

Treatment of hydraulic fracturing flowback fluid by Fe⁰-persulfate (PS) process

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Abstract. Treating hydraulic fracturing flowback fluid has been receive much attention due to its high total dissolved solid and organic matter. In this study, to remove pollutants in the influent and reduce chemical oxygen demand (COD), the process of persulfate (PS) activated by Fe⁰ was applied in the treatment of hydraulic fracturing flowback fluid. At the optimal parameters of experimental condition (Fe⁰=8 g/L, PS = 12 mmol/L, pH=7.7, temperature=25°C, reaction time=5 min), 93.6% COD (111.6 mg/L) was removed. Therefore, the Fe⁰-PS process could be proposed as a promising treatment technology for the removal of toxic and refractory hydraulic fracturing flowback fluid wastewater.

1 Introduction

Shale gas, an unconventional natural gas that exists in shale formation in adsorbed and free state, has attracted worldwide attention due to its high resource exploration potential [1-3]. The increasing exploitation of shale gas has a decisive impact on the country's political economy and other aspects. In the process of shale gas exploration, hydraulic fracturing technology, as a mean to improve shale gas production, has been widely applied. The basic idea of hydraulic fracturing is to increase the pressure in the vertical well by injecting a mixture of water, sand and chemical reagents. When the pressure rises to a certain level, it causes the horizontal rock to break away from the vertical well, releasing more shale gas and increasing production of shale gas [4, 5].

Although hydraulic fracturing technology has greatly increased the exploitation of shale gas and alleviated energy pressure, it has caused many environmental problems, such as a large amount of wastewater, impact on formation structure, noise, etc. [6-9]. The wastewater is divided into two categories: one is the fracturing flowback fluid generated in the fracturing process, and the other is the produced water generated in the continuous gas production process. Compared with produced water, the main characteristics of flowback fluid wastewater include production time concentrated, large wastewater flow and high concentration of organic and inorganic constituents [10]. If hydraulic fracturing flowback released into environment without disposal, it might threaten the human beings and wildlife. Therefore, how to treat the hydraulic fracturing flowback fluid wastewater becomes the focus of public concern.

The traditional treatment technology of hydraulic fracturing flowback mainly include recycling and underground injection, flocculation and precipitation and

membrane technology and distillation technology [1, 11, 12]. But they are limited by high capital or operating cost. Over the last decade, a great deal of interest was focused on the degradation of toxic and refractory pollutants with the advanced oxidation processes (AOPs) [13-15]. It has been reported that zero-valent iron (Fe⁰) as an environmental friendly, high reductive capacity and inexpensive material has been extensively applied to treatment/remediation of wastewater and could greatly enhanced the degradation efficiency of pollutants in wastewater [16-18]. However, its practical applications still suffer from the limitations of reactivity inhibition due to the surface passivation or narrow working pH. Persulfate (PS) as a newest oxidizing agent has recently received an attention and widely used in the chemical oxidation of wastewater/groundwater. The standard oxidation potential of PS is 2.01 V. Besides, PS can generate more powerful oxidizing agent by light, heat base, ultrasound, transition metals and other conditions. Like sulfate radical (SO₄^{•-}, E⁰=2.6V), which can largely degrade most pollutants in water without selectivity.

In this study, Fe⁰ was chosen as the ideal catalyst to active PS. Therefore, Fe⁰-PS process was set up to treatment hydraulic fracturing flowback fluid wastewater. The key operating parameters (i.e., PS dosage, Fe⁰ dosage, initial pH value, treatment temperature and treatment time) were optimized through single-factor experiments. In addition, the reaction mechanism of the Fe⁰-PS process was discussed thoroughly.

2 Experimental

2.1 Reagents

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Hydraulic fracturing flowback fluid wastewater used in this study was obtained from a shale gas well in southwest China. As shown in Table. 1, The COD, BOD₅, colority, SS, pH, conductivity and Cl⁻ were approximately 1744 mg/L, 60 mg/L, 500, 418 mg/L, 7.6, 31400 μS cm⁻² and 10200 mg/L. Fe⁰ powders and persulfate (Na₂S₂O₈, analytical) from Chengdu Kelong chemical reagent factory were used in the experiment. Other chemicals used in the experiment were of analytical grade. Deionized water was used throughout the whole experiment process.

Table 1. Characteristics of the hydraulic fracturing flowback.

Item	Units	Values
COD	mg/L	1744 ± 20
BOD ₅	mg/L	60 ± 5
Colority	Times	500±20
Suspended Solids (SS)	mg/L	418 ± 20
pH	-	7.6 ± 0.2
Conductivity	μS cm ⁻²	31400 ± 120
Cl ⁻	mg/L	10200 ± 130

2.2 Experimental procedure

In this study, the key operating parameters, including PS dosage, Fe⁰ dosage, initial pH value, treatment temperature and treatment time were investigated thoroughly by batch experiments. In each batch experiment, 300 mL hydraulic fracturing flowback was placed in a 500 mL beaker, meanwhile the different PS dosage, Fe⁰ dosage, initial pH and temperature were placed in a 500 mL flat bottom beaker. In addition, to ensure the full fluidization of the Fe⁰ powders in reaction solution, the slurry was stirred by a mechanical stirrer with a stirring speed of 350 rpm. The samples were withdrawn at pre-determined time intervals, and diluted by deionized water and filtered through a PTFE syringe filter disc (0.45 μm). And then, the COD of the samples were measured, respectively. All the experiments were conducted in triplicate and error bar represented the standard deviation of the replicate experimental data.

2.3 Analytical methods

COD and pH of the samples were measured by COD rapid analyser (Lianhua, China) and PHS-3C meter (Rex, China), respectively.

3 Results and discussion

3.1 Effect of PS dosage

Figure 1 shows the COD removal efficiency of effluents at different PS dosages (0–16 mmol/L) in Fe⁰-PS process. It can be seen from Figure 1 that lower COD removal efficiency was obtained after 30 min treatment in Fe⁰ alone process. With the increase of PS dosage (from 0 to 8 mmol/L), the COD removal efficiency improved slowly from 2.5% to 17.4%. However, when PS dosage increased from 8 to 12 mmol/L, the COD removal efficiency rapidly improved from 17.4% to 85.5%. And then COD removal efficiency did not further enhance when the PS dosage was above 12 mmol/L. On the one hand, PS could react with Fe⁰ to generate stronger oxidants (SO₄^{•-}). In addition, increase of PS dosage could also facilitate the corrosion of Fe⁰ and generate more Fe²⁺, which also react with PS to generate SO₄^{•-}. The SO₄^{•-} can effectively degrade pollutants in reaction solution without selectively to obtain higher COD removal efficiency of hydraulic fracturing flowback fluid. Furthermore, the solution pH decreased when excess PS added into solution, which might generate plenty of Fe²⁺ to scavenge the generated radicals. Therefore, the optimal PS dosage was selected as 12 mmol/L.

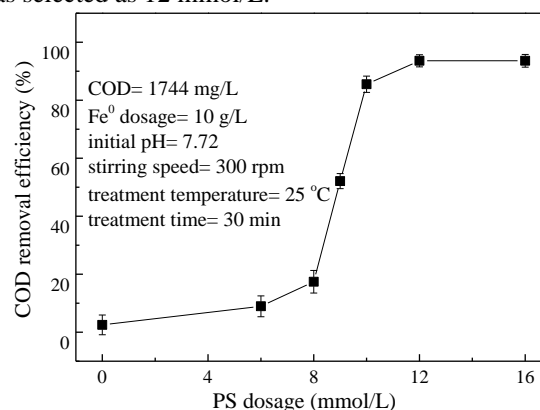


Fig. 1. Effect of PS dosage on the COD removal efficiency after Fe⁰-PS treatment.

3.2 Effect of Fe⁰ dosage

Effect of Fe⁰ dosage on the COD removal efficiency were investigated and the results was shown in Figure 2. It is apparent that the sole PS process without Fe⁰ only led to 5.14% COD removal efficiency. The results may be that the redox potential of PS is only 2.01 V, and the mineralization efficiency of pollutants through electron acceptance reaction is low. However, with the increase of Fe⁰ dosage (from 0 to 2g/L), the COD removal efficiency rapidly enhance from 10.3% to 82.6%, and then gradually improved with the further increase of Fe⁰ dosage. The results can be explained from three aspects, (i) the increase of Fe⁰ dosage could increase the amount of active site. (ii) the more Fe⁰ dosage in the Fe⁰-PS process, the more amount of corrosion products (i.e., Fe²⁺, Fe³⁺, FeOOH and Fe₃O₄, etc), which effectively activated PS to generate more SO₄^{•-}. (iii) When the Fe⁰ dosage was above the 8 g/L, the generated radicals would be scavenged by the excess Fe⁰ and its corrosion product. Therefore, the Fe⁰ dosage of 8 g/L was selected as the optimal value in the follow study.

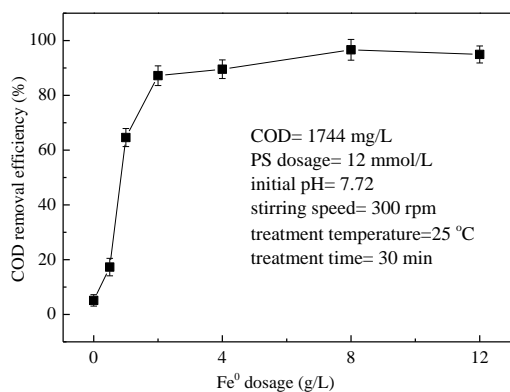


Fig. 2. Effect of Fe⁰ dosage on the COD removal efficiency after Fe⁰-PS treatment.

3.3 Effect of initial pH value

As shown in Figure 3, the COD removal efficiency were studied at different initial solution pH (2.0, 3.0, 5.0, 7.7, 9.0 and 11.0). Firstly, when initial pH was 3.0, 5.0 and 7.7 (raw water), the COD removal efficiency were 91.57%, 92.92% and 95.61%, respectively. In neutral and acid conditions, Fe⁰ reacted with H⁺ to generate more Fe²⁺, enough Fe²⁺ could activate PS to generate SO₄^{•-}. In addition, the lower initial pH can also facilitate the formation of Fenton-like reaction and improve the COD removal efficiency. However, the COD removal efficiency significantly decreased when the initial pH decreased from 3.0 to 2.0. In particular, when the initial solution pH was 2.0, the COD removal efficiency of hydraulic fracturing flowback fluid only was 68.3%. The strong acidity causes the quickly corrode of Fe⁰ and thus generate excessive Fe²⁺. The excessive generation of Fe²⁺ could scavenge the radicals in Fe⁰-PS process, leading to the reduction of the COD removal efficiency. Furthermore, under the alkaline condition, the corrosion of Fe⁰ was inhibited and the amount of Fe²⁺ decreased, which inhibited the activation of PS and reduce the COD removal efficiency. Therefore, the initial solution pH of 7.7 (raw water) was selected as the optimal value in the following experiments.

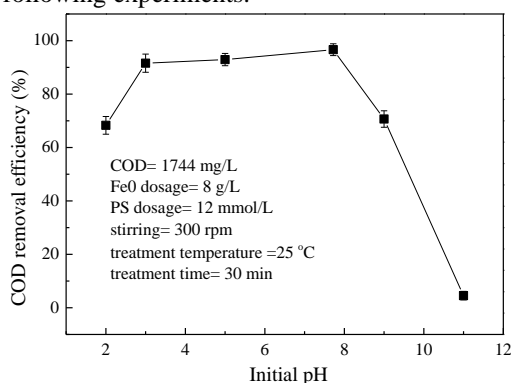


Fig. 3. Effect of initial pH on the COD removal efficiency after Fe⁰-PS treatment.

3.4 Effect of treatment temperature

Figure 4 shows the effect of treatment temperature on COD removal efficiency by the Fe⁰-PS process. It can be seen from Figure 4 that the COD removal efficiency gradually enhanced from 95.6% to 97.5% with the increased treatment temperature (from 15 °C to 35 °C), and then it gradually decreased to 93.2% when temperature improved from 35 °C to 70 °C. On the one hand, with the increase of temperature, PS can generate free radicals through thermal activation reaction. Meanwhile, with the increase of treatment temperature, the collision between molecules intensifies and the viscosity of water decreased, which is conducive to the coagulation precipitation process. Furthermore, the increase of temperature is also facilitate to the occurrence of hydrolysis reaction. However, when temperature was above 35 °C, COD removal efficiency gradually decreased with the increased treatment temperature. The results can be explained as that the higher temperature was not conducive to coagulation precipitation process. Furthermore, the higher treatment temperature would also consume a lot of energy. Although the COD removal efficiency has decreased at higher temperature, the decrease is no more than 5%, thus the temperature has little influence on the COD removal in the whole process. Therefore, the optimal treatment temperature of 25 °C was chosen as optimize the following parameter.

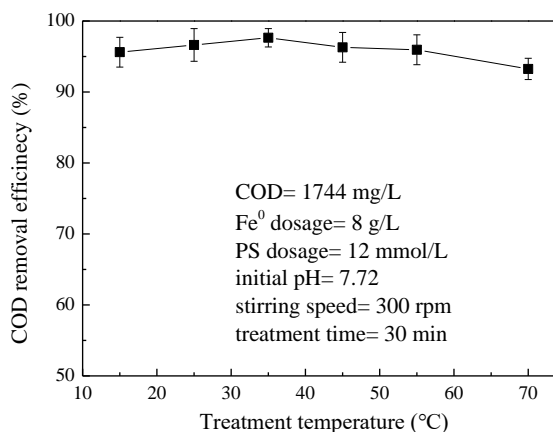


Fig. 4. Effect of treatment temperature on the COD removal efficiency after Fe⁰-PS treatment.

3.5 Effect of treatment time

Figure 5 shows the effect of treatment time on COD removal efficiency in the Fe⁰-PS process. The COD removal efficiency rapidly increased to 93.6% in the initial 5 min, and then it gradually increased to 95.0% in the following 30 min. The rapid removal of the pollutants in the initial 5 min was mainly attributed to adsorption of the Fe⁰ and the mineralized by the Fe⁰-PS process. Since the increase of treatment time would increase the operating cost, thus the optimal treatment time was 5 min.

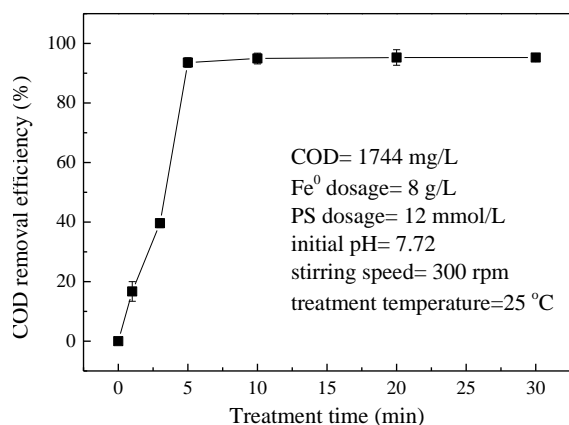


Fig. 5. Effect of treatment time on the COD removal efficiency after Fe⁰-PS treatment.

Finally, the optimal operating parameters including PS dosage (12 mmol/L), Fe⁰ dosage (8 g/L), initial pH value (7.7), treatment temperature (25 °C) and treatment time (5 min) were obtained according to the above semi-batch experiments.

3.6 Possible reaction mechanism of the Fe⁰-O₃ process

On the one hand, Fe⁰ and its corrosion products (e.g., FeOOH, FeO, Fe₃O₄, Fe₂O₃ and Fe²⁺/Fe³⁺) can effectively activate PS and generate more free radicals (SO₄^{•-}). At the same time, the generate SO₄^{•-} existed in the solution phase and degrade pollutants effectively. In addition, the pollutants in hydraulic fracturing flowback also be adsorbed by the generated iron corrosion (e.g., FeOOH, FeO, Fe₃O₄, Fe₂O₃) and form complexes. In other words, some pollutants in hydraulic fracturing flowback also could be removed by the coagulating sedimentation from the generated iron corrosion products.

4 Conclusion

In this study, the Fe⁰-PS process was developed to treat the hydraulic fracturing flowback. The Fe⁰ as a catalyst, could significantly increases the COD removal efficiency in Fe⁰-PS process (i.e., 93.6%), and was higher than those of sole Fe⁰ process (2.5%) and sole PS process (5.14%). In addition, the key operating parameters were investigated and the optimal operating parameters including PS dosage (12 mmol/L), Fe⁰ dosage (8 g/L), initial pH value (7.7), treatment temperature (25 °C) and treatment time (5 min) were obtained according to semi-batch experiments. Under the optimal conditions, the COD removal efficiency of hydraulic fracturing flowback in Fe⁰-PS process reached 93.6%, which indicated that the Fe⁰-PS process could effectively decompose the refractory pollutants in hydraulic fracturing flowback. In addition, the treatment ability of Fe⁰-PS process was much higher of Fe⁰ alone process and PS alone process. The results indicate that high treatment efficiency of Fe⁰-PS process was mainly attributed to the synergetic effects between Fe⁰ and PS. It can be concluded that the possible

reaction mechanisms of the Fe⁰-PS process consist of three parts: (i) activation of PS by Fe⁰ and its corrosion products, (ii) Fenton-like reaction in the presence of dissolved oxygen, (iii) adsorption through coagulating sedimentation of iron corrosion products. Therefore, it can be concluded that the Fe⁰-PS process can be considered as an effective, robust and feasible treatment method for hydraulic fracturing flowback.

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