment of hydraulic fracturing wastewater. The experiments used different values of flocculant, coagulant, and oxidizing agent added to the wastewater, as well as different reaction times and treatment temperatures. The use of flocculants for the pretreatment of fracturing wastewater was shown to improve treatment efficiency. The addition of 500 mg/L of polyaluminum chloride (PAC) and 20 mg/L of anionic polyacrylamide (APAM) during pretreatment resulted in a COD removal ratio of 8.2% and reduced the suspended solid concentration of fracturing wastewater to 150 mg/L. For a solution of pretreated fracturing wastewater with 12 mL of added H₂O₂, the COD was reduced to 104 mg/L when reacted at 300 °C for 75 min, and reduced to 127 mg/L when reacted at the same temperature for 45 min while using a 1 L autoclave. An optimal combination of these parameters produced treated wastewater that met the GB 8978-1996 'Integrated Wastewater Discharge Standard' level I emission standard.

Key words | COD removal ratio, flocculation, hydraulic fracturing wastewater, pretreatment, wet air oxidation

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INTRODUCTION

Hydraulic fracturing is a technique in which fluids are pumped into wells under high pressure to increase the permeability of geologic formations (Economides & Nolte 2000; Britt 2012). The chemicals used in hydraulic fracturing, which can include gelling and foaming agents, friction reducers, crosslinkers, breakers, pH adjusters, biocides, corrosion inhibitors, scale inhibitors, iron-control chemicals, clay stabilizers, and surfactants (Stringfellow *et al.* 2014), significantly increase the chemical oxygen demand (COD). During hydraulic fracturing, up to four million gallons of water-based fluid could be injected into a single drilled well to both initiate and expand fractures, and act as proppant transport (i.e., sand or ceramic materials), of which 10–70% is subsequently recovered as flowback (Lester *et al.* 2015). This impaired water stream contains high concentrations of potentially hazardous organic and inorganic constituents and it requires some degree of treatment. However, hydraulic fracturing in underground oil and gas operations produces contaminated wastewater that is difficult to treat and often characterized by high

COD, high salinity, and high concentrations of toxic elements (Gregory *et al.* 2011; Chapman *et al.* 2012; Vengosh *et al.* 2013). An example chemical profile from fracturing water of the Marcellus shale region has shown that COD values of fracturing water increase considerably with time, whereas the biochemical oxygen demand (BOD) decreases (Mehta & O'Sullivan 2015); a dynamic that implies increasing toxicity with time. Currently, the treatment of hydraulic fracturing wastewater employs methods such as chemical coagulation, chemical oxidation, advanced oxidation processes, electrocoagulation, activated carbon adsorption, biological methods, and solidification methods (Lester *et al.* 2013; Sun *et al.* 2013; Theodori *et al.* 2014; Esmaeilirad *et al.* 2015), all of which have various shortcomings. For example, some methods require complex processing equipment, high processing costs, or a large amount of oxidizing agents (Rahm *et al.* 2013), while other methods can produce additional pollutants that do not meet national wastewater discharge standards (Hladik *et al.* 2014). Treatment processes that address all types of

wastewater have not yet been developed and they must be refined and improved to increase the efficiency and reduce the economic costs of hydraulic fracturing.

The wet air oxidation (WAO) method was developed in the 1950s to treat high concentrations of toxic and hazardous biological materials in refractory wastewater. It is a chemical process that removes contaminants in the liquid phase, and it usually requires high-temperature and high-pressure conditions and an agent to oxidize organic pollutants to CO₂, water, and inorganic or small organic molecules. WAO is not only less damaging to the environment but it is also more economical compared with other advanced oxidation processes that often use harmful and/or expensive oxidizing agents, such as ozone and ultraviolet light (Fu *et al.* 2015). Compared with traditional treatments, the WAO method is advantageous because it has a wider range of application, higher efficiency, produces little secondary pollution, can reuse energy generated during the treatment process, and produces useful secondary materials (Lefèvre *et al.* 2011).

In this study, a series of orthogonal experiments were first conducted using a small, hydrothermal autoclave to determine the optimal operating parameters for the treatment of hydraulic fracturing wastewater at the laboratory scale. A larger autoclave with an inner volume of 1 L was then used to conduct a series of pilot tests at a scale more realistic for operational hydraulic fracturing. Experiments were also conducted to determine whether the pretreatment of wastewater with flocculant, prior to the application of the WAO process, further improved the efficiency of wastewater treatment. The processes of coagulation and flocculation are used extensively in the treatment of drinking water as well as in industrial processes for the removal/separation of organics/inorganics dissolved/suspended as colloids in water/solution (Verma *et al.* 2010).

MATERIALS AND METHODS

Hydraulic fracturing wastewater and chemicals

The hydraulic fracturing wastewater used in this experiment originated from an oil and gas operation in Sichuan Province (the initial composition of the wastewater is listed in Table 1). The wastewater treatment experiments in this study were conducted using polyaluminum chloride (PAC) (Runfeng Environmental Protection Co., Zhenzhou, China) and polyacrylamide (PAM) (Huafeng Water Purification Materials Co., Zhenzhou, China) as flocculants and H₂O₂ (30% mass fraction) as an oxidant.

Table 1 | Initial composition of the fracturing wastewater

Pollutant/Property	Value
COD (mg/L)	4,624
BOD ₅ (mg/L)	107
Ammonia Nitrogen (mg/L)	63
Chloride Ion (mg/L)	957
Suspended Solids (mg/L)	892
Chromaticity	15 (turbid and light yellow)
pH	7.23

Analytical methods

The COD and ammonia nitrogen concentration were measured using a COD rapid detector (Lanzhou Lian Hua 5B-3C (V8)); the BOD₅ was measured using a BOD detector (HACH, CO, USA); the chloride ion concentration was determined using an AgNO₃ titration method (GB11896-1989); the suspended solids were determined by the gravimetric method (GB11901-1989); the chromaticity was measured by the dilution method (GB11903-1989); and pH was measured using a pHS-3C digital pH meter (Shanghai Optical Instrument Factory Co., Ltd, China).

WAO processes

The experiments were conducted using two types of hydrothermal autoclaves. The smaller hydrothermal autoclaves (Swagelok Co., OH, USA) were constructed from stainless steel (SUS316) and had a 5.6 mL volume, 12 mm length, 1 mm wall thickness, and 9.5 mm diameter. A salt bath mixture with a 1:1 mass ratio of NaNO₃ and KNO₃ was used to heat the autoclave. For each experiment with the smaller autoclaves, the fracturing wastewater, H₂O₂, and distilled water were first placed into the autoclave and the autoclave was sealed. The salt bath was then heated to a specific reaction temperature and the loaded autoclave immersed in the molten salt bath to promote a reaction, while being fixed to a hydrothermal apparatus that would intermittently stir the autoclave. After a predetermined reaction period, the autoclave was placed in a water bath and cooled over several minutes to room temperature, following which the fracturing wastewater was analyzed.

Experiments were also conducted using a larger autoclave composed of a custom alloy (Harrington) with an inner volume of 1 L and a 3 kW heating system (Figure 1). For these experiments, 100 mL of distilled water was

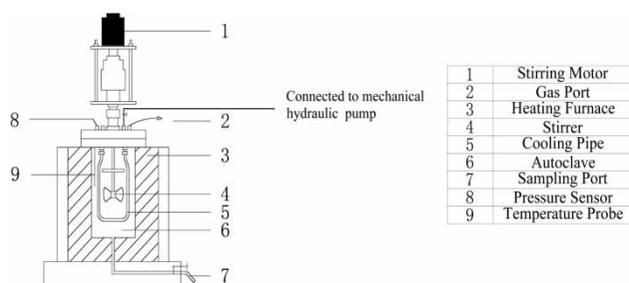


Figure 1 | Structure of the autoclave with an inner volume of 1 L.

added to the autoclave before it was sealed and heated. When the autoclave reached a predetermined reaction temperature, a valve connected to a hydraulic pump was opened and 200 mL of fracturing wastewater was pumped into the autoclave. The valve was then closed to allow the wastewater to react over a predetermined time at a specific reaction temperature. After the reaction, the autoclave was cooled to room temperature using water flow through a cooling pipe. The fracturing wastewater sample was removed from the autoclave and a COD removal ratio (%) was calculated according to

$$P = \frac{\text{COD}_0 \times \frac{V_1}{V_1 + V_2} - \text{COD}_1}{\text{COD}_0 \times \frac{V_1}{V_1 + V_2}} \times 100\% \quad (1)$$

where COD_0 is the COD of the untreated fracturing wastewater, COD_1 is the COD of the treated fracturing wastewater, V_1 is the volume of fracturing wastewater

added to the autoclave, and V_2 is the volume of distilled water added to the autoclave.

RESULTS AND DISCUSSION

Orthogonal experiments

We first conducted the orthogonal experiments using the smaller autoclaves to explore the effects of various factors and operating conditions on the efficiency of the wastewater treatment process. The orthogonal experiments were designed according to L9 (3^3) principle (three factors, three levels, nine experiments) (Deng 1994). The effects of three parameters (reaction time, reaction temperature, and oxidant dosage) were investigated in this research. If only three process factors are studied in an analysis, an orthogonal array with nine incorporations of input parameters can be employed. The L9 orthogonal array, the levels of the parameters (each parameter was designed with three levels), and the nine combinations of the factors are listed in Table 2. In Table 2, K1, K2 and K3 are the average values of COD removal of level 1, level 2, and level 3, respectively, for each factor; and R is the difference between the maximum and the minimum of the average values of the experimental results, under different levels for the same factor or range. We evaluated the effects of reaction temperature, reaction time, and amount of oxidizing agent on the COD removal ratio (Table 2).

Table 2 | Results and range analysis of orthogonal experiments

Expt #	Fracturing wastewater (mL)	H ₂ O (mL)	H ₂ O ₂ (mL)	Temperature (°C)	Reaction time (min)	COD after reaction (mg/L)	COD removal ratio (%)
1	1.5	0.135	0.045	280	15	1,911	58.7
2	1.5	0.135	0.045	310	30	534	88.4
3	1.5	0.135	0.045	340	45	421	90.9
4	1.5	0.112	0.068	310	45	325	93.0
5	1.5	0.112	0.068	340	15	489	89.4
6	1.5	0.112	0.068	280	30	640	86.2
7	1.5	0.090	0.090	340	30	312	93.2
8	1.5	0.090	0.090	280	45	466	89.9
9	1.5	0.090	0.090	310	15	895	80.6
K ₁			79.3	78.3	76.2		
K ₂			89.5	87.3	89.3		
K ₃			87.9	91.2	91.3		
R			8.6	12.9	15.1		

A maximum COD removal ratio of 93.2% was achieved using 0.09 mL of H₂O₂ for a 30 min reaction at 340 °C and the COD removal rate for the majority of experiments was >80%. This shows that the WAO process is more effective in treating fracturing wastewater than other chemical methods that produce a COD removal rate of approximately 50–90% (Fakhru'l-Razi *et al.* 2009). A comparison of the R values from the range analysis showed that, in order of importance, the three principal factors governing the efficiency of COD removal from fracturing wastewater were: reaction time > reaction temperature > oxidant dosage.

Optimization experiments

WAO experiments

A series of experiments was conducted using the larger, 1 L autoclave system to simulate more realistic conditions of fracturing wastewater treatment. The fracturing wastewater was first mixed with 12 mL of H₂O₂ at a reaction temperature of 340 °C for 30 min (Table 3); these were the optimal conditions determined from the small autoclave experiments. The fracturing wastewater COD removal ratio was 93.8% using the 1 L autoclave, i.e., similar to the efficiency achieved by the small autoclave treatment (93.2%). Using the same reaction temperature and oxidant dosage, the reaction time was then reduced from 30 to 15 min, and the fracturing wastewater COD removal ratio subsequently dropped to 91.9%. The optimal COD removal ratio of 93.8% corresponded to a COD of 191 mg/L, which exceeded the GB 8978-1996 'Integrated Wastewater Discharge Standard' level I emission standard of 100 mg/L.

Flocculation experiments using PAC

We conducted experiments to determine whether flocculant pretreatment improved the efficiency of COD removal from fracturing wastewater. PAC is a flocculant commonly used in fracturing wastewater treatment processes. To examine the effect of different amounts of PAC on flocculation efficiency, varying amounts of a 5% PAC solution were added to 100 mL of fracturing wastewater, and then stirred for

2 min at a speed of 120 rpm on a magnetic stirrer. After allowing the mixture to stand for a 10 or 30 min period, the COD of the supernatant was measured (Table 4).

It is known that higher COD removal efficiency cannot be obtained by adding more PAC (Yao *et al.* 2015). However, considering the sedimentation floc proportion, vitriol flower achieved a better sedimentation effect when the amount of PAC additive was 500 mg/L, reaching 20% of the liquid after standing for 30 min. When the amount of PAC additive was 250 mg/L, the floc sedimentation effects were poorest, the floc layer was not obvious, and almost no sedimentation effect was observed, even after standing for 30 min. Furthermore, the flocculation supernatant was measured as the chloride ion content, as shown in Figure 2. The addition of PAC did not increase the flocculation efficiency, and the experimental results were found consistent with the literature (Fakhru'l-Razi *et al.* 2009). The chloride ion content also increased with PAC and increased more rapidly when >500 mg/L of PAC was added (Figure 2). Taking the above factors into account, a PAC concentration of 500 mg/L was used in subsequent experiments.

Flocculation experiments using PAM

PAM is a coagulant commonly used in the treatment of hydraulic fracturing wastewater in various forms including anionic polyacrylamide (APAM), cationic polyacrylamide (CPAM), and nonionic polyacrylamide (NPAM). To examine the flocculation efficiencies of the different types of PAM, 20 mg/L of PAM from a 0.1% solution was added to 100 mL of fracturing wastewater, then stirred for 2 min at a speed of 120 rpm using a magnetic stirrer. After allowing the solution to stand for 10 min, the COD of the supernatant was measured (Table 5).

There was little difference between the effects of the three types of PAM on the efficiency of COD removal from fracturing wastewater. APAM and NPAM produced the same COD removal ratios, while CPAM showed slightly greater removal efficiency. However, the APAM treatment of fracturing wastewater produced a dark brown aggregate and significant flocculent precipitate, with the color of the solution changing from pale yellow to transparent, while

Table 3 | Hydrothermal experimental results (1 L autoclave)

Expt #	H ₂ O ₂ (mL)	Temperature (°C)	Pressure (MPa)	Reaction time (min)	COD after reaction (mg/L)	COD removal ratio (%)
10	12	340	22.9	30	191	93.8
11	12	340	22.9	15	251	91.9

Table 4 | Flocculation experiments using PAC

Added PAC (mg/L)	COD (mg/L)	COD removal ratio (%)	Sedimentation floc proportion (%)	
			Standing for 10 min	Standing for 30 min
0	4,624	0.0	0	0
250	4,515	2.4	0	0
500	4,486	3.0	40	20
750	4,389	5.1	60	40
1,000	4,243	8.2	90	60

the CPAM and NPAM treatments did not produce significant flocculation or sedimentation and the color of the solution remained almost unchanged. Therefore, APAM was selected for use in subsequent flocculation experiments.

Flocculation experiments using PAC and APAM

Fracturing wastewater (100 mL) was mixed with PAC solution (500 mg/L) and varying amounts of a 0.1% APAM solution, and then stirred for 2 min at a speed of 120 rpm using a magnetic stirrer. After allowing the mixture to stand for 10 or 20 min, the COD of the supernatant was measured (Table 6).

With the amount of PAC held constant, the COD removal ratio increased as the amount of APAM increased, with a maximum removal ratio of 8.2% for a 20 mg/L APAM solution. The addition of APAM enhanced sedimentation floc and after a standing period of 20 min, the sedimentation floc proportion reached equilibrium at 20%. With 20 mg/L of added APAM, the suspended solid content

of the supernatant was 150 mg/L after a standing period of 30 min, i.e., much lower than the suspended solid content of 1,064 mg/L when no APAM was added. Therefore, 500 mg/L of PAC and 20 mg/L of APAM were selected as the optimal amounts for flocculant pretreatment of fracturing wastewater.

Flocculation pretreatment + WAO

For the next set of experiments (Table 7), the fracturing wastewater was first treated with 500 mg/L of PAC and 20 mg/L of APAM. The supernatant was then treated using the WAO method. Then, 12 mL of H₂O₂ was added to 200 mL of fracturing wastewater in the autoclave and allowed to react at 300 °C for different experimental periods. The COD removal ratio was measured and calculated using Equation (1), where COD₀ was the COD of the fracturing wastewater following the pretreatment process (4,243 mg/L).

As the reaction time increased, the COD removal ratio increased. After a reaction time of 60 min, the COD of treated fracturing wastewater was 108 mg/L, i.e., close to the GB 8978-1996 'Integrated Wastewater Discharge Standard' level I emission standard (100 mg/L). As the reaction time increased from 60 to 75 min, the COD removal ratio increased by only 0.1%, suggesting that additional reaction time would not significantly increase the removal ratio of COD under the experimental conditions.

A high reaction temperature requires considerable energy consumption to maintain the critical equipment conditions. To evaluate the treatment efficiency under conditions to reduce processing costs, we conducted additional WAO experiments at lower reaction temperatures. Varying amounts of H₂O₂ were added to 200 mL of fracturing

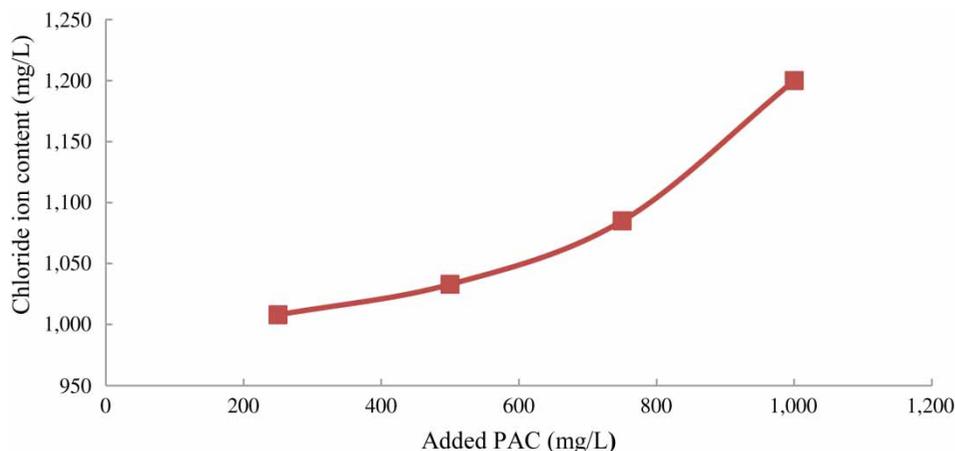
**Figure 2** | Chloride ion content response to added PAC.

Table 5 | Flocculation experiments using PAM

Type of PAM (20 mg/L)	COD (mg/L)	COD removal ratio (%)	Standing effect
APAM	4,465	3.4	Flocculation
CPAM	4,400	4.8	No Flocculation
NPAM	4,465	3.4	No Flocculation

Table 6 | Flocculation experiments using PAC (500 mg/L) and APAM

APAM amount (mg/L)	COD (mg/L)	COD removal ratio (%)	Suspended solids (mg/L)	Sedimentation floc proportion (%)	
				Standing for 10 min	Standing for 20 min
0	4,486	3.0	1,064	40	20
10	4,400	4.8	785	35	
15	4,343	6.1	765	35	
20	4,243	8.2	150	30	
25	4,457	3.6	550	25	

Table 7 | WAO experiments at 300 °C with pretreatment

Expt. #	H ₂ O ₂ (mL)	Pressure (MPa)	Reaction time (min)	COD value after reaction (mg/L)	COD removal ratio (%)
12	12	14.6	45	127	95.5
13	12	14.7	60	108	96.2
14	12	14.7	75	104	96.3

wastewater after flocculation pretreatment and reacted at 280 and 260 °C for 60 min (Table 8). The COD removal ratio increased with additional amounts of H₂O₂. For a reaction at 280 °C with 18 mL of added H₂O₂, the COD of fracturing wastewater was 127 mg/L after treatment, which was the same result as achieved for a reaction at 300 °C over 45 min with 12 mL of added H₂O₂. For a reaction at 260 °C with

Table 8 | WAO experiments at 280 and 260 °C with pretreatment

Expt. #	H ₂ O ₂ (mL)	Temperature (°C)	Pressure (MPa)	Reaction time (min)	COD value after reaction (mg/L)	COD removal ratio (%)
15	12	280	11.1	60	178	93.7
16	15	280	11.1	60	145	94.9
17	18	280	11.3	60	127	95.5
18	18	260	9.1	60	180	93.6

18 mL of H₂O₂ added, the COD was 180 mg/L after treatment, with a COD removal ratio of 93.6%, i.e., similar to the removal ratio at 280 °C using 12 mL of H₂O₂ and the same reaction time. These results suggest that the reaction temperature, reaction time, and the amount of added H₂O₂ might be complementary factors in determining the COD removal efficiency, as was also suggested by the results of the orthogonal experiments, in which the R values suggested little difference in the importance of the three factors.

For reactions with 12 mL of added H₂O₂ at 300 and 280 °C for various reaction times, the inner pressure of the autoclave was 0.2 MPa after being cooled to room temperature (25 °C). When the amount of added H₂O₂ was increased from 15 to 18 mL for a reaction at 280 °C, the inner pressure of the autoclave at room temperature increased from 0.3 to 0.4 MPa. This increase in pressure could have been due to the release of O₂ from excess, unreacted H₂O₂ (the O₂ from 6 mL of H₂O₂ can generate approximately 0.1 MPa). Therefore, additional amounts of H₂O₂ would not improve the COD removal rate, and the optimal amount of oxidant was determined to be between 12 and 18 mL.

To determine whether a treatment process that combined flocculation pretreatment with the WAO method improved COD removal compared with treatment using the WAO method alone, we undertook two experiments under the same reaction conditions. The reactions were conducted at a temperature of 300 °C for 45 min using 12 mL of H₂O₂ (Table 9).

The COD of the treated fracturing wastewater with flocculation pretreatment was 127 mg/L and the removal ratio was 95.5%. In contrast, the COD of the treated fracturing wastewater without flocculation pretreatment was 206 mg/L and the removal ratio was 93.3%. These results show that COD removal increased when fracturing wastewater was pretreated using flocculants prior to applying the WAO process. On the other hand, the color of the liquid after reaction with the flocculation pretreatment was colorless, but that without flocculation pretreatment was yellowish green. The reason for this could have been that the

Table 9 | WAO experiments at 300 °C with and without pretreatment

Flocculation pretreatment	COD value after reaction (mg/L)	COD removal ratio (%)	Color of liquid after reaction
Yes	127	95.5	Colorless
No	206	93.3	Yellowish green

fracturing wastewater was pretreated using flocculants, protecting the autoclave when conducting the WAO process.

We also conducted experiments to verify whether the use of a mechanical hydraulic pump improved the results for the WAO process. Without the use of a mechanical hydraulic pump, the fracturing wastewater was gradually heated for about 80 min in the autoclave before the reaction began at the specific reaction temperature. In contrast, when a mechanical hydraulic pump was used, the fracturing wastewater was pumped into an autoclave, pre-heated to the specific reaction temperature, and the reaction began immediately. For the experiment without the use of a hydraulic pump, 27 mL of H₂O₂ was added to 300 mL of

pretreated fracturing wastewater in the autoclave. The autoclave was then closed and heated to 280 °C. The reaction was allowed to proceed for 60 min after the reaction temperature was reached and the COD was then measured (Table 10). The final reaction conditions were the same for both experiments with and without the use of a hydraulic pump. When the mechanical hydraulic pump was used, the COD removal ratio was higher than when operating without the hydraulic pump. Without the use of a hydraulic pump, some of the H₂O₂ reacted with the fracturing wastewater during the heating process, resulting in a smaller amount of H₂O₂ available to react at the optimum WAO temperature. These results suggest that the heating rate of the autoclave in the WAO process is important; a faster heating rate produces greater COD removal from fracturing wastewater.

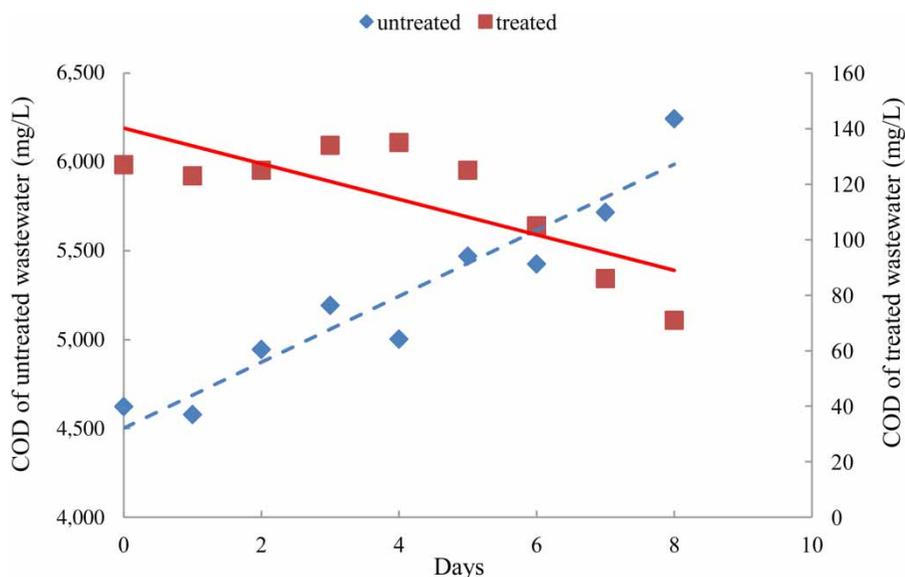
Long-term COD values at room temperature

Fracturing wastewater contains contaminants, which are both difficult to treat and highly stable. Experiments were conducted to determine whether the WAO treatment of fracturing wastewater enhanced the biodegradability of the wastewater. Untreated and treated fracturing wastewater samples (200 mL each) from experiment number 12 were left at room temperature for 8 days and the changes in COD during this period were measured (Figure 3).

The COD of untreated fracturing wastewater increased with standing time and could be related to the evaporation

Table 10 | Results with and without the use of a mechanical hydraulic pump in the WAO process

Mechanical hydraulic pump	H ₂ O ₂ (mL)	Pressure (MPa)	Reaction time (min)	COD value after reaction (mg/L)	COD removal ratio (%)
Used	18	11.3	60	127	95.5
Not used	27	11.5	60	270	94.2

**Figure 3** | Changes in COD over multiple days at room temperature.

of water from the solution. The COD of treated fracturing wastewater decreased from 127 to 86 mg/L over the first 7 days, and then decreased to 71 mg/L after 8 days. Furthermore, we tested the BOD₅ of the treated fracturing wastewater samples from experiment number 12. The BOD₅ of the measured fracturing wastewater was 24 mg/L and the BOD₅ of the untreated fracturing wastewater was 107 mg/L. The BOD₅/COD ratios of the treated and untreated fracturing wastewater were 0.19 and 0.02, respectively. These results show that the biodegradability of fracturing wastewater was enhanced by the flocculation and WAO treatments, and that the COD of treated fracturing wastewater was reduced below the GB 8978-1996 'Integrated Wastewater Discharge Standard' level I emission standard after 7 days at room temperature.

CONCLUSIONS

WAO is an effective treatment method for wastewater produced by hydraulic fracturing and it can achieve a COD removal ratio of up to 96.3%. The use of flocculants for the pretreatment of fracturing wastewater can also improve treatment efficiency. The addition of 500 mg/L of PAC and 20 mg/L of APAM during pretreatment resulted in a COD removal ratio of 8.2% and reduced the suspended solid concentration of fracturing wastewater to 150 mg/L.

An initial set of orthogonal experiments using small hydrothermal autoclaves showed that three principal factors influenced the COD removal ratio of fracturing wastewater; from most to least important, these were the reaction time, reaction temperature, and oxidant dosage. A series of optimization experiments using a 1 L autoclave shows higher reaction temperatures with increased time, and increased amounts of H₂O₂ increased the COD removal efficiency. For a solution of pretreated fracturing wastewater with 12 mL of added H₂O₂, the COD was reduced to 104 mg/L when reacted at 300 °C for 75 min, and reduced to 127 mg/L when reacted at the same temperature for 45 min. However, for a solution with 18 mL of added H₂O₂, the COD was also reduced to 127 mg/L when reacted at 280 °C for 60 min. These results suggest that the three principal factors that influence COD removal are complementary to some extent.

The biodegradability of fracturing wastewater was also enhanced using a combination of flocculation pretreatment and the WAO treatment process. The COD value of the treated fracturing wastewater after 7 days at room temperature was reduced to <100 mg/L, meeting the GB 8978-1996

'Integrated Wastewater Discharge Standard' level I emission standard.

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