Effect of Dehydration Process Conditions on Oily Sludge in a Fenton Advanced Oxidation System

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Abstract: Oily sludge is the main solid waste produced by the petrochemical industry and has attracted increasing attention due to its complex composition, containing a large number of heavy metals and organic toxic substances. Advanced oxidation technology has attracted much attention as an oily sludge treatment method as it can be used to reduce the harmful organic matter content and improve the dewatering performance of oily sludge. Taking oily sludge as the research object, this study adopted an orthogonal experimental design to investigate the water content and specific resistance of oily sludge by controlling the pH, reaction time and the mass ratio of hydrogen peroxide to ferrous sulfate (m_{H2O2}/m_{FeSO4}) of the reaction system. Results showed that the water content of oily sludge treated using the Fenton reagent was optimal under reaction conditions of pH 3, with a reaction time of 40 min and m_{H2O2}/m_{FeSO4} of 10/1. In contrast, the specific resistance of oily sludge treated using the Fenton reagent was optimal under the conditions of pH 3, with a reaction time of 50 min and m_{H2O2}/m_{FeSO4} of 14/1. Among the three factors assessed, the m_{H2O2}/m_{FeSO4} mass ratio had the greatest influence on both the water content and specific resistance of oily sludge.

1 INTRODUCTION

Oily sludge is an oily solid waste produced during the process of oil exploitation, transportation, refining and oil field oily wastewater treatment in the petrochemical industry. It generally consists of a stable suspension emulsion of oil in water (O/W), water in oil (W/O) and suspended solids. The composition of oily sludge is highly complex, containing a large amount of water and numerous refractory organic substances, heavy metals and other toxic substances, causing it to be classified as hazardous waste (Hu 2013). The high moisture content results in oily sludge having a large volume, while the untreated heavy metal residues can accumulate to dangerous concentrations which endanger human health. Extracellular polymeric substances (EPS) and metal ions are important components of oily sludge (Liu 2016). EPS accounts for about 80% of the sludge content, contributing to the formation of highly hydrated biofilms comprising various microorganisms, which adsorbs a large amount of water and constitutes the sludge floc skeleton. The EPS content has been reported to be the most important factor affecting sludge dewatering (Xiao 2017).

Previous studies have investigated the mechanism of sludge conditioning using the Fenton reaction. Hydroxyl radicals (·OH) are produced by a chain reaction in Fenton systems and have a very high redox potential (up to 2.8V), which can quickly oxidize EPS, changing the sludge structure and achieving sludge conditioning. Zhang et al. studied the changes in EPS and sludge morphology during the process of Fenton sludge conditioning via three-dimensional fluorescence electron microscopy, finding that oxidation is more important than flocculation in the process of Fenton sludge conditioning. After the oxidation of ·OH, the EPS composition and the morphology of sludge changed, resulting in a change of floc structure and particle size (Zhang 2015, Yang 2017). Xu et al. showed that

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fulvic acids disappear and that EPS was destroyed after sludge was treated using a Fenton-like system, while SEM exhibited that stable sludge flocs were destroyed using a Fenton-like system and acidification, with the water in flocs more easily released and therefore, the sludge dewatering performance improved. The floc structure of sludge changes, allowing the bound water to be released and the polymer to become smaller after EPS oxidation and degradation (Xu 2016).

Previous reports on sludge dewatering using Fenton advanced oxidation systems, have mainly focused on urban sludge, while few reports have investigated oily sludge from specific industries and there is no general consensus on the optimal Fenton reagent dosage, or conditions for the dehydration and reduction of oily sludge. This paper comprehensively analyzes the dehydration performance of oily sludge after conditioning using a Fenton advanced oxidation system. The influencing factors and optimal conditions for Fenton reaction conditioning of oily sludge were determined by investigating the changes in moisture content and specific resistance of sludge after conditioning. These findings lay a foundation for the practical application of Fenton advanced oxidation technology in the oil sludge industry.

2 MATERIALS AND METHODS

2.1 Materials

The oily sludge used in this experiment originated from Sichuan province and was produced during shale gas exploitation. The sludge was gray black with a moisture content of 30-85%, as shown in Fig. 1 and Fig. 2. According to the results of XRF analysis, the main components of the oily sludge were found to be inorganic minerals such as $BaSO_4$, CaO and Al_2O_3, as shown in Table 1. $FeSO_4$, H_2O_2 and HCl were all of analytical purity.

Figure 1: Sample of oily sludge

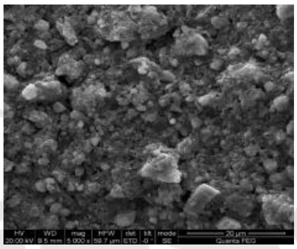

Figure 2: SEM of oily sludge.

Table 1: Composition analysis of XRF oily sludge containing oily sludge.

Components	SiO_2	CaO	Al_2O_3	BaO	SO_3	Fe_2O_3	Others
Wt (%)	39.26	15.32	11.45	10.69	8.26	5.65	9.37

2.2 Methods

Oily sludge was poured into a beaker and combined with the Fenton reagent, with continual agitation using a magnetic stirrer and the reaction maintained under different temperatures and different durations. The conditioned oily sludge was then poured into a Brinell funnel equipped with quantitative filter paper for vacuum suction filtration and dehydration. The amount of filtrate in the measuring cylinder was recorded at specific times, allowing the sludge specific resistance (SRF) to be calculated. The moisture content of sludge was determined using the gravimetric method.

3 RESULTS AND ANALYSIS

In order to establish the effect of varying pH, reaction time and m_{H2O2}/m_{FeSO4}, each factor was compared at three levels, using the $L_9(3^4)$ orthogonal table, in which A indicates pH (A_1 (pH=2), A_2 (pH=3) and A_3 (pH=4)); B indicates reaction time (B_1 (30 min), B_2 (40 min) and B_3 (50 min); C indicates the mass ratio of hydrogen peroxide to ferrous sulfate (m_{H2O2}/m_{FeSO4}) (C_1 (m_{H2O2}/m_{FeSO4}=10/1), C_2 (m_{H2O2}/m_{FeSO4}=12/1) and C_3 (m_{H2O2}/m_{FeSO4}=14/1)). Factors A, B and C are listed in columns 1, 2 and 3 of $L_9(3^4)$, respectively.

Table 2: Orthogonal experimental design.

Level	Factors		
	pH（A）	Reaction time (B)	Mass ratio（C）
1	2（A_1）	30（B_1）	10/1（C_1）
2	2（A_1）	40（B_2）	14/1（C_3）
3	2（A_1）	50（B_3）	12/1（C_2）
4	3（A_2）	30（B_1）	12/1（C_2）
5	3（A_2）	40（B_2）	10/1（C_1）
6	3（A_2）	50（B_3）	14/1（C_3）
7	4（A_3）	30（B_1）	14/1（C_3）
8	4（A_3）	40（B_2）	12/1（C_2）
9	4（A_3）	50（B_3）	10/1（C_1）

3.1 Apparent Analysis of Orthogonal Experimental Results

Results show that the appearance of oily sludge was a black solid block prior to treatment, changing to a dissolved state after pH adjustment treatment. The oily sludge expanded during treatment, with gas escaping during the reaction process. Under different reaction conditions the intensity of oily sludge expansion varied, with the resulting dried oily sludge being a black gray loose block. As shown in Fig. 2, the oily sludge is in a mass shape with an uneven surface, containing a high mass of extracellular polymer micelles which contain a large amount of bound water, which is not conducive to the dehydration of oily sludge. As shown in Fig. 4, the extracellular polymer structure was destroyed by the Fenton reaction, improving the dewatering performance of oily sludge.

Table 3 Orthogonal experimental results of oily sludge dewatering under Fenton advanced oxidation system

NO.	m_1 (g)	m_2 (g)	m_3 (g)	w_j (%)	c_j (%)	SRF (s^2/g)
1	28.8968	48.9740	46.2095	13.77	86.23	7.53×10^{14}
2	28.9030	49.0111	46.3609	13.18	86.82	1.18×10^{14}
3	28.8980	49.3161	46.6438	13.09	86.91	5.12×10^{14}
4	28.8556	49.0637	46.1923	14.21	85.79	6.87×1014
5	28.6968	48.7183	46.1493	12.83	87.17	7.13×10^{14}
6	28.8584	48.8695	45.9478	14.60	85.40	1.01×10^{14}
7	28.8651	48.9668	46.2897	13.32	86.68	3.28×10^{14}
8	31.6662	51.7520	49.0044	13.68	86.32	4.60×10^{14}
9	28.8564	48.9887	46.1100	14.30	85.70	4.04×10^{14}

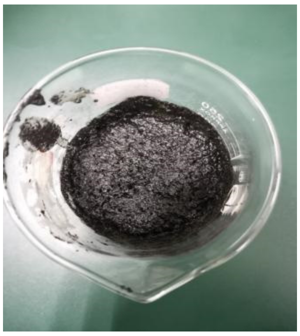

Figure 3: Oily sludge after treatment.

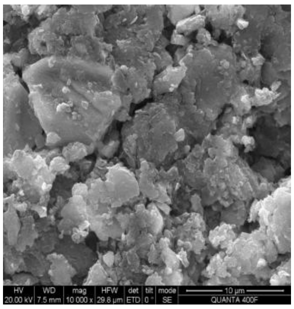

Figure 4: SEM of oily sludge after treatment.

3.2 Analysis of Water Content of Oily Sludge under Fenton Advanced Oxidation System

Analysis of orthogonal experimental results showed that the water content of treated oily sludge varied between 12-15% depending on the level of different experimental factors. The lowest treated sludge specific resistance had the highest water content of 14.60%, which was achieved under reaction conditions of pH 3, with a 50 min reaction time and m_{H2O2}/m_{FeSO4} ratio of 14/1. The lowest moisture content of 12.83% was achieved under reaction conditions of pH 3, with a reaction time of 40 min and m_{H2O2}/m_{FeSO4} of 10/1, which were the optimal experimental conditions in terms of moisture content according to the orthogonal experimental results.

Table 4 Variance analysis of moisture content.

Source	Class III sum of squares	Freedom	Mean square	F	Significance
Modified model	1.409[a]	6	0.235	0.301	0.893
Intercept	1680.453	1	1680.453	2156.240	0.000
pH (A)	0.474	2	0.237	0.304	0.767
Reaction time (B)	0.929	2	0.464	0.596	0.627
Mass ratio (C)	0.007	2	0.003	0.004	0.996
Error	1.559	2	0.779		
Total	1683.421	9			

Analysis of variance showed that among the influencing factors, pH, reaction time and m_{H2O2}/m_{FeSO4} ratio had a significant impact on the water content of oily sludge. The primary and secondary relationships among the three factors was ranked in the order of m_{H2O2}/m_{FeSO4}(C) > pH(A) > reaction time(B). The optimum level of each factor was: pH 3, reaction time of 40 min and m_{H2O2}/m_{FeSO4} of 10/1.

3.3 Analysis of Sludge Specific Resistance of Oily Sludge under Fenton Advanced Oxidation System

It was found that the specific resistance of oily sludge after treatment varied from 1.00×10^{14} - $8.00\times10^{14}s^2/g$, with the analysis of orthogonal experimental results showing that the specific resistance of oily sludge under different factor conditions varied according to both the factor and the factor level. The highest specific resistance of oily sludge (difficult to filter sludge) was $7.53\times10^{14}s^2/g$ under reaction conditions of pH 2, with a reaction time of 30 min and a m_{H2O2}/m_{FeSO4} of

10/1. In contrast, the lowest sludge specific resistance was $1.01\times10^{14}s^2/g$ under the reaction conditions of pH 3, with a reaction time of 50 min and a m_{H2O2}/m_{FeSO4} of 14/1, which were the optimal experimental conditions for specific resistance according to the orthogonal experimental results.

Table 5 Variance analysis of sludge specific resistance.

Source	Class III sum of squares	Freedom	Mean square	F	Significance
Modified model	4.50×10^{29a}	6	7.505×10^{28}	7.235	0.126
Intercept	1.85×10^{30}	1	1.846×10^{30}	177.998	0.006
pH (A)	1.62×10^{28}	2	8.106×10^{27}	0.781	0.561
Reaction time (B)	9.64×10^{28}	2	4.822×10^{28}	4.648	0.177
Mass ratio (C)	3.38×10^{29}	2	1.688×10^{29}	16.276	0.058
Error	2.07×10^{28}	2	1.037×10^{28}		
Total	2.32×10^{30}	9			

Analysis of variance showed that among the influencing factors, pH, reaction time and m_{H2O2}/m_{FeSO4} ratio had a significant impact on the specific resistance of oily sludge. The primary and secondary relationships among the three factors were ranked in the order pH(A) > reaction time(B) > m_{H2O2}/m_{FeSO4}(C). The optimum level of each factor was: pH 3, with a 50 min reaction time and m_{H2O2}/m_{FeSO4}(C) of 14/1.

4 CONCLUSION

Orthogonal experimental results for oily sludge treatment using the Fenton advanced oxidation system show that the optimal moisture content of 12.83% was achieved under the experimental conditions of pH 3, with a reaction time of 40 min and m_{H2O2}/m_{FeSO4} of 10/1. The optimal specific resistance of $1.01\times10^{14}s^2/g$ was achieved under experimental conditions of pH 3, with a reaction time of 50 min and a m_{H2O2}/m_{FeSO4} of 14/1. These results confirm that the Fenton advanced oxidation system can effectively destroy the extracellular polymer structure of oily sludge, releasing some of the bound water and converting it into free water, improving the dewatering performance of sludge.

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