The combined effects of hydrothermal treatment and $Na_2S_2O_8$/ $CuFe_2O_4$ magnetic oxidation on sludge dewaterability improvement

Yonghao Chen[#,1], Dandan Chen[#,1,2,3], Yuhao Dou[2], Min Song[1,], Feirong Peng[3]*

[1]Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 210096, China
[2]Engineering Laboratory for Energy System Process Conversion & Emission Control Technology of Jiangsu Province, School of Energy & Mechanical Engineering, Nanjing Normal University, Nanjing 210023, China
[3]China Construction Power and Environment Engineering Co., LTD, Nanjing 210017, China

Abstract. $Na_2S_2O_8/CuFe_2O_4$ addition and hydrothermal pretreatment were combined in this paper to ameliorate the dewatering performance (DP) of sludge with specific-resistance of filtration (SRF), time of capillary suction (CST), and water content (Wc) as well as water types investigated. The results shown the synergistic effect between $Na_2S_2O_8/CuFe_2O_4$ addition and hydrothermal pretreatment and the DP of sludge reached to the best when the hydrothermal temperature was 150 ºC, the addition amount of $Na_2S_2O_8$ was 0.08 mmol/g-VSS and the mass ratio of $Na_2S_2O_8/CuFe_2O_4$ was 2.0. Through the analysis of water distribution, it was also demonstrated that the sludge structure was destroyed with the surface moisture released. All the results obtained shown the significant impact of the combined methods on ameliorating DP of sludge and promoting sludge recovery and utilization.

1 Introduction

With the increase of water consumption caused by the advancement of residents' living standard, sludge as a by-product of sewage treatment has attracted more and more attention. In 2015, the sludge harmless disposal rate in China's cities was only 53%, while the 13th five-year plan requires that the sludge harmless disposal rate in prefecture-level cities reach 90% and that in county-level cities reach 75% by 2020, which is a huge challenge because of China's growing sludge production.

The current sludge treatment and disposal approaches mainly include sanitary landfill, aerobic composting, natural drying, incineration power generation, etc. Based on the principle of "stabilization, innocuity and recycling" proposed in the 13th five-year plan, treatment methods such as composting, natural drying and incineration have been advocated. However, these methods have quite high requirements for the moisture content of sludge: when sludge is composted or buried, the moisture content should be at least less than 60%; when sludge is used to improve soil properties, its moisture content should be lower than 45%; when sludge is used to make building materials, its moisture content should be less than 40%; and incineration is the most demanding for sludge moisture content, which must be less than 30%.

At present, usual dewatering methods for surplus sludge in sewage treatment plants are as follows: first add CaO to regulate the sludge properties, and then dehydrate with the plate-and-frame filter press. Although this method is very effective in decreasing the volume of sludge (the moisture content of sludge can be reduced from 99% to about 80%), it still cannot meet the above requirements. Therefore, it is necessary to pretreat the sludge, so as to further decrease the water content (Wc) of the sludge and meet the requirements of deep dewatering.

The key factor of the sludge dewatering process is the existence of extracellular polymeric substances (EPS). EPS has a high adsorption performance on water molecules, and the organic floc structure which is constituted by EPS has a fairly powerful hydroscopicity. The water molecules are restricted in the sludge, preventing the liberation of the bound water in the procedure of dewatering [1-5]. Hydrothermal pretreatment can decompose large particles of organic matter into small molecules of organic matter, and degrade insoluble organic matter into liquid phase, thus greatly improving the dewatering performance (DP) of sludge [6-7].

Advanced oxidation process (AOP) has been widely used in recent years because it can effectively degrade and mineralize organic pollutants [8-10]. The combination of hydrothermal treatment and advanced oxidation has been shown to be more effective in the treatment of spaceflight solid waste and waste drugs than hydrothermal treatment alone [11]. However, the combination of the two methods for sludge treatment has been rarely reported. Therefore, advanced oxidation technology and hydrothermal pretreatment method were combined in this paper to

* Corresponding author: minsong@seu.edu.cn
# Co-first author: Yonghao Chen and Dandan Chen. These authors contributed equally to this work.

ameliorate the DP of sludge and bring down the moisture content of sludge.

Persulfate oxidation is known as an environment-friendly process among advanced oxidation processes, which can produce high-efficiency sulfate radicals ($SO_4^{-\bullet}$). $Na_2S_2O_8$ was used as oxidizing agent in this work, and $CuFe_2O_4$ was the catalyst. Studies have shown that $CuFe_2O_4$ has higher catalytic activation performance than other metal oxides [12], which can significantly increase the concentration of $SO_4^{-\bullet}$ in solution and improve the efficiency of sludge oxidation and degradation. Moreover, $CuFe_2O_4$ is a magnetic material, which is easy to recycle and can avoid affecting the subsequent treatment of sludge after dewatering.

The aim of the current study is to estimate the combined effect of hydrothermal treatment and $Na_2S_2O_8/CuFe_2O_4$ magnetic oxidation on the DP of sludge with the influence factors like heating temperature, oxidation-catalyst amount and the ratio of $Na_2S_2O_8$ to $CuFe_2O_4$ analyzed by three evaluation indexes, specific-resistance of filtration (SRF), time of capillary suction (CST), and water content (Wc).

2 Materials and methods

2.1. Materials

The experimental sludge was taken from a sludge tank in a sewage treatment plant, which is located in Anhui province. The Wc of the sludge was 81.40%. Retrieved sludge samples were sealed in plastic bags and stored in a refrigerator at 4 ºC. The basic quality of the sludge used in this experiment is proved in Table 1. The oxidant $Na_2S_2O_8$ and the catalyst $CuFe_2O_4$ were selected to improve the DP of sludge. $Na_2S_2O_8$ (> 99%) used in this experiment, which was purchased from Sinopharm Chemical Reagent Co. LTD. (Shanghai, China), was analytically pure grade and $CuFe_2O_4$ was provided as the production process described by Ding et al. [12-14]

Table 1. Basic properties of sludge

Property	Value
pH	7.16
Water content	81.40%
Total suspended solids (TSS)	1.86×10^5 mg/L
Volatile suspended solids (VSS)	3.45×10^3 mg/L

Table 2. Main mechanical parameters of the reactor

Parameter	Value
Nominal capacity	2 L
Working pressure	≤20 MPa
Working temperature	≤350 ºC
Heating power	2 kW
Stirring speed	20~750 r/min

The high pressure hydrothermal reactor used in this experiment is produced by an automatic control reactor company in Shandong province. The main mechanical parameters are offered in Table 2.

2.2 Experimental methods

Each sludge sample was made by mixing sludge and distilled water, whose total mass was 1kg and the Wc was adjusted to 90%. $Na_2S_2O_8$ and $CuFe_2O_4$ were put into the container in some predetermined ratios. The heating was performed with a stirring speed of 150 r/min for an hour and the products were deposited at 4 ºC in the freezer for follow-up analyses.

To study the influence of the $Na_2S_2O_8/CuFe_2O_4$ ratio on sludge dewatering performance, the mass ratio of $Na_2S_2O_8/CuFe_2O_4$ was set at 1.0, 2.0, 5.0 and 10.0 while $Na_2S_2O_8$ was added at three addition amounts: 0.06, 0.08 and 0.12 mmol/g-VSS. To evaluate the impact of the heating temperature, the temperature in the reactor was set to 110, 130, 150 and 180 ºC while $Na_2S_2O_8$ was added at a fixed amount of 0.08 mmol/g-VSS and the mass ratio of $Na_2S_2O_8/CuFe_2O_4$ was 2.0. And samples were labeled according to the working condition. For example, 150-0.08-2.0 means the heating temperature is 150 ºC, the addition amount of $Na_2S_2O_8$ is 0.08 mmol/g-VSS and the mass ratio of $Na_2S_2O_8/CuFe_2O_4$ was 2:1. In particular, zero represents no heating or addition.

2.3 Analytical methods

2.3.1 SRF, CST and Wc

Evaluation methods of sludge dewatering performance were sludge filtration performance, dewatering rate and dewatering degree, and the corresponding indexes were specific-resistance of filtration (SRF), time of capillary suction (CST) and water content (Wc).

The SRF is the resistance when dry sludge is put on the filtration scope under a fixed pressure. And the value was calculated by the Carmen filtration equation after a Buchner funnel experiment [15]. The CST is the time required for the free moisture in sludge to filter a certain distance on chromatographic filter paper, so it can indicate the filtration rate of sludge. The Wc was measured at 105 ºC for 8 h in a drying oven after the sludge went through the same filtration process. The filtration process was conducted by a simple hydraulic filter device at 0.8 MPa [16].

2.3.2 Water distribution of sludge

According to the changes of sludge drying rate and binding energy, the water in the sludge was classified into four types: free moisture, pore water, surface moisture and bound water [17-19].

In this paper, the content of these four kinds of water was measured by thermal drying method, which was first proposed by Smollen in the quantitative study of biological sludge bound water [20]. The experimental device was made as described by Deng et al. [21], it was connected to a computer and can record the weight of sludge in real time.

Table 3. Evaluation indexes of dewatering performance and water distribution of sludge at different conditions.

Sample	SRF (×10^{10} s^2/kg)	CST (s)	Wc (%)	Free moisture	Pore water	Surface moisture	Bound water	Free moisture + Pore water
Raw sludge	110.49	348	76.81	13.76	35.59	23.74	16.71	49.35
150-0-0	97.70	157	62.38	19.93	49.78	8.59	11.10	69.71
110-0.08-2.0	125.10	430	57.65	9.08	47.63	18.84	13.90	56.71
130-0.08-2.0	106.93	192	55.88	19.34	47.85	7.32	16.06	67.19
150-0.08-2.0	53.67	144	51.57	26.61	39.80	9.53	13.64	66.41
180-0.08-2.0	2.34	130	50.62	28.83	39.78	7.54	13.44	68.61
0-0.08-1.0	99.36	293	63.12	25.67	36.09	12.46	15.43	61.76
0-0.08-2.0	57.78	236	62.73	24.16	39.94	7.90	17.69	64.10
0-0.08-5.0	72.78	279	64.02	10.98	47.56	14.23	17.57	58.54
0-0.08-10.0	85.38	291	64.26	16.82	37.26	14.01	22.04	54.08
0-0.06-2.0	86.18	295	64.21	9.54	45.07	15.13	18.57	54.61
0-0.12-2.0	85.19	288	65.31	17.16	49.78	8.02	13.79	66.94

3 Results and discussion

3.1 Dewatering performance of sludge

The estimate indexes (SRF, CST, and Wc) of DP of sludge at various conditions are provided in Table 3. The data show that the combined method of hydrothermal treatment and $Na_2S_2O_8$/$CuFe_2O_4$ addition is more effective than the individual processes.

The combined method has a pretty high effect, for example, three indexes under the condition of 150-0.08-2.0 were reduced by 51.4%, 58.6% and 32.9%, respectively.

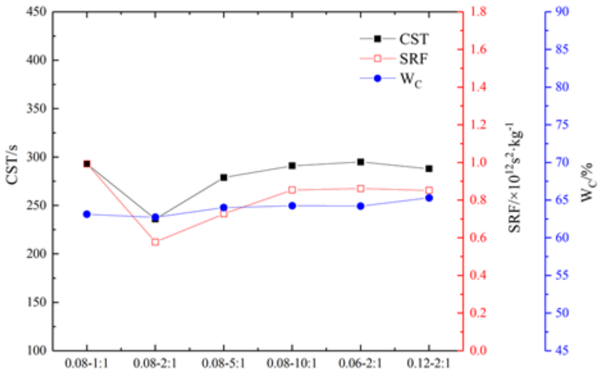

Fig. 1. Sludge dewatering properties of different $Na_2S_2O_8$/ $CuFe_2O_4$ additions

In order to estimate the impact of the addition amount of $Na_2S_2O_8$/$CuFe_2O_4$ on the DP of sludge, the addition amount of $Na_2S_2O_8$ was controlled at 0.06, 0.08 and 0.12 mmol/g-VSS, and the mass ratios of $Na_2S_2O_8$ and $CuFe_2O_4$ were 1:1, 2:1, 5:1 and 10:1. According to Fig. 1, when the addition amount was 0.08-2.0, the SRF and the CST reached the lowest values at 0.5778×10^{12} s^2/kg and 236 s, respectively. However, the dewatering degree of sludge was little affected, indicating that the influence of oxidative pretreatment on the DP of sludge was more about improving the filtration performance and dewatering rate of sludge.

In the study of the influence of hydrothermal reaction temperature, the adding amount of $Na_2S_2O_8$ was 0.08 mmol/g-vss, and the mass ratio of $Na_2S_2O_8$/$CuFe_2O_4$ was 2.0. As shown in Fig. 2, with the increase of temperature, the three indexes showed a significant trend of decline, and the SRF even dropped to 0.0234×10^{12} s^2/kg at 180 ºC. Since there was no significant difference in Wc between 150 ºC and 180 ºC (differ by 0.95%), 150 ºC was the optimal reaction temperature in consideration of the energy consumption of the hydrothermal reaction.

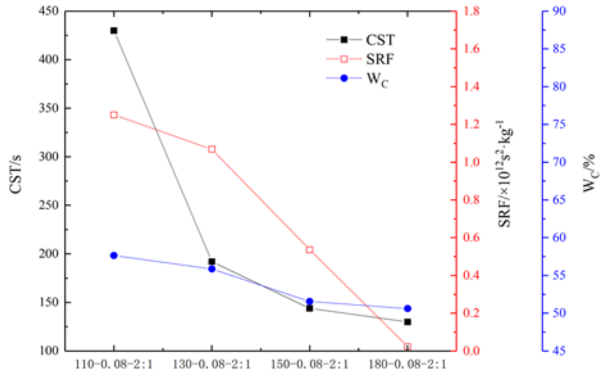

Fig. 2. Sludge dewatering properties of different hydrothermal reaction temperatures

3.2 Water distribution of sludge

The water contents of four kinds (free moisture, pore water, surface moisture and bound water) are also provided in Table 3. The method to calculate water distribution from sludge drying curves was described by Chen et al. [22] For free moisture and most pore water can be separated mechanically, the sum of them (Fm+Pw, Free moisture + Pore water) is listed separately as a representation of the extent to which sludge can be dehydrated. The maximum value of the Fm+Pw was 69.71%, indicating that the hydrothermal method was more conducive to reducing the binding water which was the most difficult to remove from the sludge. After thermal hydrolysis pretreatment, the hydrophilic capacity of the sludge cut down and the conversion of the bound water in the sludge into free moisture was promoted. The proportion of moisture that can be removed from the sludge after pretreatment by combined hydrothermal and advanced oxidation was 66.41%, lower than hydrothermal pretreatment alone, but its free moisture content was up to 26.61%, so the moisture content of sludge cake was lower after mechanical dewatering.

Fig. 3 shows the sludge drying curves of different pretreatment methods. It can be seen that after advanced oxidation, hydrothermal method and combined treatment, the sludge drying rate was significantly accelerated, and the constant rate stage lasted longer, indicating that the content of free moisture in the sludge increased. And combined with the data in Table 3, pore water content in the sludge was increasing, showing that after various pretreatment, the mechanical structure of sludge was changed, releasing the moisture in sludge cells, leading to the reduction of surface moisture and bound water content, which was transformed into pore water and free moisture that can be mechanical removed easily.

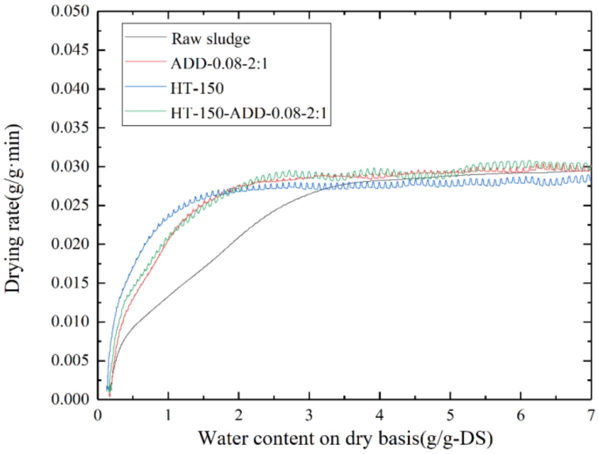

Fig. 3. Sludge drying curves of different pretreatment methods

Water distribution of sludge in different conditions is revealed in Fig. 4 and Fig. 5. In Fig. 4, the two lowest points of the red-blue boundary lines appear under the conditions of 0.08-2.0 and 0.12-2.0, respectively, corresponding to Fm+Pw values of 64.10% and 66.94%, indicating that the mass ratio of 2.0 was optional and the higher the amount of addition, the greater the change of the Wc in the sludge, and the more Wc can be separated from the sludge. And as can be seen from Fig. 5, when the hydrothermal temperature exceeds 130 ºC, the moisture content that can be removed from the sludge increases significantly, accounting for more than 66%, which is consistent with the change in the DP of the sludge above.

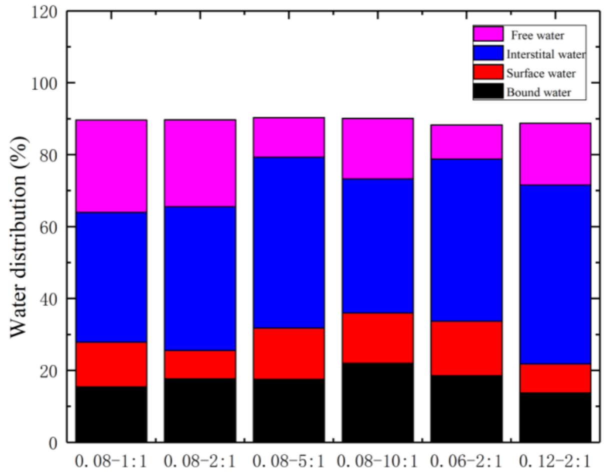

Fig. 4. Water distribution of sludge at different $Na_2S_2O_8$/ $CuFe_2O_4$ additions

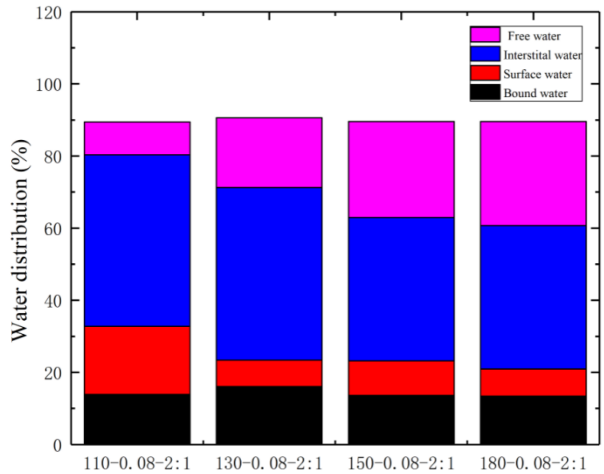

Fig. 5. Water distribution of sludge at different hydrothermal reaction temperatures

4 Conclusion

The combined effects of $Na_2S_2O_8$/$CuFe_2O_4$ magnetic oxidation and hydrothermal method on sludge dewatering performance and sludge water distribution were investigated in this paper. The results revealed that $Na_2S_2O_8$/$CuFe_2O_4$ addition and hydrothermal process could both ameliorate the DP of sludge and increase the proportion of the moisture content that can be mechanically removed.

The synergistic effect between hydrothermal pretreatment and $Na_2S_2O_8$/$CuFe_2O_4$ addition ameliorated the DP of sludge observably. The influences of the heating temperature, oxidation-catalyst amount and the ratio of $Na_2S_2O_8$ to $CuFe_2O_4$ on the DP of sludge shown that the effect of the mass ratio of $Na_2S_2O_8$/$CuFe_2O_4$ is greater than that of the addition with the optimized condition of 0.08-2.0 obtained. Besides, the filtration performance of sludge was improved by about 97.88%, the dewatering rate was improved by about 62.64%, and the Wc in final sludge cake was decreased to 50.62% when the treatment condition was 180-0.08-2.0. When the heating temperature increased to 150 ºC, the three values changed to 51.43%, 58.62% and 51.57% respectively. It demonstrated that 150-0.08-2.0 is the optimal reaction condition since sludge dewatering performance can be effectively improved.

In addition, the floc structure of sludge was destroyed under the combined pretreatment. The EPS was hydrolyzed, releasing the surface moisture in the sludge and converting it into free moisture and pore water. When the hydrothermal reaction temperature exceeds 150 ºC, the content of free moisture increased significantly, the degree of sludge dewatering was ameliorated and the Wc of final sludge cake was greatly decreased. By the way, the recovery rate of $CuFe_2O_4$ was over 50%.

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