

## Application of Fenton's reagent combined with sawdust on the dewater ability of oily sludge

Ying Li<sup>†</sup> and Ke-Jian Ji

*Norinco Group China North Material Science  
and Engineering Technology Group Corporation  
Jinan, 250031, China*

<sup>†</sup>E-mail: 59854177@qq.com

Hao Guo

*Combustion and Environmental Technology Research Center,  
Shanghai Jiao Tong University  
Shanghai 200240, China*

Su-Ping Feng

*Environmental Science and Engineering School,  
Shandong University  
Jinan 250100, China*

The dewater ability of oily sludge by application of Fenton's reagent and sawdust was investigated. The results showed that the two main indexes, capillary suction time and specific resistance to filtration, which are used to evaluate the effect of dewater ability of the raw oily sludge, were reduced from 1750 s and  $13.8 \times 10^{12}$  m/kg to 185 s and  $1.5 \times 10^{12}$  m/kg, respectively. By optimizing experimental conditions, the best dosage of  $H_2O_2$ ,  $Fe^{2+}$  and sawdust and the best reaction time were determined to be 170 mL/L, 216 mg/L, 50 wt. % and 40 min, respectively. Besides, the dry matter contents of sludge cakes and the properties of the supernatant were analyzed. The final results indicated that the oily sludge is more suitable for further treatment after combined process with Fenton's reagent and sawdust.

**Keywords:** Oily Sludge; CST; SRF; Fenton's Reagent; Dewater Ability.

### 1. Introduction

With the development of world economy, the demand of oil is increasing all the time. Abundant of oily sludge will be generated from oil exploration, transportation, and refining and consumption processes [1]. At present, almost 60 million tons of oily sludge will produce all over the world each year, and the annual output of oily sludge in China is 5 million tons. Until the beginning of 2014, about 1 billion tons untreated oily sludge existed around

the world [2, 3]. Oily sludge includes moisture, organic matter and solid residue, and these materials constitute multiphase mixture system. Because of different area and refined way, the moisture content of oily sludge is in commonly 40~99wt% [4, 5]. Fenton's reagent refers to the ferrous ions react with hydrogen peroxide, and produce high reactivity of the hydroxyl free radical reagent. In recent years, Fenton's reagent is applied more and more extensively in the oily sludge treatment. It's mainly using the strong oxidizing of hydroxyl radicals to destroy the emulsion structure and macromolecular organic matter of oily sludge, and reduce the difficulty of the subsequent processing. This paper investigated the dewater ability of oily sludge by application of Fenton's reagent and sawdust, in order to identify the best condition of dewatering performance.

## 2. Experimental Methods and Materials

### 2.1. Experimental materials

Oily sludge samples derived from sludge storage tank in Zhongyuan Oilfield Sixth Plant Union Station. The oily sludge in sludge storage tank was mixed well and uniform in texture. The samples were kept in plastic bucket with cover, avoid shaking during the transportation process, and stored in refrigerator at 4 C as soon as possible.

Physicochemical characteristics of the raw oily sludge are shown in Table 1.

Table 1. Physicochemical characteristics of the raw oily sludge

Parameters	Units	Value
pH	—	7.43
solid content	%	7.96
moisture content	%	87.01
oil content	%	5.03
SRF	$\times 10^{12}$ m/kg	13.8
Capillary Suction Time(CST)	s	1750

Sawdust derived from Huangtai furniture factory in Jinan. The saw dust was sieved and make sure the sizes of the samples were less than 2mm. The samples were dried for 4 hours under 80°C, and stored tightly sealed until ready for use.

### 2.2. The experiment reagent and instrument

H<sub>2</sub>O<sub>2</sub>, FeSO<sub>4</sub>·7H<sub>2</sub>O (AR);  
CST determinator, Triton, 304M;  
Vacuum pump, SHZ-D(III)

### 2.3. Experimental procedure

(1) We adjust the PH of Oily sludge to 3, add a certain amount of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , stir until  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  dissolves, add different amount of  $\text{H}_2\text{O}_2$  and reaction fully. Then, we will measure the changes of CST and SRF for making sure the best reaction time of Fenton's reagent and the best dosage of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$ .

(2) On the basis of in the previous step, we add the sawdust which was sieved and dried. Then, we will measure the CST and SRF of the mixture for making sure the best dosage of sawdust.

(3) We measure TOC and the content of iron ions of supernatant which was from oily sludge treated by Fenton's reagent and Fenton's reagent/sawdust, respectively, to inspect dewatering performance.

## 3. Results and Discussion

### 3.1. Effect of volume of $\text{H}_2\text{O}_2$ on dewater ability of oily sludge

$\text{H}_2\text{O}_2$  has extremely oxidability in the acidic condition. It can transfer bounder water to free water by decomposing the colloid and emulsifying structure in order to improve the dewater ability of oily sludge.

In this experiment, each 100ml of oily sludge sample had mixed with  $\text{H}_2\text{O}_2$  at dosage of 11 to 22ml respectively. The Figure 1 shows the relationship between  $\text{H}_2\text{O}_2$  dosage and oily sludge dewaterers ability.

As you can see from Figure 1, in the beginning stage, the dewater ability of oily sludge had been improved with the  $\text{H}_2\text{O}_2$  dosage increased which be indicated by CST and SRF decreased smoothly; when the dosage of  $\text{H}_2\text{O}_2$  reached 17ml, SRF and CST dropped to the minimum which were 1046s and  $8.3 \times 10^{12}\text{m}$  respectively. However, excessive dosages of  $\text{H}_2\text{O}_2$  made SRF and CST enhanced a little, because overdosing caused more organic matters of sludge were decomposed by Fenton's reagent. Its particle size became smaller, which directly deteriorate the dewater ability of sludge.

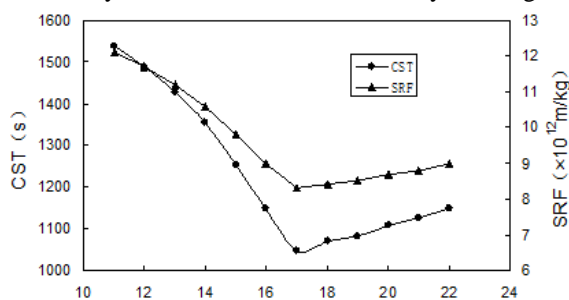


Fig. 1. Effect of volume of  $\text{H}_2\text{O}_2$  on dewater ability of oily sludge.

Therefore, the best dosage of  $\text{H}_2\text{O}_2$  for the best dewatering performance of oily sludge was 17mL/100mL

### 3.2. Effect of dosage of catalyst on dewater ability of oily sludge

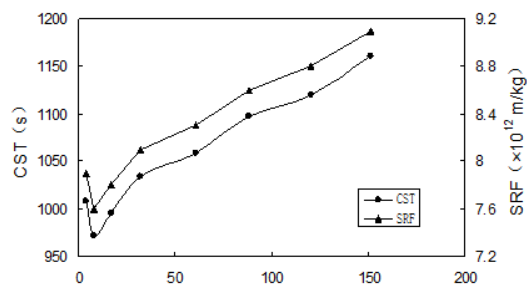


Fig. 2. Effect of dosage of catalyst on dewater ability of oily sludge.

As shown in Figure 2, it is limited to improve the dewatering effect of oily sludge, when the dosage of  $\text{Fe}^{2+}$  catalyst was low in the oily sludge. However, with the increasing dose of  $\text{Fe}^{2+}$ , the CST and SRF values of oily sludge also increased.  $\text{Fe}^{2+}$  shows catalytic effect on composition of  $\text{H}_2\text{O}_2$ , the colloid and emulsion structure of oily sludge can't be destroyed very soon, due to the low concentration of  $\text{Fe}^{+2}$  wouldn't decompose  $\text{H}_2\text{O}_2$  to form enough OH. When increasing the concentration of  $\text{Fe}^{2+}$ , the excess  $\text{Fe}^{2+}$  (partly transformed into  $\text{Fe}^{3+}$ ) will generate colloid, which will further increase the CST and SRF values of oily sludge. The more dose of  $\text{Fe}^{2+}$ , the more obvious effect on the dehydration of oily sludge, which is similar to the results of Liu Huan et al [6]

Therefore, the effects of dewater will be better when the catalyst of  $\text{Fe}^{2+}$  is at a dose of  $7.77 \times 10^{-5}$  mol/L. Under these conditions, the CST and SRF values of oily sludge were reduced to 971 s and  $7.6 \times 10^{12}$  m/kg respectively.

### 3.3. Effect of reaction time on dewater ability of oily sludge

Under the condition of using optimal  $\text{H}_2\text{O}_2$  and catalyst dosage, reaction time on the influence of oily sludge dewatering performance, the results shown in Figure 3.

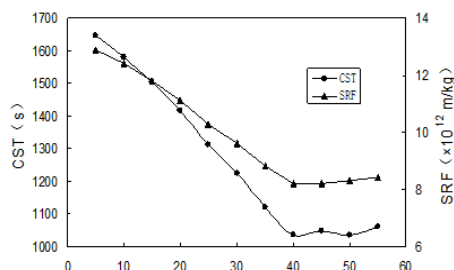


Fig. 3. Effect of reaction time on dewater ability of oily sludge.

As the Figure 3 shown, during the first 40 mins, CST and SRF of sludge declined gradually; the values became steady after 40 mins. The reason of the phenomenon was Fenton's reagent and oily sludge have not been mixed evenly, therefore only a part of sample could react with  $\bullet\text{OH}$  of Fenton's reagent. In the following stirring process, reaction rate of Fenton's reagent have been promoted by  $\bullet\text{OH}$  further blended with oily sludge. After the reaction to a certain extent, with the consumption of  $\text{H}_2\text{O}_2$ , the  $\bullet\text{OH}$  concentration is also declining, and the reaction rate would be reduced. And thus, the best oily sludge dewatering performance appears when the reaction time was 40 minutes, and the CST and SRF values of oily sludge which was treated were 1035 s and  $8.2 \times 10^{12}$  m/kg.

### 3.4. Effect of sawdust on dewater ability of oily sludge

In sludge dewatering process, sawdust is widely use as a leavening agent. It can provide skeletal structure in the sludge filtration and dewatering, thus easier to sludge dewatering and subsequent drying [7]. The effect of sawdust on dewater ability of oily sludge was shown in Figure 4.

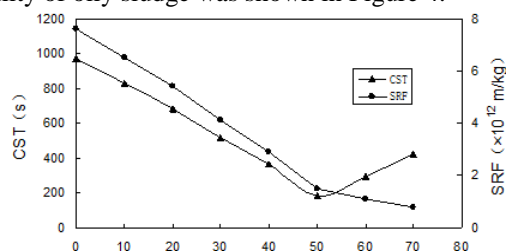


Fig. 4. Effect of sawdust dosage on dewater ability of oily sludge.

Figure 4 shows the performance that added waste wood sawdust to the treated oily sludge by Fenton's reagent. With the waste wood sawdust adding amount increasing, CST decreased gradually; however, when the amount of waste wood sawdust exceeded the dry mass of oily sludge 50wt. %, the CST

had rising and SRF had declined during whole reaction process. Because of the waste wood sawdust was a fluffy and easy to absorb moisture material and the oily sludge had high water content, the skeleton function of the waste wood sawdust was much larger than that of the water absorption in the filtration process. Nonetheless, its water absorption ability cannot be ignored with water content of oily sludge lost when the dose had been increased to a certain extent.

In conclusion, when the dose of sawdust was 50wt. %, oily sludge was treated by Fenton's reagent and sawdust, the CST and SRF values of oily sludge were reduced to 185s and  $1.5 \times 10^{12}$  m/kg.

### 3.5. Researches on products gained from oily sludge dewatering

In order to understanding the dewatering performance of Fenton reagent and sawdust, We measure moisture contents of sludge cakes which was from oily sludge treated by Fenton's reagent and Fenton's reagent/sawdust, respectively, and TOC, the content of iron ions and PH of supernatant. The results are shown in Table 2.

Table 2. Analysis of products gained from oily sludge dewatering.

Treatment Type	Moisture contents of sludge cakes (%)	Supernatant		
		pH	contents of Fe (mg/L)	contents of TOC(mg/L)
Fenton's reagent	67.5	2.65	1320	95.7
Fenton's reagent+sawdust	68.1	2.64	1130	86.8

As shown in Table 2, the moisture contents of sludge cakes which combined treatment with Fenton's reagent and sawdust were higher than which treatment with Fenton's reagent only. This is due to the dried sawdust will absorb a part of moisture during filtration process. Besides, PH of the supernatant of these two processes was the same, and it's reduced than before. This is because Fenton's reagent can turn the insoluble organic matter in oily sludge into soluble organic acids; it's also the reason of TOC of the supernatant increased after the treatment. The lower PH of the supernatant was conducive to the precipitation of Fe, so the Fe content in the supernatant was much higher.

## 4. Conclusions

Combined treatment with Fenton's reagent and sawdust can improve the dewater ability of oily sludge. Under the optimal conditions, the CST and SRF were reduced from 1760s and  $13.8 \times 10^{12}$  m/kg to 185s and  $1.5 \times 10^{12}$

m/kg, respectively. Dissolved organic matter, especially the acidic organic compounds in the supernatant after dewatered increased and PH reduced.

### References

1. Y. Zhou, W. Wei, G. F. Wu, J. H. Zhu, K. Zhang, Oil field oil sludge dewatering technology present situation and development [J], Chemical Management, 2014(29):167-167.
2. L.J. da Silva, F.C. Alves, F.P. de França, A review of the technological solutions for the treatment of oily sludges from petroleum refineries[J], Waste Management & Research, 2012 (30): 1016-1030.
3. Zhu Jiamusi, Study and analysis on the physical and chemical properties of oily sludge [D], Zhejiang University, 2014.
4. V.S. Cerqueira, R.P. Maria do Carmo, F.A. Camargo, F.M. Bento, Comparison of bioremediation strategies for soil impacted with petrochemical oily sludge[J], International Biodeterioration & Biodegradation, 2014(95): 338-345.
5. Y. Jiang, C.C. Zhao, D.F. Zhao, Oily sludge characteristics and treatment methods [J], Oilfield environmental protection, 2006 (15): 38-41.
6. H. Liu, J. Yang, Y. Shi, Y. Li, S. He, C. Yang, H. Yao, Conditioning of sewage sludge by Fenton's reagent combined with skeleton builders [J], Chemosphere, 2012 (88): 235-239.
7. C.V. Owens Jr, C. Lambright, K. Bobseine, B. Ryan, L.E. Gray Jr, B.K. Gullett, V.S. Wilson, Identification of estrogenic compounds emitted from the combustion of computer printed circuit boards in electronic waste[J], Environmental science & technology, 2007 (41): 8506-8511.