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Experimental study of treatment processes for shale gas fracturing flowback fluid in the eastern Sichuan Basin

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ABSTRACT

The toxicity of shale gas fracturing flowback fluid in the eastern Sichuan Basin was investigated and proven to be nontoxic. Based on the water quality characteristics of the fracturing flowback fluid in this area, an experimental study of treatment processes was conducted considering the coagulation–Fenton oxidation processes. Orthogonal and single-factor experiments were carried out for the coagulation and Fenton oxidation processes, respectively. The appropriate values of the various factors affecting the coagulation and Fenton oxidation experiments were determined according to the results. Subsequently, the water quality of the effluent treated by the coagulation–Fenton oxidation processes was evaluated, and the result showed that the water quality requirements for underground injection were met. Finally, the performances of slick water prepared by the effluent were evaluated, and the results showed that the slick water met the demands of fracturing operations and could be reused for further fracturing jobs.

Keywords: Shale gas; Fracturing flowback fluid; Toxicity test; Treatment processes; Underground injection; Recycling

1. Introduction

In recent years, with technology breakthroughs in shale gas exploration and development in China, shale gas, i.e. an unconventional oil and gas resource, has been attracting increasing attention. Currently, the two main technologies for the economical production of shale gas are horizontal wells with long perforating intervals using multistage fracturing technology and hydraulic fracturing using slick water (a common fracturing fluid). The construction and operation of shale gas wells consume large amounts of water (between 1 and 4 million gallons of water are needed per well on average) [1]. Furthermore, the slick water fracturing fluid contains a variety of chemical additives, including clay stabilizer, friction reducer, scale inhibitor, biocide, and surfactant [2]. Nevertheless, significantly more additives are utilized in horizontal drilling than in vertical drilling [3]. After hydraulic fracturing, flowback fluid begins to flow back through the well casing to the wellhead, and the volume of the

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flowback fluid may account for less than 30% to more than 70% of the original fracturing fluid volume in various basins and shale gas plays [4]. Because the flowback fluid contains a large amount of organic and inorganic pollutants, such as oil, high mineral ions, formaldehyde, and guanidine gum [5], the wastewater is characterized by high total suspended solids (TSS), high chemical oxygen demand (COD), high total dissolved solids (TDS), and a high degree of biodegradable difficulty.

Because of the differences between shale gas and conventional oil and gas, such as in the fracturing fluid system, geological structure and fracturing technologies, the fracturing flowback fluids of shale gas and conventional oil and gas have different components. Thus, the treatment processes for flowback fluid from conventional oil and gas are not fully compatible with fracturing flowback fluid from shale gas. The research, exploration, and development of shale gas in China are still at the exploratory stage, and at the present, there have only been a few research investigations on the treatment technologies for shale gas fracturing flowback fluid in China. In addition, the water quality of the flowback fluid is influenced by the quality of water used in the fracturing fluid, the type of chemical additive and its abundance in the fracturing fluid, the chemical constitution of the geological reservoir, and the residence time of the flowback fluid on the ground [6]. The water qualities of the flowback fluid in different shale basins are not the same, and there are significant differences in some of the indexes; thus, the treatment processes of shale gas fracturing flowback fluid in foreign countries cannot simply be applied to the flowback fluid in China.

Due to the geological characteristics of the distribution of shale gas resources, the form of multiple cluster wells is typically used in shale gas development to realize commercial-scale production, where the volume of flowback fluid is extremely large. If the flowback fluid is not effectively treated, soil, surface water, and groundwater can be easily contaminated and can even cause considerable damages to human health [7,8]. Treating shale gas fracturing flowback fluid effectively is of great significance to decrease the discharge of contaminants and promote the development of the shale gas industry. Thus, this paper investigated experimental studies of treatment processes for the shale gas fracturing flowback fluid in the eastern Sichuan Basin. The results are expected to provide a reference for the research and development of treatment technologies of fracturing flowback fluid in China.

2. Toxicity test and water quality characteristics of the flowback fluid in the eastern Sichuan Basin

2.1. Toxicity test of flowback fluid in the eastern Sichuan Basin

Three tests were conducted on the flowback fluid taken from an onsite raw pond in the eastern Sichuan basin to test its toxicity, including the integral skin toxicity test of rabbits, eye irritation toxicity test of rabbits, and acute oral toxicity test of Kunming mice. The results showed that the flowback fluid led to no irritable reactions to the integral skins and eyes of the rabbits. In the acute oral toxicity test of Kunming mice, no poisoning or death occurred when the maximum dosage of mouse lavage was administered (46,400 mg/kg, i.e. 9 times higher than the standard limit set at 5,000 mg/kg in Chemicals Toxicity Test Instruction [9]). Therefore, the flowback fluid in the eastern Sichuan Basin was nontoxic.

2.2. Water quality characteristics of the flowback fluid in the eastern Sichuan Basin

The superficial characteristics of the flowback fluid were its pungent odor, nigrescence, high turbidity, and greasiness on the surface. After one hour of immobility, its color changed from black to canary yellow and produced black sediments on the bottom of the beaker. The supernatant of the flowback fluid was used to test its water quality, and the comparison between the water quality of the flowback fluid and the China groundwater standard for central drinking water systems (CGSCDS) in the Quality Standard for Groundwater [10] is given in Table 1.

3. Experiment design

3.1. Experimental methods and experimental apparatus

Three main management options exist for the flowback fluid in China: (1) inject the fluid underground through a disposal well (onsite or offsite); (2) reuse for a future fracturing job after being treated; and (3) haul to a wastewater treatment facility and then discharge to the surface water. Underground injection into disposal wells requires reduced concentrations of TSS, oil, and grease as well as reduced mean diameters of the suspended particles. The concentrations of TSS, oil, and grease, heavy metal ions, organics, and bacteria must be reduced if the flowback fluid is reused for a future fracturing job after being treated. When discharging the treated flowback fluid to surface water, the concentrations of TSS, oil, and grease, heavy metal

Table 1
Water quality of the flowback fluid and CGSCDS

Parameter	Flowback fluid	CGSCDS
pH	7.17	6.5–8.5
COD (mg/L)	1,802.7	≤3.0
TSS (mg/L)	455	–
Transparency (cm)	10.6	–
Viscosity (mPa s)	0.9685	–
Calcium (mg/L)	420.66	–
Magnesium (mg/L)	68.90	–
Barium (mg/L)	198.82	≤1.0
Strontium (mg/L)	86.75	–
Manganese (mg/L)	2.00	≤0.1
Plumbum (mg/L)	1.48	≤0.05
Iron (mg/L)	0.43	≤0.3
TDS (mg/L)	28,900	≤1,000
Chloride (mg/L)	19,200	≤250
Hardness (as $CaCO_3$, mg/L)	1,334.19	≤450
Oil and grease (mg/L)	17.3	≤0.1
Mid-value of suspended particles’ diameter (μm)	11.6	–

ions, organics, and TDS must be reduced; furthermore, desalination is a major technical difficulty of this management option. In comparing these three management options, the first one is low cost and facile, whereas the third option requires a high cost and is rather difficult, and the second one is modest in both difficulty and cost [11].

Based on the analysis above, both underground injection and reusing the flowback fluid for a future fracturing job after treatment were targeted in this experiment. Considering the water quality characteristics of the shale gas fracturing flowback fluid in the eastern Sichuan Basin, the coagulation–Fenton oxidation processes were chosen to treat the wastewater. The coagulation process involves coagulation, flocculation, and sedimentation, which destabilizes small colloidal particles first and then forms larger and heavier aggregates, which can be removed by conventional physical treatments. Fenton oxidation is an advanced oxidation process (AOP) in which hydrogen peroxide (H_2O_2) is mixed with a Fe^{2+} catalyst to generate a highly reactive hydroxyl radical ($OH^{\cdot}$), which has tremendous oxidation power and can oxidize various organic contaminants non-selectively to harmless end products, such as H_2O and CO_2 [12]. The coagulation and Fenton oxidation processes are frequently used in wastewater treatments, and nearly all of the materials that are added in both processes will be removed from the wastewater. For example, coagulant and flocculants added in the coagulation process, Fe^{2+} and SO_4^{2-} added in the Fenton oxidation process, will form sediments and then be removed; excessive H_2O_2 added in the Fenton oxidation process will be dispelled by added sodium hydroxide (NaOH). Therefore, these two processes have nearly no impacts on the environments of the groundwater and surface water. Furthermore, there is not a limit on the concentrations of the materials added in both processes according to CGSCDS, except for SO_4^{2-} (≤250 mg/L) and Fe (including Fe^{2+} and Fe^{3+}, ≤0.3 mg/L). There is limited information on the Fenton oxidation for treating shale gas fracturing flowback fluid in full-scale facilities. Bench-scale and field studies are also scarce. The published literature investigating petroleum refinery effluent treatment with Fenton oxidation appears to be more common, and this process is able to achieve excellent organic removal efficiency (TOC = 70%, DOC = 90%, and COD = 98% at the optimum conditions) [13,14]. Moreover, Fenton oxidation is widely used to treat a large variety of industrial wastewater, such as chemical, plastics, textile, maintenance, explosives, abrasive, and deinking.

The coagulation process was used to reduce the concentrations of TSS, oil and grease, heavy metal ions, organics, and bacteria and to reduce the mean diameter of the suspended particles. COD removal, the size of the flocs, and its density degree are the composite indicators for evaluating the effect of the coagulation process. The Fenton oxidation process was used to further reduce the concentrations of TSS, oil and grease, heavy metal ions, organics, and bacteria; COD removal is a composite indicator used to evaluate the effect of this process. Because the cost of Fenton’s reagent is higher, coagulation was utilized prior to Fenton oxidation to pretreat the flowback fluid, which reduced both the difficulty of Fenton oxidation and the cost of the treatment. Sodium hydroxide (NaOH) and vitriolic acid (H_2SO_4) were used to regulate the appropriate pH conditions of the reaction system. Both of these compounds are pH regulators and precipitating agents of several heavy metal ions (Ba^{2+}, Sr^{2+}, Mg^{2+}, Ca^{2+}, $Mn^{2+,}$ Pb^{2+}, Fe^{3+}, and so on). The experimental procedures of the treatment processes are shown in Fig. 1.

Orthogonal and single-factor experiments were carried out in the coagulation process and Fenton oxidation process, respectively, to determine the appropriate values of various factors affecting these processes. Experiments using an orthogonal design allow several affecting factors to be simultaneously determined efficiently and effectively, and one can significantly reduce the time needed for the experimental investigation by applying this method [15]. A single-factor experiment examines one affecting factor at a time instead of all factors simultaneously; it can determine an appropriate value of the affecting factor rapidly. The orthogonal experiment was designed to address the favorable ranges of various affecting factors and their primary and secondary sequences. After the orthogonal experiment, a single-factor experiment was conducted under certain conditions to determine the appropriate value of each affecting factor sequentially according to their primary and secondary sequences.

3.1.1. Coagulation experiment

After one hour of immobility, 500 ml of the supernatant of the flowback fluid was poured into a 500-ml beaker. NaOH or H_2SO_4 was used to regulate the pH value, and the solution in the 500-mL beaker was placed in a blender. A certain amount of coagulant and flocculant was added to the solution under rapid stirring (300 r/min). Then, it was stirred slowly (50 r/min) for 5 min after 2 min of rapid stirring. Afterward, the beaker was allowed to stand for a certain time, and the COD of the supernatant in the beaker was measured. In the orthogonal experiment, the type of coagulant, concentration of coagulant, concentration of PAM flocculants, pH value, and standing time were chosen as factors that influenced coagulation. The orthogonal design was adopted using five factors and five levels, and a L_{25} (5^6) orthogonal table was chosen in the coagulation experiment.

3.1.2. Fenton oxidation experiment

Five hundred milliliters of the effluent of the coagulation process was poured into a 500-mL beaker. NaOH or H_2SO_4 was used to regulate the pH value, and a certain amount of $FeSO_4{\cdot}7H_2O$ was added. Then, the beaker was placed in a blender and on a thermostatic water bath, in which the temperature was set to a certain value. The solution was stirred evenly, and a certain amount of 30% H_2O_2 was placed in the beaker. Afterward, the solution was stirred for a certain time (300 r/min), and NaOH was used to regulate the pH value to 8 to dispel the remaining H_2O_2 in the beaker. Finally, the COD of the supernatant in the beaker was measured after leaving the solution alone for 2 h. In the orthogonal experiment, the pH value, amount of 30% H_2O_2, concentration of Fe^{2+}, temperature of the Fenton oxidation reaction, and stirring time are chosen as the factors that influence the Fenton oxidation. The orthogonal design was adopted in five factors and five levels, and a L_{25} (5^6) orthogonal table was chosen in the Fenton oxidation experiment.

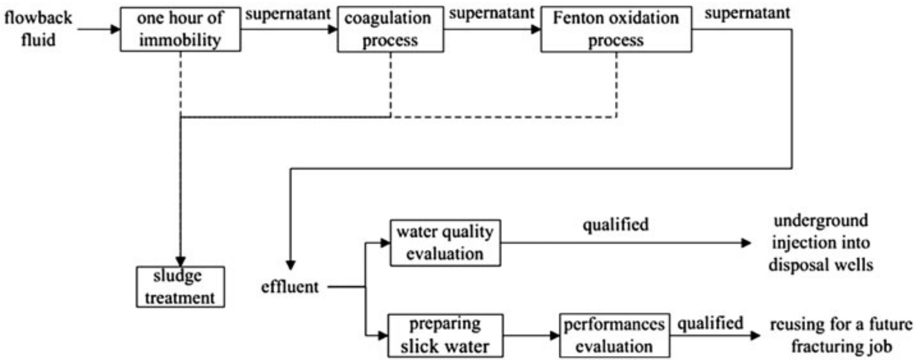

Fig. 1. Experimental procedures of the treatment processes for flowback fluid.

3.2. Methods of statistical analysis

The data obtained from the orthogonal experiment of coagulation and Fenton oxidation processes were evaluated via range analysis and analysis of variance (ANOVA).

The range analysis was estimated by the value of $\bar{K}$, which was the mean value of each response variable (the removal efficiency of contaminants in this paper) for the corresponding affecting factors at each level. The preliminary optimal values of various factors that influence the effect of the orthogonal experiment are determined according to the value of $\bar{K}$.

ANOVA was applied to determine which factor affected the removal efficiency of contaminants more significantly [16]. This statistical approach computed quantities, such as sums of squares (SS), degrees of freedom (DF), variance (V), *F*-ratio, and relative percentage contribution (PC%), among all factors. The "*F*-ratio" is a well-known statistical parameter in the ANOVA table that is equal to the ratio of the factor variance to the error variance. The *F*-test indicates which factor has a significant effect ($p < 0.05$) on obtaining the maximum removal efficiency of contaminants. Furthermore, the values of PC% can also be used to determine which factor has a greater effect on the removal efficiency of contaminants. All of the aforementioned statistical parameters were calculated based on methods described in the literature [17].

In the single-factor experiments of the coagulation and Fenton oxidation processes, each experiment was repeated three times to increase the precision and reduce random error. The confidence limits (μ) of the experimental data in the single-factor experiment were computed by Eq. (1):

$$\mu = \bar{x} \pm t \times \frac{s}{\sqrt{n}} \tag{1}$$

where $\bar{x}$ is the mean value, n is the number of replicate experiments and s is the standard deviation. The value of t relies on the degree of confidence and the number of DF. A confidence degree of 95% was used in the single-factor experiments.

4. Results and discussion

4.1. Coagulation experiment

4.1.1. Orthogonal experiment

The results of the range analysis (Table 2) and ANOVA (Table 3) of the orthogonal experiment are presented below.

The values of PC% (Table 3) were used to determine the primary and secondary sequences of the various factors that influenced the effect of COD removal in the coagulation experiment, which were the concentration of the coagulant, type of coagulant, pH value, time of standing, and concentration of PAM flocculants. According to the range analysis (Table 2), comprehensive COD removal of PAC was the highest according to the mean values ($\bar{K}$) of various coagulants, and the size of the flocs and its density degree were larger than that of other coagulants. Thus, the coagulating effect of PAC was determined to be the best. The preliminary optimal values of various factors that influenced the effect of coagulation were determined according to the $\bar{K}$ values of each COD removal for the corresponding factors at each level. The results were as follows: the concentration of the PAC coagulant was 100 mg/L, the concentration of the PAM flocculant was 20 mg/L, the pH value was 8, and the time of standing was 90 min.

4.1.2. Single-factor experiment

4.1.2.1. Influence of the concentration of the PAC coagulant. For this experiment, the concentration of the PAM flocculants was 20 mg/L; the time of standing was 90 min; the pH value was 8; and the concentrations of the PAC coagulant were 30, 50, 60, 70, 80, 90, 100, and 120 mg/L, respectively. The relationship between COD removal, the COD value of the effluent, and the concentration of the PAC coagulant is shown in Fig. 2.

As shown in Fig. 2, COD removal was the highest (42.7%) when the concentration of the PAC coagulant was 80 mg/L. COD removal reduced gradually when the concentration of the PAC coagulant was higher or lower than 80 mg/L. This behavior may be because when the concentration of the PAC coagulant was too low, the surface potentials of the colloidal particles were relatively higher, causing the electrostatic repulsions among the colloidal particles to be relatively larger. Thus, it was difficult to form larger flocs, and the settling speed of the flocs was lower. As the concentration of the PAC coagulant increased gradually, the surface potentials of colloidal particles reduced gradually, and the electrostatic repulsions among the colloidal particles were gradually lowered and became lower than the attractive forces among the colloidal particles. Thus, the colloidal particles flocculated rapidly, and the size of the flocs and its density degree were greater, causing the removal of COD to increase gradually. When the concentration of the PAC coagulant increased continuously above 80 mg/L, the

Table 2
Results and range analysis of the orthogonal experiment

Trial no.	A[a]	B[b]	C[c]	D[d]	E[e]	$(R\%^{f})_1$	$(R\%)_2$	$(R\%)_3$	Average $R\%$
1	$Al_2(SO_4)_3$	30	5	2	5	21.8	20.1	20.8	20.9
2	$Al_2(SO_4)_3$	50	10	4	10	32.8	30.1	32.2	31.7
3	$Al_2(SO_4)_3$	100	15	6	30	40.9	40.7	39.6	40.4
4	$Al_2(SO_4)_3$	150	20	8	60	36.1	36.9	37.4	36.8
5	$Al_2(SO_4)_3$	200	25	10	90	27.1	28.6	28.6	28.1
6	$AlCl_3$	30	10	6	60	29.2	27.8	27.6	28.2
7	$AlCl_3$	50	15	8	90	38.6	37.3	38.4	38.1
8	$AlCl_3$	100	20	10	5	32.8	32.7	32.3	32.6
9	$AlCl_3$	150	25	2	10	20.5	22.6	22.0	21.7
10	$AlCl_3$	200	5	4	30	20.5	22.1	21.6	21.4
11	PAC	30	15	10	10	34.3	34.5	33.8	34.2
12	PAC	50	20	2	30	34.5	35.0	38.2	35.9
13	PAC	100	35	4	60	40.9	41.7	38.9	40.5
14	PAC	150	5	6	90	39.9	38.1	39.6	39.2
15	PAC	200	10	8	5	31.4	32.8	32.1	32.1
16	PFC	30	20	4	90	34.8	34.5	33.9	34.4
17	PFC	50	25	6	5	30.1	30.6	32.9	31.2
18	PFC	100	5	8	10	36.0	36.1	35.0	35.7
19	PFC	150	10	10	30	33.8	33.0	32.2	33.0
20	PFC	200	15	2	60	26.0	26.9	27.2	26.7
21	PAFC	30	25	8	30	35.9	34.1	35.3	35.1
22	PAFC	50	5	10	60	40.6	42.6	40.7	41.3
23	PAFC	100	10	2	90	35.7	35.9	37.0	36.2
24	PAFC	150	15	4	5	26.9	27.1	26.4	26.8
25	PAFC	200	20	6	10	27.9	28.9	28.1	28.3
$\bar{K}_1$	31.6	30.6	31.7	28.3	28.7	–	–	–	–
$\bar{K}_2$	28.4	35.6	32.2	31.0	30.3	–	–	–	–
$\bar{K}_3$	36.4	37.1	33.2	33.5	33.2	–	–	–	–
$\bar{K}_4$	32.2	31.5	33.6	35.5	34.7	–	–	–	–
$\bar{K}_5$	33.6	27.3	31.3	33.8	35.2	–	–	–	–

[a] Type of coagulant.

[b] Concentration of coagulant, mg/L.

[c] Concentration of PAM flocculants, mg/L.

[d] pH value.

[e] Time of standing, min.

[f] COD removal, %.

surfaces of the colloidal particles became unstable again, and part of the flocs floated up, lowering its density degree and deteriorating the coagulation effect. Therefore, the appropriate concentration of the PAC coagulant was 80 mg/L.

4.1.2.2. Influence of the pH value. For this experiment, the concentration of the PAM flocculant was 20 mg/L; the time of standing was 90 min; the concentration of the PAC coagulant was 80 mg/L; and the pH values were 5, 6, 7, 8, 9, 10, and 11, respectively. The relationship between COD removal, the COD value of the effluent and the pH value is shown in Fig. 3.

As presented in Fig. 3, COD removal increased gradually when the pH value increased. COD removal was the highest (42.7%) when the pH value was 8, and COD removal declined when the pH value was more than 8. This trend can be explained by the fact that the pollutants were eliminated primarily due to the production of a large amount of $[Al(OH)_3(H_2O)_3]_x$. When the pH value was less than 7, Al^{3+} and $Al(OH)_2^+$ were generated at greater quantities than $Al(OH)_3$, and the size of the flocs and its density degree were smaller, causing the settling speed of the flocs was lower and the coagulation effect was worse. When the pH value was more than 9, a chemical

Table 3
ANOVA table of the orthogonal experiment

Source	SS	DF	Variance	*F*-ratio[a]	PC (%)
A	169.1	4	42.3	7.4	20.0
B	311.7	4	77.9	13.6	36.9
D	160.4	4	40.1	7.0	19.0
E	158.1	4	39.5	6.9	18.7
C	19.0	4			
Error	26.9	4			
Error$^{\Delta b}$	45.9	8	5.7	–	5.4
Total	845.0	24	–	–	100.0

[a] $F_{\text{significant}}$ (4, 8; 0.05) = 3.8.

[b] When the SS value of one factor is smaller than that of the error, combine them to produce a new error (error$^{\Delta}$).

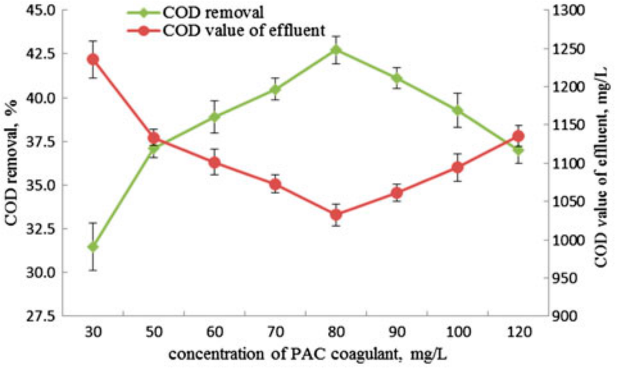

Fig. 2. Relationship between COD removal, the COD value of the effluent and the concentration of the PAC coagulant.

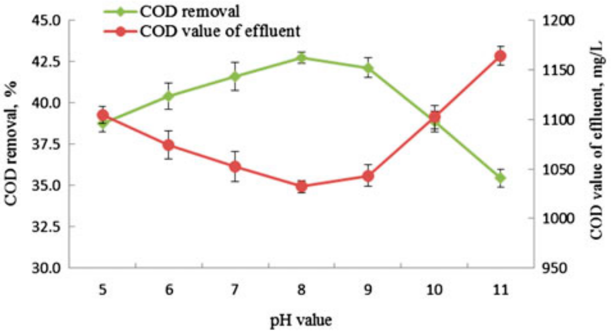

Fig. 3. Relationship between COD removal, the COD value of the effluent and the pH value.

reaction occurred between $Al(OH)_3$ and OH^- in the flowback fluid and generated AlO^{2-}; the coagulation effect became worse. Thus, the appropriate pH value was 8. Using NaOH to regulate the pH value of the flowback fluid to 8 cannot only create an appropriate pH condition for the reaction system but also act as a precipitating agent of Mg^{2+}, Fe^{3+}, Mn^{2+}, and Pb^{2+}, thus reducing their concentrations in the flowback fluid.

4.1.2.3. *Influence of the time of standing.* Here, the concentration of the PAM flocculant was 20 mg/L; the concentration of the PAC coagulant was 80 mg/L; pH value was 8; and the times of standing were 10, 20, 30, 45, 60, 75, and 90 min, respectively. The relationship between COD removal, the COD value of the effluent, and the time of standing is shown in Fig. 4.

As shown in Fig. 4, COD removal increased gradually as the time of standing increased. COD removal increased slowly when the time of standing exceeded 60 min. When the time of standing was not sufficiently long, the size of the flocs and its density degree were small. When the time of standing reached a certain value (>60 min), the size of the flocs and its density degree were large. Thus, when the time of standing was 60 min, coagulative precipitation was nearly completed. Hence, the appropriate time of standing was 60 min and the COD removal was 42.3%.

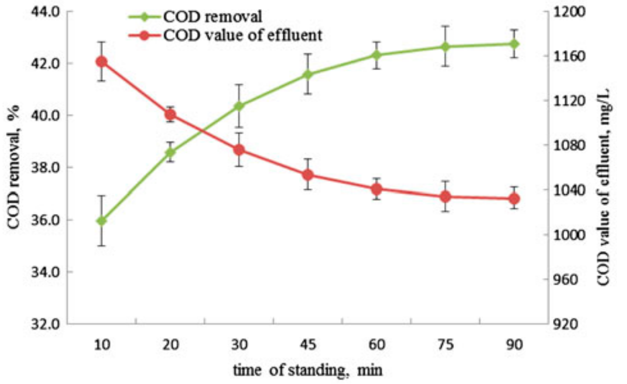

Fig. 4. Relationship between COD removal, the COD value of the effluent and the time of standing.

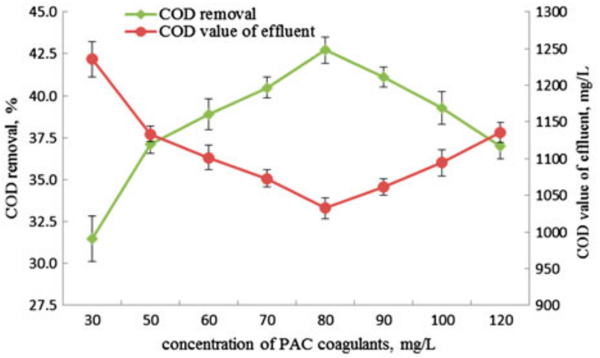

Fig. 5. Relationship between COD removal, the COD value of the effluent and the concentration of the PAM flocculants.

4.1.2.4. Influence of the concentration of PAM flocculants. For this experiment, the concentration of the PAC coagulant was 80 mg/L; pH value was 8; the time of standing was 60 min; the concentrations of the PAM flocculants were 5, 10, 15, 20, 25, 30, and 40 mg/L, respectively. The relationship between COD removal, the COD value of the effluent and the concentration of the PAM flocculants is presented in Fig. 5.

As presented in Fig. 5, COD removal was the highest (42.8%) when the concentration of the PAM flocculants was 15 mg/L. COD removal declined gradually when the concentration of the PAM flocculants was higher or lower than 15 mg/L. PAM is a type of polymer flocculant, and its main function in coagulative precipitation is to induce an adsorption bridging action. The adsorption bridging action was more effective when the concentration of the PAM flocculants was moderate, causing the size of the flocs to be large and the settling speed to be rapid; thus, COD removal was high. If the concentration of the PAM flocculants was too high, the adsorption bridging action deteriorated and COD removal reduced. Meanwhile, the residues of PAM in the supernatant increased the COD value of the effluent. Therefore, the appropriate concentration of the PAM flocculants was 15 mg/L.

4.1.3. Water quality of the effluent after the coagulation process

The water quality of the effluent after the coagulation process is shown in Table 4.

4.2. Fenton oxidation experiment

4.2.1. Orthogonal experiment

The results of the range analysis (Table 5) and ANOVA (Table 6) of the orthogonal experiment are presented below.

From the values of PC% (Table 6), the primary and secondary sequences of the various factors that influenced the effect of COD removal in the Fenton oxidation experiment was determined to be the pH value, the amount of 30% H_2O_2, the concentration of Fe^{2+}, the time of stirring, and the reaction temperature. According to the range analysis (Table 5), the preliminary optimal values of the various factors that influenced the effect of Fenton oxidation were determined according to the values of each COD removal for the corresponding factors at each level. The results were as follows: the pH value was 3, the amount of 30% H_2O_2 was 6 mL/L, the concentration of Fe^{2+} was 15 mmol/L, the time of stirring was 150 min, and the reaction temperature was 40℃.

4.2.2. Single-factor experiment

4.2.2.1. Influence of the pH value. For this experiment, the amount of 30% H_2O_2 was 6 mL/L; the concentration of Fe^{2+} was 15 mmol/L; the time of stirring was

Table 4
Water quality of the effluent after the coagulation process

Parameter	Concentration	Parameter	Concentration
pH	7.76	Strontium (mg/L)	55.01
COD (mg/L)	1,030.4	Manganese (mg/L)	0.63
TSS (mg/L)	32	Plumbum (mg/L)	0.58
Transparency (cm)	>30	Iron (mg/L)	0.37
Viscosity (mPa s)	0.8768	TDS (mg/L)	27,800
Calcium (mg/L)	198.48	Chloride (mg/L)	19,200
Magnesium (mg/L)	54.86	Hardness (as $CaCO_3$, mg/L)	721.52
Barium (mg/L)	65.27	Oil and grease (mg/L)	9.2
Mid-value of suspended particles' diameter (μm)			5.8

Table 5
Results and range analysis of the orthogonal experiment

Trial no.	A^a	B^b	C^c	D^d	E^e	$(R\%^f)_1$	$(R\%)_2$	$(R\%)_3$	Average $R\%$
1	2	4	10	25	30	25.7	24.3	24.1	24.7
2	2	6	15	30	60	55.1	56.4	56.2	55.9
3	2	8	20	40	90	57.4	58.0	58.9	58.1
4	2	10	25	50	120	45.1	45.8	45.0	45.3
5	2	12	30	60	150	35.0	35.7	34.9	35.2
6	3	4	15	40	120	65.2	66.5	66.0	65.9
7	3	6	20	50	150	66.6	67.2	67.8	67.2
8	3	8	25	60	30	50.9	52.4	52.4	51.9
9	3	10	30	25	60	43.7	43.1	42.5	43.1
10	3	12	10	30	90	32.5	32.2	32.5	32.4
11	4	4	20	60	60	51.4	51.8	51.3	51.5
12	4	6	25	25	90	60.8	59.8	58.5	59.7
13	4	8	30	30	120	56.3	56.1	56.8	56.4
14	4	10	10	40	150	46.1	46.9	47.4	46.8
15	4	12	15	50	30	36.7	37.8	36.8	37.1
16	5	4	25	30	150	44.6	44.1	45.7	44.8
17	5	6	30	40	30	40.3	40.9	42.1	41.1
18	5	8	10	50	60	40.0	40.4	39.0	39.8
19	5	10	15	60	90	44.3	42.7	42.9	43.3
20	5	12	20	25	120	28.7	28.2	27.4	28.1
21	6	4	30	50	90	21.6	21.3	22.8	21.9
22	6	6	10	60	120	21.5	20.6	20.3	20.8
23	6	8	15	25	150	23.6	23.9	22.7	23.4
24	6	10	20	30	30	15.5	14.9	14.9	15.1
25	6	12	25	40	60	9.8	9.6	10.3	9.9
$\bar{K}_1$	43.8	41.8	32.9	35.8	33.9	–	–	–	–
$\bar{K}_2$	52.1	48.9	45.1	40.9	40.0	–	–	–	–
$\bar{K}_3$	50.3	45.9	44.0	44.4	43.1	–	–	–	–
$\bar{K}_4$	39.4	38.7	42.3	42.3	43.3	–	–	–	–
$\bar{K}_5$	18.2	28.6	39.6	40.5	43.5	–	–	–	–

[a] pH value.

[b] Amount of 30% H_2O_2, mL/L.

[c] Concentration of Fe^{2+}, mmol/L.

[d] Reaction temperature, ℃.

[e] Time of stirring, min.

[f] COD removal, %.

Table 6
ANOVA table of the orthogonal experiment

Source	SS	DF	Variance	F-ratio[a]	PC%
A	3,695.7	4	923.9	74.2	61.7
B	1,238.2	4	309.6	24.9	20.7
C	476.7	4	119.2	9.6	8.0
D	200.4	4	50.1	4.0	3.3
E	332.1	4	83.0	6.7	5.5
Error	49.8	4	12.4	–	0.8
Total	5,993.0	24	–	–	100.0

[a] $F_{\text{significant}}$ (4, 4; 0.05) = 6.4.

150 min; the reaction temperature was 40℃; and the pH values were 2, 3, 3.5, 4, 5, 6, and 7, respectively. The relationship between COD removal, the COD value of the effluent and the pH value is shown in Fig. 6.

As shown in Fig. 6, the pH value had a large influence on COD removal in Fenton oxidation reaction. COD removal initially increased and then decreased as the pH value increased. COD removal was the highest (66.2%) when the pH value was 3.5. This trend was due to the existence of iron ions, which depended on the pH condition of the reaction system. When the pH value was too low, Fe^{3+} could not easily be reduced to Fe^{2+}, and Fe^{2+} could not easily catalyze

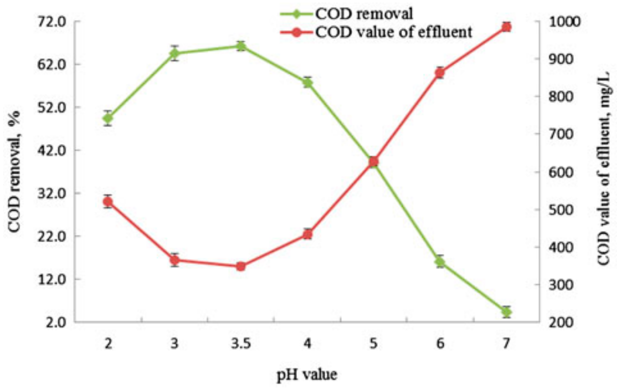

Fig. 6. Relationship between COD removal, the COD value of the effluent and the pH value.

H_2O_2 to produce OH$^\bullet$. When reaction system was neutral or alkaline, the production of OH$^\bullet$ was hindered, and hydroxide precipitation of Fe^{2+} or/and Fe^{3+} occurred. Hence, the appropriate pH value of the reaction system was 3.5. Utilizing H_2SO_4 to regulate the pH value of the effluent from the coagulation process to 8 cannot only create an appropriate pH condition for the reaction system of Fenton oxidation but also act as the precipitating agent of Ca^{2+}, Ba^{2+}, Sr^{2+}, and Pb^{2+}, thus reducing their concentrations.

4.2.2.2. Influence of the amount of 30% H_2O_2. Here, the concentration of Fe^{2+} was 15 mmol/L; the time of stirring was 150 min; the reaction temperature was 40℃; the pH value was 3.5; and the amounts of 30% H_2O_2 were 2, 4, 6, 8, 10, and 12 mL/L, respectively. The relationship between COD removal, the COD value of the effluent, and the amount of 30% H_2O_2 is presented in Fig. 7.

As shown in Fig. 7, COD removal initially increased and then reduced with the amount of 30% H_2O_2 raised. COD removal was the highest (66.2%) when the amount of 30% H_2O_2 was 6 mL/L. The reason was that when the amount of H_2O_2 increased from 2 to 6 mL/L gradually, the production of OH$^\bullet$ increased and COD removal increased gradually. After increasing the amount of H_2O_2 to a certain value, a portion of the Fe^{2+} was oxidized by excessive H_2O_2, and the concentration of Fe^{2+}, i.e. the catalyst of H_2O_2, decreased. This not only wasted H_2O_2 but also restrained the generation of OH$^\bullet$. Thus, the appropriate amount of 30% H_2O_2 was 6 mL/L.

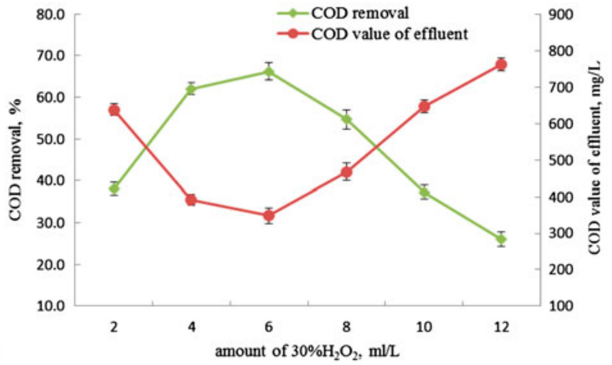

Fig. 7. Relationship between COD removal, the COD value of the effluent and the amount of 30% H_2O_2.

4.2.2.3. Influence of the concentration of Fe^{2+}. Here, the dosage of 30% H_2O_2 was 6 mL/L; the time of stirring was 150 min; the reaction temperature was 40℃; the pH value was 3.5; and the concentrations of Fe^{2+} were 5, 10, 15, 20, 25, and 30 mmol/L, respectively. The relationship between COD removal, the COD value of the effluent and the concentration of Fe^{2+} is shown in Fig. 8.

As shown in Fig. 8, COD removal initially increased and then decreased slowly with the concentration of Fe^{2+}. COD removal was the highest (66.2%) when the concentration of Fe^{2+} was 15 mmol/L. The amount of OH$^\bullet$ produced by the catalytic reaction was lower when the concentration of Fe^{2+} was inadequate. When the concentration of Fe^{2+} was excessive, part of H_2O_2 was reduced and some of Fe^{2+} was oxidized, wasting both chemicals and making the effluent more yellow. Therefore, the appropriate concentration of Fe^{2+} was 15 mmol/L.

4.2.2.4. Influence of the time of stirring. Here, the amount of 30% H_2O_2 was 6 mL/L; the reaction temperature was 40℃; the pH value was 3.5; the concentration of Fe^{2+} was 15 mmol/L; and the times of stirring were 10, 30, 60, 90, 120, and 150 min, respectively. The relationship between COD removal, the

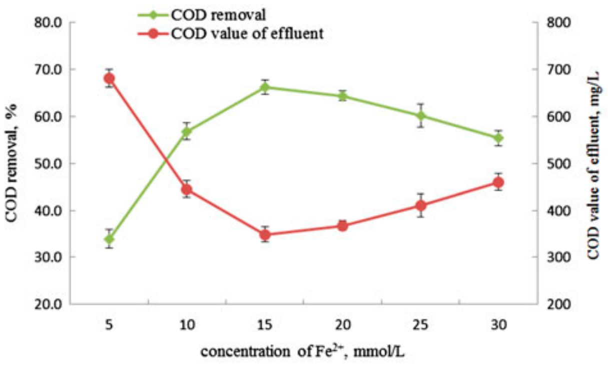

Fig. 8. Relationship between COD removal, the COD value of the effluent and the concentration of Fe^{2+}.

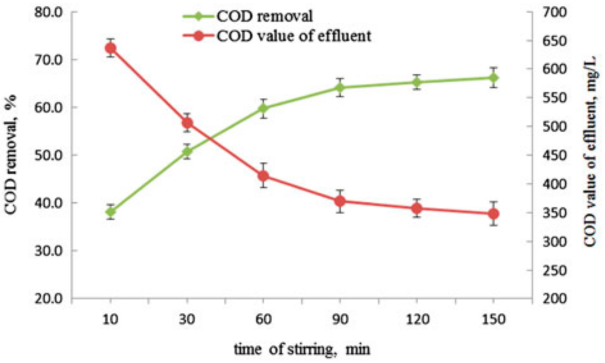

Fig. 9. Relationship between COD removal, the COD value of the effluent and the time of stirring.

COD value of the effluent, and the time of stirring is presented in Fig. 9.

As shown in Fig. 9, COD removal increased continuously with the time of stirring. As the time of stirring exceeded 90 min, COD removal increased slowly. Thus, the Fenton oxidation reaction was almost completed when the time of stirring was 90 min. Thus, the appropriate time of stirring was 90 min and the COD removal was 64.1%.

4.2.2.5. Influence of the reaction temperature. Here, the amount of 30% H_2O_2 was 6 mL/L; the pH value was 3.5; the concentration of Fe^{2+} was 15 mmol/L; the time of stirring was 90 min; and the temperatures of reaction were 25, 30, 40, 50, 60, and 70℃, respectively. The relationship between COD removal, the COD value of the effluent, and the reaction temperature is shown in Fig. 10.

As shown in Fig. 10, COD removal increased first and then decreased with increasing reaction temperature. COD removal was the highest (64.1%) when the reaction temperature was 40℃. This can be attributed to the fact that with the increase in the reaction temperature, the reaction rate of Fenton oxidation increased, and the production of OH˙ increased. Thus, the degradation speeds of the organics increased, and COD removal increased. When the reaction temperature was excessively high, some of H_2O_2 broke down into O_2 and H_2O, and COD removal decreased. Therefore, the appropriate reaction temperature was 40℃.

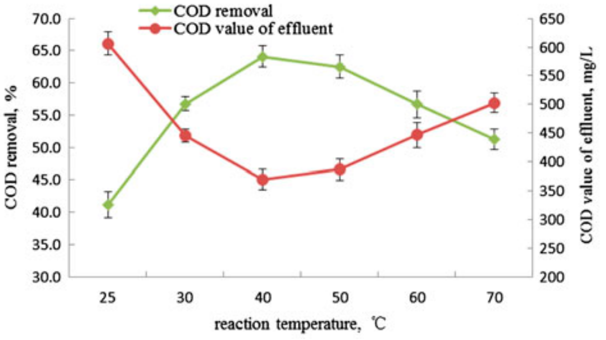

Fig. 10. Relationship between COD removal, the COD value of the effluent and the reaction temperature.

4.2.2.6. Influence of the number of times of 30% H_2O_2 addition. For this experiment, the concentration of Fe^{2+} was 15 mmol/L; the pH value as 3.5; the time of stirring was 90 min; the reaction temperature was 40℃; the total added amount of 30% H_2O_2 was 6 mL/L; and 30% H_2O_2 was added once (0 min), twice (0 and 45 min), three times (0, 30 and 60 min), and four times (0, 22.5, 45, and 67.5 min). When 30% H_2O_2 was added in a series of steps, the added amount at each step equaled the total added amount divided by the number of steps. The relationship between COD removal, the COD value of the effluent, and the number of times of 30% H_2O_2 addition is shown in Fig. 11.

As shown in Fig. 11, adding H_2O_2 in steps helped to improve COD removal. As the number of times 30% H_2O_2 was added increased, the degree of homogenization increased, which reduced the disadvantages of the amount of 30% H_2O_2 being insufficient or excessive. By comprehensively considering the operability of the addition and COD removal, the optimal number of times of 30% H_2O_2 addition was determined to be 4 and the COD removal was 69.6%.

4.2.3. Water quality of the effluent after the coagulation–Fenton oxidation processes

The water quality of the effluent after the coagulation–Fenton oxidation processes is shown in Table 7.

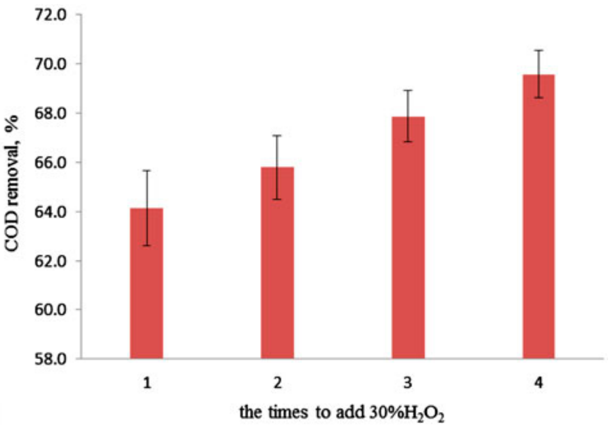

Fig. 11. Relationship between COD removal, the COD value of the effluent and the number of times 30% H_2O_2 was added.

Table 7
Water quality of the effluent after the treatment of the coagulation–Fenton oxidation processes

Parameter	Concentration	Parameter	Concentration
pH	8.00	Strontium (mg/L)	12.75
COD (mg/L)	313.6	Manganese (mg/L)	0.60
TSS (mg/L)	13	Plumbum (mg/L)	0.19
Transparency (cm)	>30	Iron (mg/L)	0.08
Viscosity (mPa s)	0.8591	TDS (mg/L)	27,300
Calcium (mg/L)	19.41	Chloride (mg/L)	19,000
Magnesium (mg/L)	33.41	Hardness (as $CaCO_3$, mg/L)	186.05
Barium (mg/L)	27.65	Oil and grease (mg/L)	5.3
Mid-value of suspended particles’ diameter (μm)			3.7

A comparison of Tables 1 and 7 indicates after the treatment of coagulation–Fenton oxidation processes, the concentrations of TDS and chloride decline slightly, the concentrations of various heavy metal ions, hardness, TSS, COD, and oil and grease decrease sharply and the mid-value of suspended particles’ diameter decreases significantly. The viscosity of the effluent is nearly equal to that of clean water, and the effluent is transparent.

5. Evaluation of effluent after the treatment of coagulation–Fenton oxidation processes

5.1. Water quality evaluation

The water quality indexes of re-injected wastewater are recommended by China’s National Development and Reform Commission (NDRC) in the petroleum and natural gas industry standard of Recommended Practice for Produced-water Reinjection in Gas Field [18]. The comparison between the recommended water quality indexes of re-injected wastewater and the water quality of the effluent after the coagulation–Fenton oxidation processes is presented in Table 8.

As shown in Table 8, the water quality of the effluent met the water quality requirements for underground injection. Thus, the effluent was qualified to be injected into disposal wells.

5.2. Performances evaluation

The performances of slick water prepared by the effluent were evaluated, and the results of the evaluation and the performance requirements of slick water according to the local petroleum and natural gas standards in the Technical Specifications of Sliding Water for Fracturing [19] published by the Sichuan Institute of Standardization are compared in Table 9.

As presented in Table 9, the performances of slick water prepared by the effluent treated by the coagulation–Fenton oxidation processes met the performance requirements of slick water. Therefore, the effluent was qualified to be reused to prepare slick water for a future fracturing job.

5.3. Evaluation of the influence of fracturing fluid or flowback fluid leakage on regional groundwater quality

Modern technologies used in shale gas development are not free from environmental hazards, especially those related to regional drinking water qualities. An ongoing public concern has arisen regarding issues of the groundwater quality in shale basins due to several possible hydrofracturing-related cases (Pavillion in Wyoming, Parker County in Texas, Dimock in Pennsylvania and so on) [20]. A comparison of the water quality of slick water prepared by the effluent and CGSCDS is shown in Table 10.

Table 8
Comparison between the recommended water quality indexes of re-injected wastewater and the water quality of the effluent after the coagulation–Fenton oxidation processes

Parameter	pH value	Oil and grease (mg/L)	TSS (mg/L)	Mid-value of suspended particles’ diameter (μm)
Recommended water quality indexes[a]	6–9	<30	≤15	≤8
Water quality of effluent	8.00	5.3	13	3.7

[a] When the permeability of the reservoir is less than 2 μm^2.

Table 9
Comparison between the performances of slick water prepared by the effluent and the performance requirements of slick water

Parameter	Slick water prepared by the effluent	Performance requirements of slick water
pH value	8.0	6–8
Apparent viscosity	5.1	≤10.0
Surface tension	24.4	≤28.0
Interfacial tension	0.36	≤1.0
Resistance-reducing	69.0%	≥50.0%
Compatibility with formation water	No sedimentation or flocculation	No sedimentation or flocculation

Table 10
Water quality of slick water prepared by the effluent and CGSCDS

Parameter	Flowback fluid	CGSCDS
pH	8.0	6.5–8.5
COD (mg/L)	332.5	≤3.0
TSS (mg/L)	19	–
Transparency (cm)	>26	–
Viscosity (mPa s)	0.6153	–
Calcium (mg/L)	19.87	–
Magnesium (mg/L)	34.58	–
Barium (mg/L)	29.72	≤1.0
Strontium (mg/L)	12.86	–
Manganese (mg/L)	0.62	≤0.1
Plumbum (mg/L)	0.21	≤0.05
Iron (mg/L)	0.10	≤0.3
TDS (mg/L)	27,850	≤1,000
Chloride (mg/L)	19,000	≤250
Hardness (as $CaCO_3$, mg/L)	192.02	≤450
Oil and grease (mg/L)	5.5	≤0.1
Mid-value of suspended particles' diameter (μm)	3.9	–

As presented in Tables 1 and 10, the values of several quality indexes of fracturing fluid and flowback fluid exceeded the standard limits in CGSCDS. Fracturing fluid or flowback fluid may migrate through induced fractures or natural fractures or through an inappropriately sealed cement annulus between the casing and wellbore outside the target formation. Although the fractures of the shale reservoir extend up to ~460 m above the top of some horizontal wells, this is still ~1,600 m or more below freshwater aquifers [21]. Despite allegations of harm to groundwater caused by hydrofracturing or drilling, evidence of harm to freshwater aquifers caused by shale gas development is insufficient. Despite installation of surveillance wells, clear linkages between the deterioration in groundwater quality and hydrofracturing activity have not been demonstrated.

Not all injected fracturing fluid (approximately 30–70%) will recover during the flowback period, and the potential migration pathways and ultimate dispositions of the uncovered portions of the injected fracturing fluid must be known. However, if reliable baseline information is available, it is easy to blame any incidents caused by shale gas extraction activities. Thus, it is important to establish reliable baseline information. It is also critical to enhance drilling and cementing practices to reduce the odds of fluid transport to freshwater aquifers. Furthermore, a system of comprehensive risk assessment is needed to evaluate the likely impacts of fracturing fluid or flowback fluid leakage on local groundwater quality.

6. Conclusions

1. Shale gas fracturing flowback fluid in the eastern Sichuan Basin was nontoxic.
2. The coagulation–Fenton oxidation processes were utilized to treat shale gas fracturing flowback fluid in the eastern Sichuan Basin. The

appropriate values of the various factors affecting the coagulation and Fenton oxidation experiments were addressed. In the coagulation experiment, PAC should be chosen as the coagulant with a concentration of 80 mg/L. The concentration of the PAM flocculants should be 15 mg/L, the pH value should be 8, and the time of standing should be 60 min. In the Fenton oxidation experiment, the total amount of 30% H_2O_2 should be 6 mL/L, the concentration of Fe^{2+} should be 15 mmol/L, the pH value should be 3.5, the time of stirring should be 90 min, the reaction temperature should be 40℃, and 30% H_2O_2 should be added in four steps.

(3) The water quality of the effluent after the coagulation–Fenton oxidation processes was evaluated and was found to meet the water quality requirements for underground injection.

(4) The performances of slick water prepared by the effluent treated by coagulation–Fenton oxidation processes met the performance requirements of slick water.

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