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Research on Characteristic of $Fe^{2+}/S_2O_8^{2-}$ Composite CaO Synergetic Conditioning for Municipal Sludge

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Abstract

For the problem as high energy consumption and sludge increment during the municipal sludge management process with advanced oxidation technology of sulfate radical, the $Fe^{2+}/S_2O_8^{2-}$ composite CaO reaction system was set up. Meanwhile, systematical studies had been carried out for coordinated conditioning of municipal concentrated sludge. The scientific process parameters were determined with the help of sludge capillary suction time, sewage sludge moisture content and other core indicators and the effect of traditional polyacrylamide flocculation method, Fenton method and activated persulfate method were compared. The results showed that in the neutral concentrated sludge conditioning, there were outstanding advantages for $Fe^{2+}/S_2O_8^{2-}$ composite CaO reaction system compared with Fenton, CPAM, and $SO_4^{-}\cdot$ methods and the optimal parameters for dosage were as follows: $S_2O_8^{2-}$: 80 - 120 mg·g^{-1} DS, n(Fe^{2+}):n(SPS) = 0.8:1, CaO: 200 mg·g^{-1} DS. To achieve similar performance index, the dosage of Fe^{2+} per ton for sludge could be reduced by 20%, the loss rate for iron in filtrate was 0.5%, dewatering of sludge by suction filtration was within 50 s and the moisture content for dewatering cake was 53.7%, which significantly improved the economy and practicability of $SO_4^{-}\cdot$ advanced oxidation technology, and the results were expected to form a useful supplement to the popularization and application of $SO_4^{-}\cdot$ advanced oxidation technology.

Keywords

Sludge Conditioning, Fe^{2+}, Persulfate, Quicklime, Economy, Municipal Sludge

1. Introduction

Wet sludge (water content of about 98%) was a by-product of municipal sludge, which resulted in low treatment rate, complex composition, huge output and severe problem of secondary pollution due to high disposal investment and operating costs [1]. Sludge conditioning could improve the efficiency of thickening and dewatering and promote its stabilization and harmlessness by changing the properties of sludge solid particles and their arrangement. Sludge disposal technology had long been a question of great interest in a wide range of fields. It had previously been observed that the chemical conditioning method had obvious advantages of stronger applicability, simpler, superior effect, shorter cycle and lower cost. Traditional cationic polyacrylamide (CPAM) conditioning method could reduce the moisture content of the dehydrated cake to 75% - 85%, but there were problems of toxicity and refractory degradation, and the sludge was easy to rot and smell, it was difficult to meet the requirements of national standards for sludge landfill (<60%), incineration (<50%), and building materials (<40%) [2] [3] [4]. Data from several advanced studies suggest that the oxidant sludge conditioning method could cause the partial oxidation and reorganization of extracellular polymer (EPS), thereby changing the floc structure, which could significantly improve the dewatering performance of sludge and reduce the amount of sludge [5]. Among them, activated persulfate oxidation technology is a new type of advanced oxidation technology with sulfate free radicals ($SO_4^- \cdot$) as the main active substance, which has stronger oxidation ability, wider pH range of use, and better storage and transportation, which had been applied in the study of soil and groundwater organic pollutants in remediation and sludge conditioning [6]. Liu *et al.* found that persulfate conditioning thickened sludge could effectively destroy the EPS organic matter of the sludge and release intracellular water, reduce the capillary water absorption time of the sludge, and significantly reduce the specific resistance and moisture content of the sludge, and the moisture content of the dehydrated cake could be reduced to 80% [7] [8], but the compressibility of the mud cake was unfavorably enhanced, and the efficiency of sludge dewatering was poor [9]. Therefore, recent investigators had examined the effects of physical conditioning agents (quicklime, fly ash, phosphogypsum, etc.) on $SO_4^- \cdot$ advanced oxidation technology, which probably formed a stable, permeable, rigid lattice structure, and further reduced the specific resistance and compressibility of sludge [10] [11] [12]. Li *et al.* found that the moisture content of the dehydrated cake could be reduced to 54.09% which pleasurably met the key needs of China's municipal sludge deep dewatering (<60%) in the future under the conditions of sodium persulfate (SPS) 320 mg/gDS, n(Fe^{2+}):n(SPS) = 1.5:1, lime 400 mg/gDS, fly ash 500 mg/gDS [12]. However, there were problems such as high energy consumption, large amount of chemicals, high treatment costs, and sludge increments, which had adverse impacts to improve its technical advantages and application prospects.

In this paper, the study of the synergistic sludge deep dewatering process formed by cell-breaking reagent (MS_2O_8) + activator (Fe^{2+}) + framework construct (CaO) was explored on. The research data in this thesis was drawn from three main sources: sludge capillary water absorption time (*CST*), moisture content of the dehydrated cake (*Wc*) and sludge dewatering time (*Tc*). An army of parameters and liquid phase product characteristics of persulfate-skeleton construct coordination was obtained, and compared those with typical Fenton, CPAM, etc. among domestic and foreign results. Results indicated that this research would contribute to a deeper understanding of a useful resource application of activated persulfate oxidation technology.

2. Experimental Materials and Methods

2.1. Test Materials

The sample was the concentrated sludge (water content of about 95%) produced in the sewage treatment process of Second Wastewater Treatment Plant of Everbright Water (Jinan) Ltd. The physical and chemical properties were shown as follows: pH 7.6, water content 98%, ash content 0.54%, and organic matter content 1.25%.

2.2. Main Reagents and Instruments

Six-joint stirrer (JJ4A, Changzhou Jintan); Capillary water absorption time tester (DP-304M, British Triton); STOC tester (TOC-L CPN, Japan Shimadzu); ion chromatography (CIC-D100, Qingdao Shenghan); ICP-MS (ICP-MS7500a, Agilent, USA); pH meter (BRCN, Zhejiang Brown); suction filter (VF204A, Sciencetool, USA); jack-type filter press (Homemade); electric heating blast drying box (DHG, Shanghai Binglin).

$K_2S_2O_8$, $Na_2S_2O_8$, $FeSO_4 \cdot 7H_2O$, CaO were all analytically pure (>99.9%); Cationic polyacrylamide was industrial grade.

2.3. Analysis Methods

Main indicators: *CST*, *Wc*, *Tc*.

The moisture content of the dehydrated cake was measured by gravimetric method; the capillary water absorption time was measured by a capillary water absorption time tester (DP-304M, British Triton); the filtrate after dehydration was analyzed by STOC tester (TOC-L CPN, Japan Shimadzu), Ion Chromatography (CIC-D100, Qingdao Shenghan) and ICP-MS (ICP-MS7500a, Agilent, USA); the sludge dewatering time was defined as the time required to completely filter 500 mL of sludge (suction pressure 0.1 Mpa).

The experimental data is the average data of three parallel experiments.

2.4. Experimental Method

The main steps were shown in **Figure 1**. Experimental procedure and main parameters reference [12]: Take 500 mL of experimental sludge → add persulfate → react for 5 min (stirring rate is 300 $r \cdot min^{-1}$) → add Fe_2SO_4 solution → react for 10

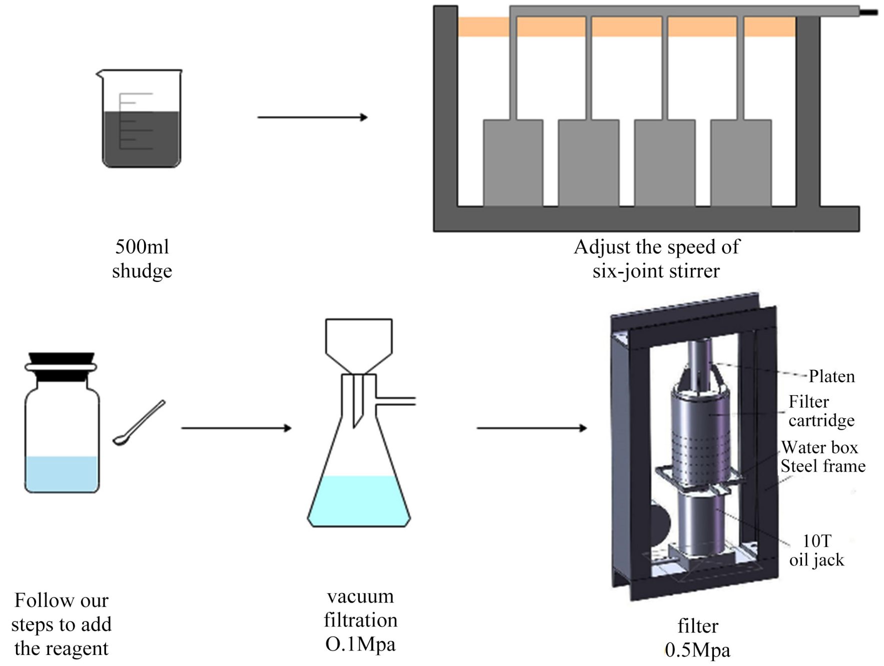


Figure 1. The experimental steps used in this research.

min (stirring rate is 150 r·min^{-1}) → add quicklime → rapid stirring for 30 s (300 r·min^{-1}), slow stirring for 2 min (150 r·min^{-1}) → vacuum filtration dehydration (0.1 Mpa) → jack press filter dehydration (0.5 Mpa). In the single factor experiment, the relevant steps were adjusted according to the different types of conditioning agents.

3. Results and Discussion

3.1. Determination of the Optimal Dosing Ratio of Fe^{2+} and MS_2O_8

As mentioned in the literature review, the theoretical dosage ratio of Fe^{2+} to MS_2O_8 was 1:1. When the two dosing ratio exceeds 1:1, the excess Fe^{2+} would react with $SO_4^{2-}\cdot$ to consume free radicals, which would dreadful to the structure destruction of sludge flocs, and caused unfavorable effectiveness [13] [14] [15] [16]. Several reports had shown that when the dosage ratio was in the range of 0.8:1 to 1.1:1, the effectiveness was almost equivalent. The mechanism was that persulfate could self-decompose or decompose by minerals in the soil to reduce Fe^{2+} consumption [17], and this could result in a significant impact on the cost of $SO_4^{-}\cdot$ advanced oxidation technology. Considering this, the paper had carried out a detailed study on the dosage ratio of Fe^{2+} and MS_2O_8 in the range of 0.6:1 - 1.4:1. Especially, when the ratio was close to 1:1, the ratio gradient scale was reduced to 0.1. The influence of the addition ratio on *CST* and *Wc* were shown in **Figure 2**.

As shown in **Figure 2**, comparing with no conditioner, *CST* value dropped rapidly from 68.7 s·L/g SS to 36.3 s·L/g SS with conditioner as a radio of 0.6:1, were an average decline in the proportion of 47.2%. And the moisture content

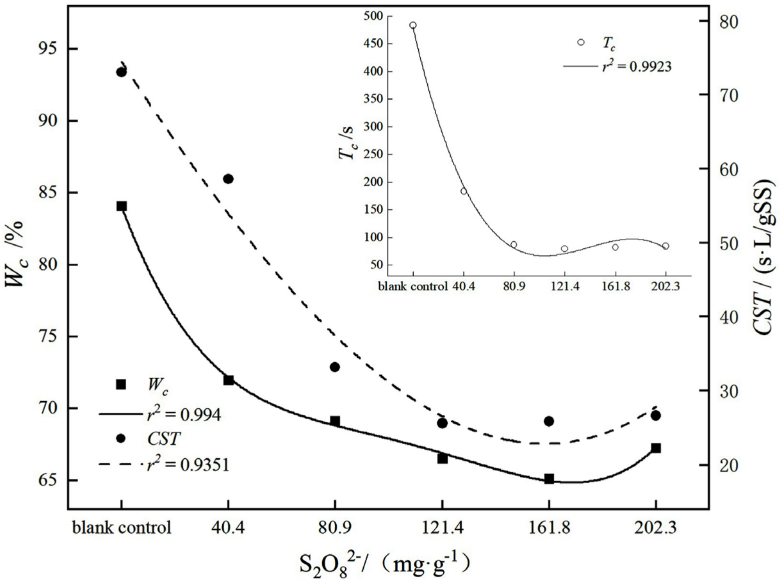


Figure 2. Effect of Fe^{2+} and persulfate addition ratio on sludge dewatering performance.

also declined from 93.0% to 85.0% or less, with a decrease of 8.6%. However, when the ratio of those two additions increased, *CST* value did not show a trend of decreasing, conversely, the *CST* value increased when the ratio exceed 0.8:1. the *CST* value started from 32.9 s·L/g SS continued to increase after the minimum value, and the moisture content of the corresponding dehydrated cake also presented a fluctuating distribution, and *Wc* fluctuated between 78% and 82%. No significant differences were found when the two dosing ratios are 0.8:1 or 1.2:1, *Wc* was similar, reaching a minimum of 78% - 79%. The two dosing ratios of 0.8:1 had the most significant effect, when enlarged the ratios, *Wc* did not have an apparent decrease.

Therefore, it could be concluded that Fe^{2+} acted as an initiator to activate MS_2O_8 to produce $SO_4^{-}\cdot$ from **Figure 2**. In the first place, $SO_4^{-}\cdot$ degraded the organic matter in the flocs, effectively destroyed the structure of the sludge flocs, forced the sludge to release more intracellular water and increase free water in the sludge. The sludge was relatively easier to be filtered than the initial configuration, and the residual moisture in the cake was reduced which had a valid promotion effect on dehydration. Apparently, *CST* value and *Wc* showed better conditioning effects than the blank control group. There is one more point, Fe^{2+} would react with $SO_4^{-}\cdot$, $SO_4^{-}\cdot$ lost the opportunity of partial oxidation to attack the organic matter of sludge flocs when the dosage ratio of Fe^{2+} and MS_2O_8 exceeded 0.8:1, thereby the overall oxidability and damaging were retarded, and the dehydration speed was slower as a result. In summary, these results showed that there was a more pleasurable and accurate chemical dosage ratio, namely, n(Fe^{2+}): n(SPS) was 0.8:1, so as to achieve the same conditioning index (*CST* reduction rate was about 47%). Clearly, the amount of sludge Fe^{2+} reagent could be reduced by 20% with a ton of pollution on average, and the iron loss rate was also reduced. At the same time, the concentration of Fe^{3+} ion in the filtrate was greatly reduced, which could reduce the difficulty and cost of subsequent filtrate wastewater treatment, and improve the economics and practicality of advanced SO_4-·oxidation technology.

3.2. The Influence of the Dosage of Activated Persulfate on Sludge Dewatering Performance

A stronger relationship between Fe^{2+} and $S_2O_8^{2-}$ has been reported in many literatures, the dosage of medicament directly affected the destruction degree of sludge flocs and the subsequent physical dehydration treatment effect. The scientific dosage of activated persulfate could further reduce the cost per ton of sludge treatment, and avoid the introduction of excessive SO_4^{2-} and other impurity ions in the system at the same time. This similar results were also reported by Zhen *et al.* [14], who studied the effect of potassium persulfate dosage in the range of 0.1 - 1.5 $mmol \cdot g^{-1}$ VSS on the sludge *CST* time, and pointed out that the effect was better at 1.2 $mmol \cdot g^{-1}$ VSS. Regrettably, the significant decrease interval (0.1 - 0.9 mmol/gVSS) had not been explored in depth by Zhen *et al.*, which would be an appreciable effect on the economics and practicality of advanced $SO_4^{-}\cdot$ oxidation technology. This section made a careful plans based on the determined optimal dosing ratio n(Fe^{2+}):n(SPS) = 0.8:1 to further evaluate the reaction system, and effect of activated persulfate dosage on the dewatering performance of sludge was compared with the research results of literature [12]. For this reason, this paper selected 0 - 220 $mg \cdot g^{-1}$ DS in experiment, and introduced the sludge dewatering time (*Tc*) as a consideration index.

It could be seen from **Figure 3** that with the addition of the $Fe^{2+}/S_2O_8^{2-}$ system, the sludge *CST* decreased rapidly from 73 s·L/g SS to less than 25 s·L/g SS and then tended to slope gently. *Wc* dropped to 65% when the amount was 161.8 $mg \cdot g^{-1}$ DS. *CST* had been reduced to within 86 s when the dosage is 80.9 $mg \cdot g^{-1}$ DS, and the lowest was 82 s (161.8 $mg \cdot g^{-1}$ DS), which indicated that the sludge conditioning level represented by this dosage had been completely matched in the later physical dehydration process. Continuous increase addition of persulfate would not increase the dehydration speed significantly. **Figure 3** showed that when the dosage of activated persulfate was 80 - 120 $mg \cdot g^{-1}$ DS, *Wc* dropped below 70% to reach a relatively ideal moisture content level, and the later change trend for *CST* and *Wc* value were basically in agreement, the declines were slowed down significantly. It was noteworthy that when the dosage of activated persulfate was more than 161.8 $mg \cdot g^{-1}$ DS, *Wc* would unexpectedly increase instead. These results suggested that when the dosage of activated persulfate increased to a certain extent, the destructive effect of the sludge flocs was enhanced. But there was a critical point, beyond this critical point, the particle size of the solid sludge was too small to compress and deform during the mechanical dehydration process which would have exactly the reverse effect.

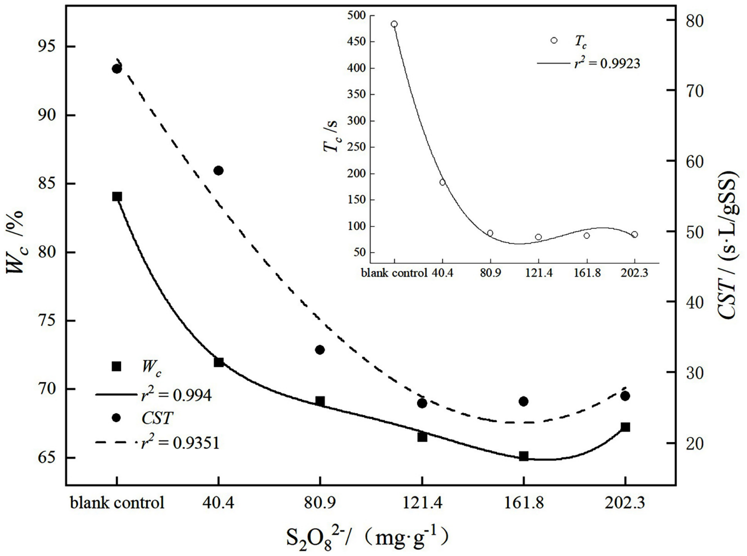


Figure 3. Effect of persulfate dosage on sludge dewatering performance.

According to the existing research conclusions, the conditioning level (water content < 70%) of the sludge under this dosing parameter was equivalent to the performance index of the sludge in the literature [18]. It was recommended that the sludge floc peroxidation should be fully considered in the process of technical application. In view of negative effects and comprehensive technical and economic effects, it was advisable to control the dosage of activated persulfate within 80 - 120 $mg \cdot g^{-1}$ DS.

3.3. The Effect of pH on Sludge Dewatering Performance

Prior studies had noted that Fenton-like oxidation technology had broader requirements for the acidity and alkalinity of the reaction environment than Fenton technology [19]. The scientific pH value of the reaction environment could play a key role in the chemical reaction and sludge dewatering effect. Based on the above-mentioned n(Fe^{2+}):n(SPS) and persulfate dosage parameters, this section paid more attention to the influence of the reaction pH on the sludge dewatering performance.

As Shown in **Figure 4**, the first and foremost, the influence of pH on *Wc* presented an arc-shaped bowl shape, which appeared the neutral point as the symmetry axis. *Wc* decreased with the increase of pH, and the lowest *Wc* was 70.9%. With the increase of the alkaline of the reaction, t *Wc* gradually increased, which showed the chemical pretreatment was completely invalid. This outcome was contrary to the literature [8] and that [18], the positive correlation between water content and pH under the conditions of HSO_5^- reagent (HSO_5^- concentration 0.9 mmol/gVSS, n(Fe^{2+})/n(HSO_5^-) = 0.9) was given [8], and the literature [18] kept behind (CaO: 70 $mg \cdot g^{-1}$ DS, Fe^{2+}: 50 $mg \cdot g^{-1}$ DS; H_2O_2: 30 $mg \cdot g^{-1}$ DS). This section obtained the relatively best cost-effective n(Fe^{2+}):n(SPS) and dosage and other parameters which were especially suitable for neutral reaction environment without pH adjustment. Thus indicated more significant superiority to further

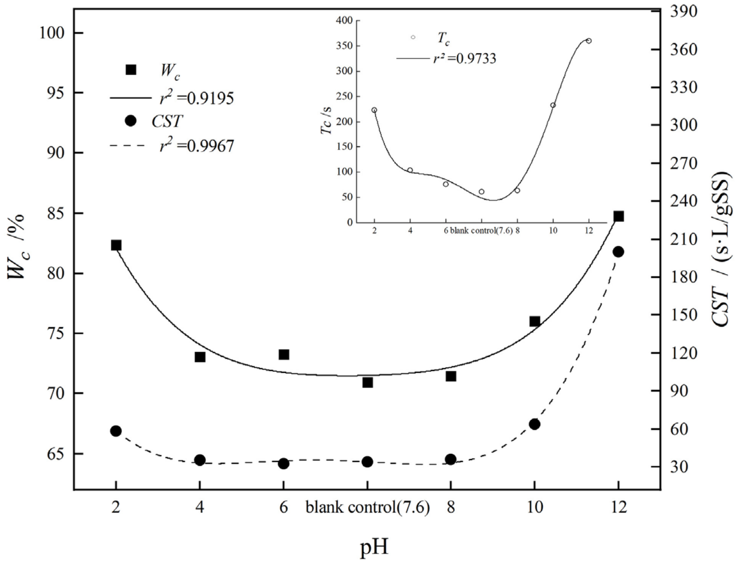


Figure 4. Effect of pH on sludge dewatering performance.

simplify the complexity and cost of the sludge pretreatment process. There is one more point, there was a significant difference between the change rule of *CST* and *Wc*. Under acidic and neutral conditions, *CST* value remained relative stable, with a fluctuation range of less than 6%, when pH exceeded 8, *CST* value gradually increased to 205 s·L/g SS (pH = 8), and the sludge dewatering rate dropped rapidly. It could be inferred that: 1) the oxidation performance of $SO_4^{-}\cdot$ radicals were weakened in a strong acid reaction environment (pH = 2 - 4), and *Tc* and *Wc* were relatively higher; 2) the process parameters we recommended were especially suitable for a neutral reaction environment (pH = 6 - 8), the sludge treatment effect was the most ideal, *CST* value and *Wc* reduction rates are 53.5% and 16.5% respectively. A possible explanation for those might be the introduction of race amounts of OH·system where OH· and $SO_4^{-}\cdot$ existed simultaneously. The combination of the two could trigger a more violent oxidation reaction and destroy the extracellular polymer of sludge. This phenomenon had also been preliminary showing by Liang, Su *et al.* [20]; 3) the process parameters we recommended were not suitable for alkaline reaction environment (pH = 10 - 12). The strong alkaline reaction environment would significantly inhibit the activity of Fe^{2+}, which was related to the rapid precipitation of Fe^{2+} ions at higher pH. It also deflected the excitation of free radicals, reduced the cracking effect on the extracellular polymer of the sludge, and weakened the flocculation effect of the sludge itself, so the sludge had a poor dewatering effect and high water content. *Wc*, *CST* and *Tc* could not give us the desired value.

In fact, the pH value of the sludge produced by municipal sewage treatment plants was usually between 6.5 and 8, which was almost close to a neutral reaction environment and very consistent with the process parameters recommended by this research. The conclusion of this paper was beneficial to reduce the unit sludge treatment cost and reduce excess anions and cations. It was of significance to practical guiding significance for effective reducing of the cost and complexity of leachate treatment. However, in some special industries, such as electroplating, mining, etc., the sludge produced by the treatment was particular acidic, and a small amount of alkaline substance was essential to be appropriately adjust the pH value of the sludge reaction environment. These would be helpful to reduce the moisture content of the dehydrated filter cake and reduce the time for sludge dehydration, ensuring the satisfactory effect of sludge regulation.

3.4. The Effect of CaO Addition Amount on Sludge Dewatering Performance

The addition of skeleton constructs (quicklime, fly ash, phosphogypsum, etc.) could effectively solve the problem of high compressibility of activated persulfate oxidation conditioning sludge. Compared with other physical conditioning agents, the amount of CaO was considered to be carried out at minimal cost, which effectively reduced the specific resistance of sludge and the moisture content of sludge [10] [21]. Coupled with quicklime in the $Fe^{2+}/S_2O_8^{2-}$ oxidation system, as a dual conditioning method, the dewatering channel of sludge could be more unobstructed which was beneficial to promote sludge dewatering speed, and the moisture content of the sludge cake was expected to drop below 60% to meet the future of China's municipal sludge deep dewater Key needs. In this section, a detailed study on the amount of CaO added was studied to effectively alleviate the increase in mud cake caused by the addition of the skeleton construct.

As shown in **Figure 5**: 1) when the CaO addition amount was in the small dose range (0 - 100 $mg \cdot g^{-1}$ DS), with the CaO addition amount gradually increasing, the sludge dehydration time decreased rapidly, the dehydration velocity increases rapidly, and the time required for dehydration changes from 105 s (0 $mg \cdot g^{-1}$ DS) to 78 s (100 $mg \cdot g^{-1}$ DS), and the dehydration velocity increased by nearly 26%; 2) when CaO addition was at the conventional research dose (100 - 400 $mg \cdot g^{-1}$ DS), with the increase of CaO addition, the decreasing trend of sludge dewatering time and dehydrated cake moisture content were obviously weakened, the minimum dehydration time was 40s and the most desirable Wc was 55.34% (400 $mg \cdot g^{-1}$ DS); 3) When the amount of CaO exceeded 400 $mg \cdot g^{-1}$ DS, Tc increases slightly, and Wc was no longer significantly decreasing; 4) the change trends of CST and Wc corresponding to Tc were similar. In the early stage, the two indexes decreased rapidly with the increase of CaO addition. When the amount of CaO added exceeded 200 $mg \cdot g^{-1}$ DS, the CST value basically fluctuated around 38 s, the minimum was 36s (300 $mg \cdot g^{-1}$ DS), and the reduction of conditioning effect was no longer remarkable. These showed that, on the one hand, calcium ions in quicklime could be combined with negative charged groups in extracellular polymers to increase the strength of sludge flocs, which was beneficial to the removal of bound water during post-treatment. On the other hand, the inorganic components in the quicklime could be used as the skeleton of the sludge, reducing the compressibility of the sludge, greatly shortening the dewatering time of the sludge, and improving the dewatering efficiency of the sludge.

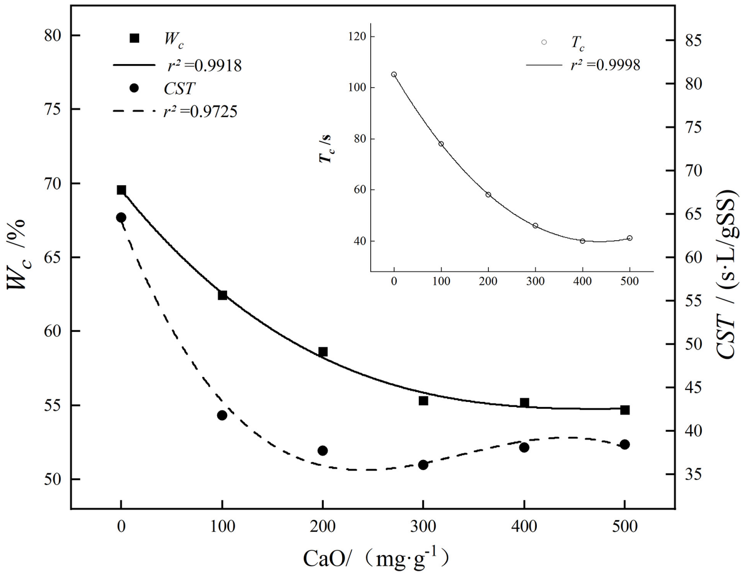


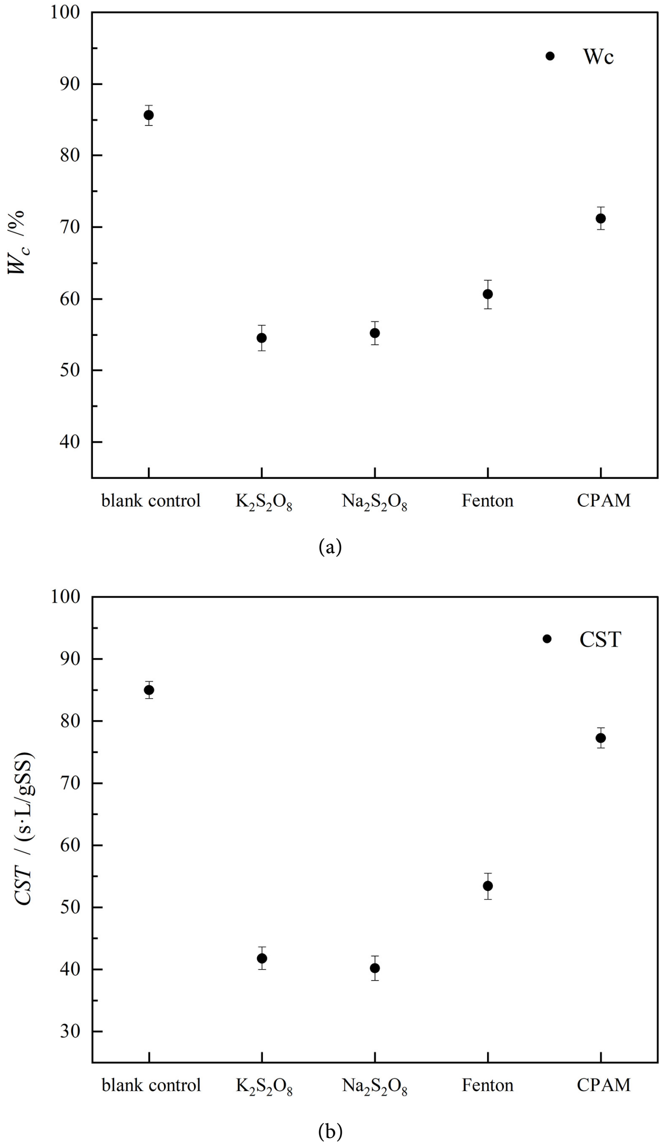
Figure 5. Effect of Cao dosage on sludge dewatering performance.

Considering the above research conclusions, combined the growth of sludge weight caused by the addition of skeleton constructs, it was recommended that the most suitable for practical application of the scale for CaO and activated persulfate was less than 200 mg·g^{-1} DS. For the acidic sludge, the amount of quicklime added could be increased as appropriate. On the one hand, the pH value of the sludge liquid could be effectively adjusted to a neutral point, which was conducive to floc destruction and recombination. On the other hand, the addition of quicklime could also greatly shorten the sludge dewatering time, but it was recommended to no more than 400 mg·g^{-1} DS.

3.5. Comprehensive Comparative Analysis with Typical Sludge Conditioning Methods

Based on the current research of sludge conditioning, a set of data of the typical $Fe^{2+}/S_2O_8^{2-}$ composite CaO conditioning method, Fenton oxidation method and CPAM conditioning method were summarized and analyzed. Among them, the Fenton oxidation method quoted from Liu Peng *et al.* [22], and the CPAM conditioning method quoted from Liu Lirong *et al.* [23]. The reaction conditions were shown in **Table 1**.

After different conditioning reactions, *CST* and *Wc* were measured. It could be seen from **Figure 6**, the $Fe^{2+}/S_2O_8^{2-}$ composite CaO conditioning method had obvious advantages over the Fenton oxidation method and the CPAM conditioning method, especially in the *CST* value and moisture content index. The Fenton oxidation method had relatively stringent requirements for the pH of the reaction (pH = 3 - 4). Compared with the $Fe^{2+}/S_2O_8^{2-}$ + CaO compound conditioning process, Fenton oxidation had a limited application prospects due to the potential safety hazards of storage and transportation caused by the usage of hydrogen peroxide and the corrosion of acid filtrate [24]. The commonly CPAM method improved the sedimentation performance and dewatering performance of the sludge, but still had problems such as larger dosage, higher cost and secondary pollution [18]. Clearly, it was impossible to add a pure coagulant to meet the key needs of China's municipal sludge deep dewatering in the future.



(a)

(b)

Figure 6. Dewatering effect of three conditioning methods. (a) Water content of dehydrated cake; (b) Capillary water absorption time.

Table 1. Partial sludge conditioning reaction parameters.

Conditioning method	pH	Add amount	Reaction time	references
Fenton	4	Fe^{2+} 0.9 g/L; H_2O_2: 5.0 g/L	30 min	[22]
CPAM method	7.6	70 mg/L	5 min	[23]
$Fe^{2+}/S_2O_8^{2-}$ composite CaO	7.6	Fe^{2+} 18.9 mg/gDS; $S_2O_8^{2-}$ 81 mg/gDS; CaO 200 mg/g	20 min	This article

Table 2 showed the typical research results of different advanced oxidation technologies for sludge conditioning. It could be summarized: 1) in the categories of reaction type, activated persulfate was better than Fenton oxidation method for deep dewatering of sludge. The *CST* reduction rate was highest, and it had the advantages of high efficiency and simple operation, would have more research potential and application prospects; 2) in the reaction conditions, the conditions determined by this research were milder, suitable for most of the original conditions of municipal sludge, and could effectively reduce the cost of reagents and the input of excess ions, and reduce the filtrate treatment pressure; 3) in the following influence, the time required for the dehydration in this research was significantly reduced and the moisture content was distinctive more pleasurable .

3.6. Analysis and Comparison of Filtrate

The $Fe^{2+}/S_2O_8^{2-}$ composite CaO sludge conditioning method could destroy the sludge floc structure and reduce the organic matter content in the dewatered sludge. The STOC index detection could effectively reflect the solubility of total organic carbon in filtrate and the degree damage for sludge EPS. So the filtrate after $Fe^{2+}/S_2O_8^{2-}$ composite CaO conditioning was subjected to STOC detection and partial anion and cation analysis. The test results were shown in **Figure 7**.

From **Figure 7**, the STOC of the filtrate from the blank control group and CPAM method were nearly identical (105 mg/L), and the filtrate STOC content of $Fe^{2+}/S_2O_8^{2-}$ composite CaO sludge conditioning method (sodium persulfate and potassium persulfate seemed similar) was surprisingly 580.5 mg/L, the Fenton filtrate STOC content was 305 mg/L, the activated persulfate compound CaO conditioning method significantly improved the total organic carbon concentration in the sludge filtrate and he degree damage for sludge EPS. After measurement, the content of iron ions in the sludge dewatering filtrate was 1.9 mg/L (equivalent to 0.095 mg/gDS), and the iron loss rate was 0.5%, which was better than the lowest value of 0.6% in the literature [18], 99.5% iron stayed in the filter cake. These shows that: 1) the activated persulfate compound CaO conditioning method had a strong destructive effect on the extracellular polymer in the sludge, dissolving a large amount of organic matter, and the efficiency of EPS cracking was greatly higher; 2) Fenton oxidation method could crack the sludge EPS by oxidation as well but the weaker effect indicated that the application of this oxidation system to sludge conditioning still needed further improvement; 3) the higher STOC value indicated the higher total organic carbon concentration in the filtrate, which further proved that the activated persulfate compound CaO conditioning method synergistically improved dewatering performance of the sludge; 4) in view of the better inherent effect of the filtrate itself [29] [30], it was recommended that the filtrate should be returned to the sludge thickening tank to give full use of the chemical effects of the residual cell breaker and activator to improve the sewage treatment economical, and reduce the operating cost of sewage treatment plants.

Table 2. Comparison of advanced oxidation parameters.

Conditioning method	Medicine ratio	Initial *CST*	Reaction *pH*	*CST reduction rate*	*Wc*	references
$Fe^{2+}/S_2O_8^{2-}$ + CaO + fly ash	$S_2O_8^{2-}$: 320 mg/gDS, CaO: 400 mg/g, fly ash: 500 mg/g, n(Fe^{2+}):n(SPS) = 1.5	/	6.89	/	54.9%	[12]
$Fe^{2+}/S_2O_8^{2-}$	Fe^{2+}: 1.5 mmol/gVSS, $S_2O_8^{2-}$: 1.2 mmol/gVSS, n(Fe^{2+}):n(SPS) = 1.25	210 s	6.95	88%	/	[14]
$Fe^{2+}/S_2O_8^{2-}$	Fe^{2+}: 23.52 mg/gDS, $S_2O_8^{2-}$: 80 mg/gDS, n(Fe^{2+}):n(SPS) = 1	47.2 s	6.5 - 7.5	60%	78.51% (Room temperature)	[16]
Heat activated $S_2O_8^{2-}$ + Biological activated carbon	$S_2O_8^{2-}$: 120 mg/gVSS, Biochar: 150 mg/gVSS	1 (Standardized unit)	No adjustment	−5.03 (Standardized unit)	42.6% (70˚C)	[25]
UV + Fenton	H_2O_2: 4 g/L, Fe^{2+}: 0.6 g/L		~3		76.36%	[26]
Fenton	H_2O_2: 3g/L, Fe^{2+}: 0.3 g/L H_2O_2/Fe^{2+} = 8 - 12:1	53.9 - 72.8 s	~3	67.8%	72%	[27]
$Fe^{2+}/S_2O_8^{2-}$	Fe^0: 15 g/L, $S_2O_8^{2-}$: 4 g/L	/	~7	50.2%	/	[28]
$Fe^{2+}/S_2O_8^{2-}$ + CaO	Fe^{2+}: 18.9 mg/gDS, $S_2O_8^{2-}$: 81 mg/gDS, CaO: 200 mg/g, n(Fe^{2+}):n(SPS) = 0.8	73 s	~7	53.5%	53.7%	This article

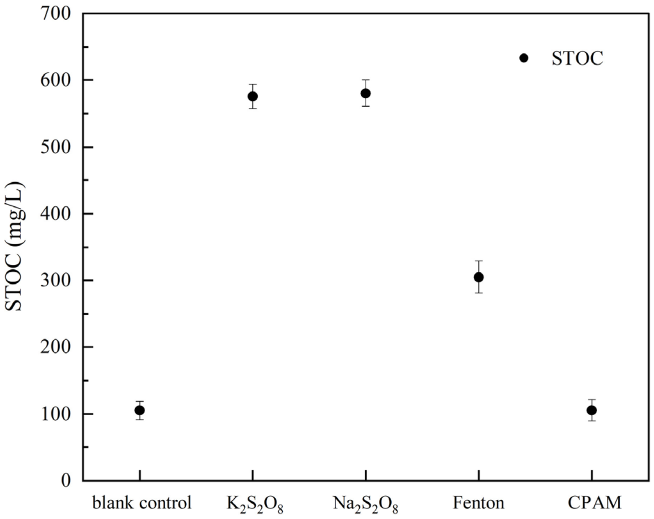


Figure 7. STOC content in filtrate of several sludge conditioning methods.

4. Conclusions

The $Fe^{2+}/S_2O_8^{2-}$ composite CaO method conditioned neutral thickened sludge under these parameters ($S_2O_8^{2-}$: 80 - 120 mg·g^{-1} DS, n(Fe^{2+}):n(SPS) = 0.8:1, CaO: 200 mg·g^{-1} DS), achieved the same performance (CST reduction rate was about 47%), the Fe^{2+} dosage per ton of sludge could be reduced by 20%, the iron loss rate in the filtrate was 0.5%, and the suction filtration dehydration time was less than 50 s, the moisture content of the dehydrated cake was satisfying 53.7%.

The $Fe^{2+}/S_2O_8^{2-}$ composite CaO conditioning method avoided the strict requirements of the Fenton method for the acidity and alkalinity of the reaction environment, decreased the danger and corrosion problems caused by hydrogen peroxide. Simultaneously, $Fe^{2+}/S_2O_8^{2-}$ composite CaO conditioning method reduced the large dose, high cost and secondary pollution effects of the CPAM method. Compared with similar persulfate activation methods, these results had obvious advantages in terms of chemical dosage, CST value, water content of dehydrated cake, EPS cracking rate and iron loss rate, which could more likely meet the needs of future Chinese cities ($Wc < 60\%$).

Although the conditioning method adopted in this experiment has a good effect on sludge dehydration, the selection of skeleton construction body needs to be discussed in the future, and more environmentally friendly skeleton materials, such as biomass, need to be developed to enhance the recycling performance of sludge.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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