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Research Article

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Effect of zero-valent iron activated sodium hypochlorite on sludge dewatering performance

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Abstract: Zero-valent iron (ZVI) activated sodium hypochlorite (NaClO) was used to condition sludge to improve sludge dewatering, and the mechanism of its effect on sludge cracking and dewatering performance was systematically investigated. The dewatering performance of sludge was measured by detecting capillary suction time (CST) and sludge specific resistance (SRF). The evolution patterns of substances such as ammonia nitrogen (NH_4-N), chemical oxygen demand (COD), soluble phosphorus (SRP), extracellular polymeric substances (EPS) (including soluble EPS (S-EPS), loosely bound EPS (LB-EPS), and tightly bound EPS (LB-EPS)), the study quantitatively and qualitatively analysed the migration patterns of organic substances within and outside sludge cells, clarifying the intrinsic connection between sludge disintegration and dewatering performance. The results showed that under the optimal treatment conditions (pH=3+Fe powder 75mg/gDS+ NaClO100mg/gDS) the CST of ZVI-NaClO treated sludge decreased from 192.7 s to 51.3 s; the SRF decreased from 2.05×10^9 S^2/g to 1.35×10^9 S^2/g; and NH_4-N in the supernatant increased from 4.14 mg/L to 8.64 mg/L; DP increased from 0.47 ug/mL to 1.12 ug/mL; and

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COD increased from 960.5 mg/L to 2323.8 mg/L. Additionally, the synergistic effect of acidified ZVI-NaClO can oxidise and degrade organic matter in sludge, reducing glutamic acid and humic acid components in the three types of EPS in sludge. Therefore, the acidified ZVI-NaClO system can disrupt the structure of sludge flocs and efficiently degrade extracellular polymers (EPS), significantly improving sludge dewatering efficiency and providing a physical-chemical foundation for subsequent sludge reduction and resource utilization.

Keywords: sludge dewatering, zero-valent iron, sodium hypochlorite, extracellular polymeric substances (EPS), free radical oxidation

1. Introduction

As the global economy continues to grow and urbanise, the scale of construction and degree of treatment of urban and rural wastewater treatment plants are expanding and increasing[1]. This has led to a significant increase in sludge production as well[2]. Sludge contains various potentially toxic substances such as heavy metals, pathogens, and organic pollutants[3]. If not properly treated, it may cause secondary pollution to the environment and even pose a threat to human health[4]. Therefore, there is a need to urgently adopt economic and effective measures for sludge, not only to achieve the reduction and resourceful disposal of sludge, but also to reasonably degrade a large number of sludge pollutants, to ensure the harmless integration of sludge into the ecosystem[5]. Sludge flocs

40 are composed of microbial aggregates and extracellular polymers (EPS)[6]. And EPS is
41 considered to be of considerable importance in the removal of pollutants from wastewater,
42 bioflocculation, and sedimentation[7]. Due to its gel-like network structure, excessive EPS
43 content can make the sludge highly hydrophilic, which is not sufficient to break down the
44 structure of EPS and convert the bound water into free water using conventional methods,
45 resulting in extreme deterioration of the dewatering effect[8].

46 Currently, widely used technologies for sludge pre-treatment are microwave pre-
47 treatment[9], ultrasonication and acidification[10], and advanced oxidation process (AOP)[11].
48 Among these methods advanced oxidation process (AOP) is considered an effective
49 strategy for efficient sludge reduction and subsequent disposal[5]. For example, activated
50 sludge pretreatment using Eletro-Fenton was found to produce highly reactive
51 homogeneous hydroxyl radicals, which contribute to the rapid release of free water from
52 sludge flocs and improve sludge dewatering performance[12]. AOP hydrothermal treatment
53 based on sulfate radicals was found to accelerate the destruction of microbial cells, protein
54 hydrolysis, and mineralisation processes and improve sludge dewatering performance by
55 detecting EPS and TOC[7]. Dewatering of streptomycin mycelial residue (SMR) was tested
56 by Fenton conditioning and found that SMR can disrupt floc/mycelial cells to release
57 intracellularly bound water and construct hydrophobic channels in the floc to facilitate
58 further water removal[13].

59 Hypochlorite is a potent oxidant capable of generating a wide range of reactive
60 species that produce highly efficient free radicals with significant oxidising properties

61 (ClO^-, Cl^-, and Cl^{2-})[14]. In water treatment, sodium hypochlorite is widely used as a
62 disinfectant and bleaching agent to treat organic pollutants[15]. And Fe^{2+} can catalyse
63 sodium hypochlorite, causing it to generate HClO in aqueous solution[16]. And since the O-
64 Cl bond is easily broken at room temperature, the release of the extremely oxidising ClO
65 may lead to the production of oxygen radicals (-OH) (see Eq. 2), which is conducive to the
66 cracking of the EPS structure[17]. ClO^- is a major factor in the treatment and decomposition
67 of organic pollutants by hypochlorite, which contributes to the resource recovery of sludge
68 dewatering and disposal[15]. The Fe^{3+} generated (see Eq. 2) also has a flocculating effect on
69 sludge[17-19]. However, excess hypochlorite increases the alkalinity of the system,
70 contributing to an increase in the concentration of HClO and OH^-, which in turn destroys
71 the EPS structure and reduces the dewatering efficiency[20].

$$ClO^- + H_2O \rightarrow HClO + OH^- \quad (1.)$$

$$HClO + Fe^{2+} \rightarrow Fe^{3+} + -OH + Cl^- \quad (2)$$

72 Studies have shown that the Fe^{2+}/NaClO process is more economical than the Fenton
73 process for wastewater treatment, and NaClO is a suitable alternative to H_2O_2 in large-scale
74 wastewater treatment plants[21]. Fe^{2+}/NaClO can degrade sludge macromolecular organic
75 matter efficiently while maintaining stable dewatering efficiency[16]. Therefore, the
76 advanced oxidation technology based on activated NaClO has a very good application
77 prospect. In this paper, we mainly investigated the sludge conditioning strategy based on
78 the generation of Fe^{2+} from zero-valent iron (ZVI) catalyzing the generation of activated
79 radicals from NaClO under acidic conditions, and regulated the amount of Fe^{2+}generation

and NaClO dosage, and explored the main organic substances inside and outside the sludge cell by analysing the capillary suction time (CST), the specific resistance of sludge (SRF), the migration of organic substances in the EPS, and the zeta potential of sludge under under different conditions (such as pH and NaClO).

2. Experiments and Test Methods

2.1 Source of raw sludge

The sludge samples used in the experiment were collected from the return sludge system from the second tank to the anaerobic tank of a municipal wastewater treatment plant in Wuhan City, which mainly treats the domestic wastewater. The samples were filtered through a 30-mesh standard sieve to remove coarse particles and impurities, and then the upper layer of the clear liquid was poured off after 2 h of sedimentation under laboratory conditions, and finally stored in a refrigerated environment at a constant temperature of 4° C to maintain microbial activity. The basic properties of sludge are shown in Table 1:

Table 1 sludge properties

Water content	pH	Suspended solids (SS)/(g • L^{-1})	Volatile suspended solids (VSS)/(g • L^{-1})
97.3%~98.0%	7.2~7.6	25~29	16~ 23

2.2 Experiment and Test Method

200 ml of sludge with a moisture content of about 97% was taken into a 500 ml flask, and the pH, the dosage of NaClO and Fe powder were controlled by the single-variable

98 method, respectively (HCl was added to adjust the pH to 2, 3, 4 etc, and the pH was
99 adjusted one pH at a time); NaClO dosage ranged from 50 mg/gDS to 150 mg/gDS, with an
100 incremental increase of 50 mg/gDS; and the dosage of Fe powder was 0 mg/gDS to 100
101 mg/gDS, with an incremental increase of 25 mg/gDS. The mixture was stirred at a speed of
102 200 rpm, and samples were taken at intervals of 15 minutes, 30 minutes, and 60 minutes for
103 sludge CST testing. The optimal conditions were determined based on the CST results,
104 including the optimal pH, iron powder dosage, NaClO dosage, and optimal treatment time.
105 Under the optimal experimental parameters, seven groups of tests were set up as
106 shown in table 2.. Firstly, CST, SRF, particle size, viscosity, and zeta potential were
107 detected at the optimum time (30 min). Then, 50 mL sludge was taken and centrifuged at
108 4000 r/min to extract extracellular polymers (EPS), including soluble EPS (S-EPS), loosely
109 bound EPS (LB-EPS), and tightly bound EPS (TB-EPS) by the thermal extraction
110 method[ ]. The sludge supernatant was subsequently assayed for detecting ammonia
111 nitrogen (NH_4-N), COD, and dissolved phosphorus (SP) contents by standard methods.
112 Protein (PN) and polysaccharide (PS) contents of the EPS was measured by the rapid
113 Lowry kit method and the sulfuric acid-anthraquinone method, respectively. The changes in
114 fluorescent analogues were also analysed by 3D-EEM detection.
115 **Table 2 Experimental parameter settings**

Group	Iron powder (mg/gDS)	NaClO (mg/gDS)	PH
1	0	0	Initial value

2	75	0	Initial value
3	0	0	3
4	75	0	3
5	75	100	3
6	0	100	Initial value
7	75	100	Initial value

116

117 **2.3 Other measure methods**

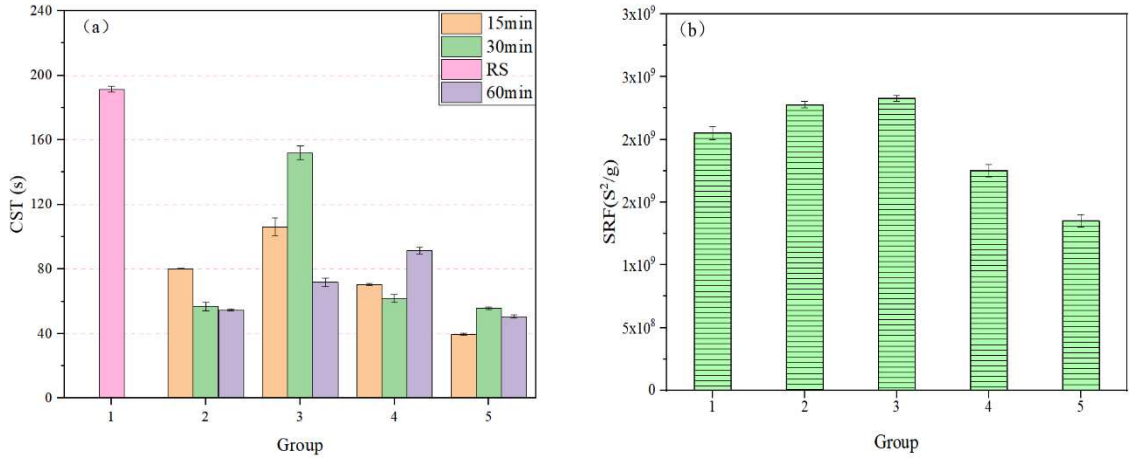
118 The main reagents include reduced iron powder, standard substance of hydrochloric
119 acid titration solution, and sodium hypochlorite solution (all of the above are analytically
120 pure). The main equipment includes a CST tester (Tritonel304M, UK), a UV-visible
121 spectrophotometer (UV-6100S, Shanghai Kunke Instrument Co., Ltd.), The changes in
122 fluorescent analogues were also analysed by 3D-EEM detection three-dimensional
123 fluorescence excitation-emission spectrometer (3D-EEM, FL7000, Japan).Zeta potential
124 was confirmed by a Nanoparticle Size and Zeta Potential Analyzer (Zetasizer Nano ZS90,
125 Malvern, UK). Active group was characterized by Electron Paramagnetic Resonance
126 Spectrometer (ESR, JEOL FA-200). The size of sludge particles were determined using a
127 laser particle size analyzer (BT-9300H, Bettersize China)

3. Results and Discussion

3.1 Analysis of sludge dewatering performance

The variation of CST and SRF of conditioned sludge under different conditions is shown in Fig.1. The CST and SRF of the raw sludge were 192.7 s and 2.05×10^9 S^2/g. In the group of iron powder only, the CST decreased to 54.3 s, a reduction of 71.8%, and the SRF increased to 2.28×10^9 S^2/g. For the group of pH=3, the CST increased slightly and then decreased, which increased to 149.2 s at 30 min; At the same time, SRF increased to 2.33×10^9 S^2/g. It was shown that acidification of sewage sludge below pH 5.49 increased with the degree of sludge dewatering, but the dewatering efficiency was extremely low[22, 23]. The CST and SRF are extremely high due to the presence of large amounts of EPS[24]. In the group dosed with Fe powder at pH=3, the CST first decreased and then increased, falling to a minimum of 63.6 s at 30 min, with a decrease of 67%, and a decrease of 51.7%, while it increased to 93 s at 60 min; the SRF decreased to 1.75×10^9 S^2/g, a decrease of only 15%. In the group dosed with iron powder and NaClO at pH=3, the CST decreased sharply to 51.3 s after 60 min of reaction, with a decrease of up to 73.7%; the SRF decreased significantly to 1.35×10^9 S^2/g, with a maximum decrease of 34%. Research has found that the use of sodium hypochlorite alone can cause a decrease in sludge dewatering performance and a significant increase in capillary suction time (CST) [25]. This may be because the unactivated sodium hypochlorite only oxidises the cell interior without destroying the EPS layer, and the sludge dewatering performance deteriorates, which is

148 similar to the study [26]. However, when Fe powder is added alone, under neutral conditions,
149 the oxidation rate of ZVI is slow, and insufficient free radicals are released, making it
150 ineffective in breaking down EPS and improving sludge dewatering. Studies have shown
151 that under acidic conditions, the formation of Fe^{2+} from ZVI is accelerated, and Fe^{2+} reacts
152 with sodium hypochlorite solution through a Fenton-like reaction to generate hydroxyl
153 radicals and chlorine radicals[27]. It can effectively destroy the EPS structure, trigger the
154 cracking of sludge flocs and cell lysis, and promote the release of bound water into free
155 water and transfer to the liquid phase, thus improving the efficiency of dewatering[28]. It
156 indicates that sodium hypochlorite activated by acidified ZVI has significantly improved
157 the performance of sludge dewatering.ZVI continuously provides Fe^{2+}, NaClO acts as an
158 oxidant, and both of them form an oxidation-reduction cycle under acidic conditions to
159 achieve efficient cracking of EPS.



160 **Fig.1 Sludge dewatering under different treatment conditions: (a) CST; (b) SRF**

161 **3.2 Migration of substances in the sludge supernatant**

162 The concentration variation of ammonia and nitrogen content in the supernatant of

different sludge samples is shown in Fig. 2(a). The NH_4-N content in the raw sludge was 4.15 mg/L. For the iron powder alone group, iron powder would promote the hydrolysis of sludge protein[29]. For the pH=3 group, the NH_4-N concentration in the supernatant was the highest, reaching 9.68 mg/L. This may be due to the acidic environment damaging the cell membranes of granular sludge, causing them to disintegrate, with intracellular proteins and nucleic acids rapidly hydrolysing into amino acids and nucleotides, and deamidating to form NH_4-N in the acidic environment. Continuing to add iron powder to sludge at pH=3 will increase pH, resulting in a shift in ammonia form to NH_3 and volatilisation losses, resulting in a decrease in ammonia content[30]. For the sodium hypochlorite alone group, the NH_4-N content decreased compared to the original mud. For the group with sodium hypochlorite and iron powder, it can be seen that the increase of ammonia-nitrogen content in the supernatant was not significant and only reached 4.23 mg/L. At pH=3, the NH_4-N content in the supernatant of the group with iron powder and NaClO reached 8.64 mg/L, which was significantly higher than that in the original mud. It suggests that ZVI activates NaClO under acidic conditions to generate $\cdot OH$, which degrades organic matter in the supernatant, especially protein-like substances, and thus releases a large amount of ammonia nitrogen[31]. The remaining iron ions may form precipitates that adsorb part of the ammonia nitrogen, resulting in lower ammonia nitrogen content compared to sludge alone under acidic conditions.

The concentration variation of COD content in the supernatant of different sludge samples is shown in Fig. 2(b). The COD content in the original sludge was 960.5 mg/L. For

184 the Fe powder alone and pH=3 groups, the COD in the sludge was reduced due to the
185 reduction and coagulation of Fe powder to remove part of the organic matter and the
186 coagulation and precipitation of part of the organic matter due to the charge neutralisation
187 under strong acidic conditions; when the two were mixed, the COD in the sludge was
188 reduced only slightly due to the reduction/coagulation[29]. For the NaClO group alone, the
189 COD content reached 1648.8 mg/L. Some studies have shown that when NaClO interacts
190 with sludge, the generated ·OH oxidises part of the organic matter in the sludge
191 supernatant, destroying the sludge structure and increasing the organic matter in the sludge
192 supernatant, resulting in an increase of COD in the sludge[25]. For the group at pH=3, with
193 the addition of iron powder and NaClO, the COD content in the supernatant was the
194 highest, reaching 2323.8 mg/L. It indicates that the Fe^{2+}generated by this system intensified
195 the generation of • OH to a certain extent, which mineralised the soluble organic matter
196 and reduced the hindrance of hydrophilic substances to the dewatering, which contributed
197 to the increase of COD[32].

198 The concentration variation of dissolved phosphorus content in the supernatant of
199 different sludge samples is shown in Fig. 2(c). The content in the original sludge was 0.47
200 ug/mL and the content of dissolved phosphorus in the 2~ 7 groups was 0.57 ug/mL, 1.93
201 ug/mL, 2.08 ug/mL, 1.12 ug/mL, 1.12 ug/mL, and 2.26 ug/mL, respectively. Similarly, it
202 can be seen that the activation of the NaClO group by Fe powder was more effective in
203 acidic conditions, releasing the phosphorus-containing material from it and oxidising it.
204 Controlling PH=3, the experimental group with or without iron powder, the dissolved

phosphorus increased to about two times of the original sludge, mainly because the solid inorganic phosphorus can be dissolved under acidic conditions, and the group with NaClO and iron powder at the same time, the increase in solubility was lower, primarily because NaClO can react with divalent iron to form trivalent iron under acidic conditions, causing the soluble phosphorus generated by the dissolution and oxidation of organic matter to re-precipitate; In the group where NaClO and iron powder were added, NaClO can oxidise part of the phosphorus-containing organic matter to release soluble phosphorus.

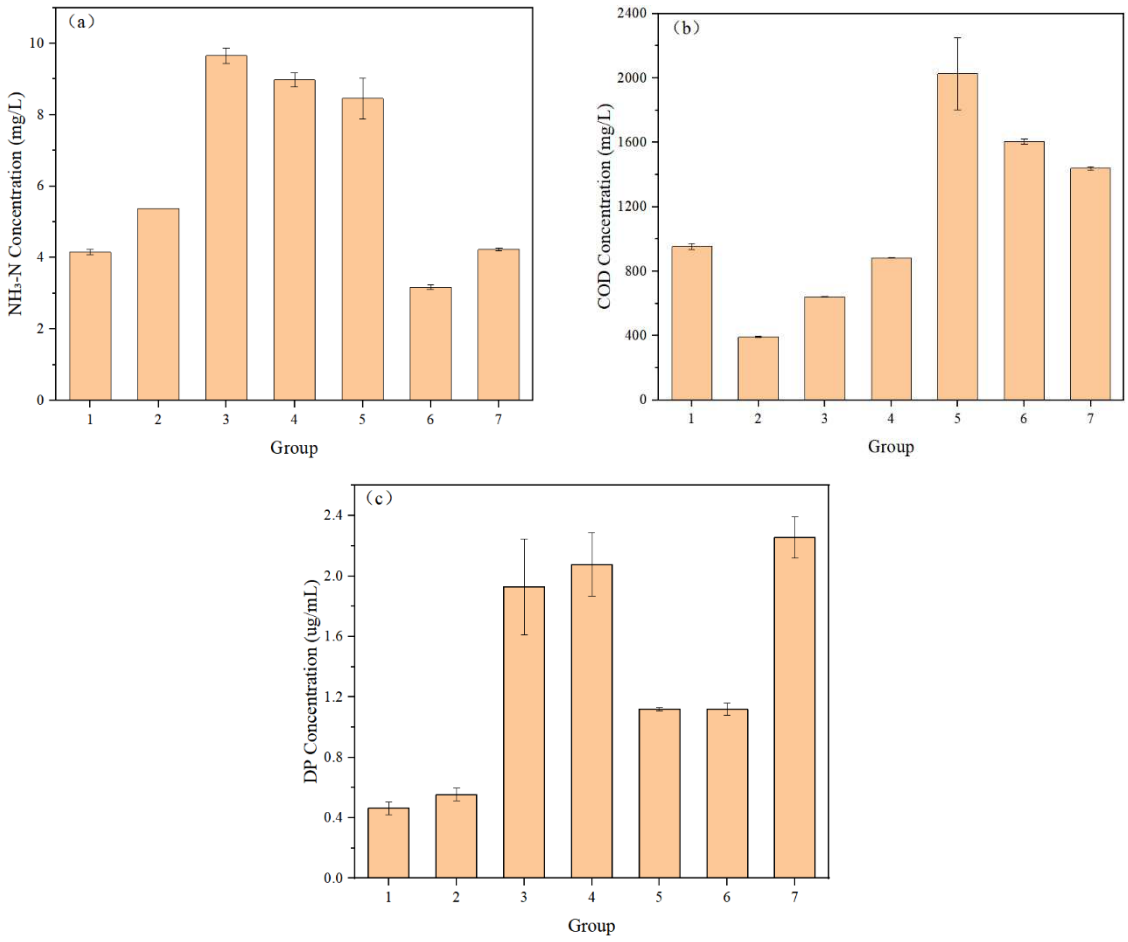


Fig. 2 Changes of ammonia nitrogen (a), COD (b), and dissolved phosphorus (c) in the supernatant.

3.3 Migration analysis of substances in sludge EPS

EPS is mainly a polymer complex composed of proteins and polysaccharides, which plays an important role in microbial adhesion and structural integrity of sludge[28]. The variation of PN and PS content in sludge EPS is shown in Fig. 3. The contents of PN and PS in TB-EPS of raw sludge were 547.0 mg/L and 57.3 mg/L, which were much higher than those in S-EPS of 94.0 mg/L and 12.8 mg/L. For the group of sodium hypochlorite alone, the S-EPS and LB-EPS were substantially higher compared to the raw sludge. Hypochlorite generates hypochlorous acid by a hydrolysis reaction with a large number of reactive radicals (i.e., OH^-, Cl^-, and ClO^-), which decompose the sludge flocs[26]. However, probably due to the limited oxidative capacity of the unactivated NaClO, it is difficult to mineralise the organic matter completely, but instead, small molecule water-soluble intermediates were generated, which led to an increase in the concentration of soluble organic matter in the S-EPS and LB-EPS. And under the condition of pH=3, the polysaccharides in TB-EPS were significantly reduced to 11.99 mg/L, which was 79% less, while the LB-EPS was significantly increased to 35.54 mg/L. The main reason may be that the acidification-induced led to the lysis of microbial cells in the sludge, which increased the content of the outer layer of EPS (including the mucus EPS and the LB-EPS) and the deflocculation of sludge flocs. Therefore, the efficiency of sludge dewatering after acidification is low[22]. For the group with iron powder and sodium hypochlorite, although it cracked the EPS, the content of S-EPS and LB-EPS increased dramatically, probably due to the generation of complexes that encapsulated the proteins and polysaccharides and

prevented them from being oxidised. It has been reported that acidic pH values are more conducive to enhancing the catalytic effect of Fe^{2+} on sodium hypochlorite for sludge dewatering[33]. Therefore, under acidic conditions, the protein in TB-EPS of sludge conditioned by the zero-valent Fe-activated NaClO system decreased to 387 mg/L, which was 29.3% lower relative to the original sludge, and the polysaccharide decreased to 30.14 mg/L, which was 45.6% lower relative to the original sludge. The decrease of TB-EPS and the increase of S-EPS could effectively improve the performance of sludge dewatering[34]. It was shown that the reduction of PN concentration in EPS could significantly improve the dewatering performance of residual sludge, while PS had little effect on the dewaterability[35]. It is noteworthy that the synergistic effect of ZVI-NaClO under acidic conditions resulted in the greatest reduction of PN. Therefore, this system can effectively improve the performance of sludge dewatering.

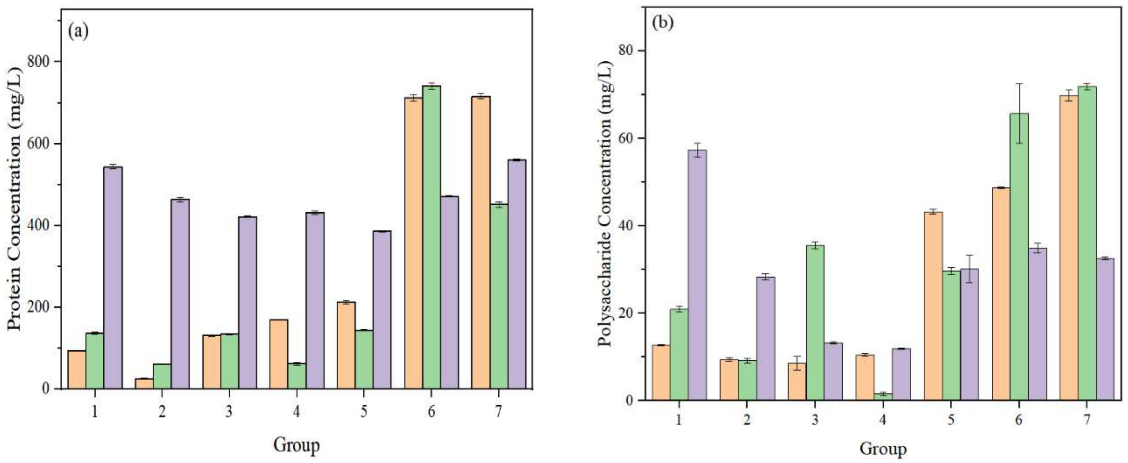


Fig. 3 Variation of protein and polysaccharide contents in EPS: (a) protein; (b) polysaccharide

3.4 Analysis of sludge particle properties

The changes of sludge zeta potential under different NaClO and ZVI dosages are shown in Fig. 4. In the group where NaClO was added alone, the negative potential was significantly enhanced, reaching -23.1 mV, indicating that NaClO oxidised the original structure of the sludge, releasing more hydrophilic substances. When iron powder and NaClO were added together, the potential decreased further, reaching -32.5 mV. Generally, the lower the Zeta potential, the stronger the classical repulsive interaction, making it difficult for the sludge to aggregate [36]. When iron powder was added alone, the Zeta potential change was small, at -17.0 mV. At pH = 3, H^+ compresses the double layer, neutralising the negative charge, reducing the Zeta potential's negative charge to -5.6 mV. At pH = 3, when iron powder and NaClO were added, the Zeta potential's negative charge significantly weakened and approached neutrality, reaching -4.36 mV. This may be because iron powder generates Fe^{2+} under acidic conditions and catalyses the production of •OH radicals from NaClO, which oxidise the negatively charged groups in EPS, thereby disrupting the flocculent structure. Additionally, cations reduce the electrostatic repulsion of sludge flocculents, leading to charge neutralisation [37].

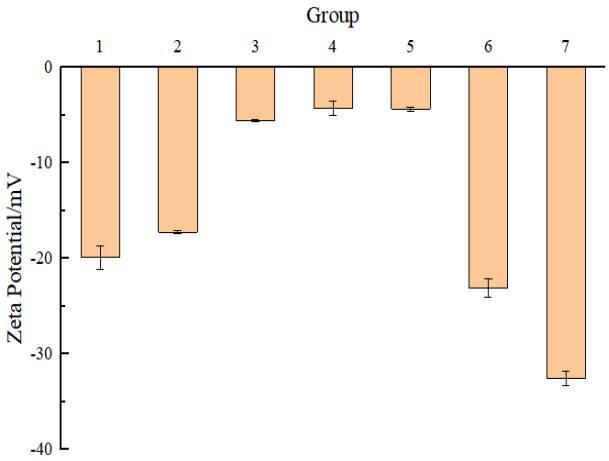


Fig. 4 Variation of zeta potential of sludge

The sludge particle sizes at different NaClO and ZVI dosages are shown in Fig. 5. The sludge particle sizes of all samples were in the range of 1~200 μm. In the pH=3 group and the group with iron powder at pH=3, the sludge particle sizes did not change significantly after treatment. Whereas, the particle size of sludge samples in the group with NaClO and iron powder significantly increased compared to the original sludge size, which may be due to the effect of electrical neutralisation and adsorption bridging, resulting in a significant increase in the floc size[38]. The changes of sludge D_{10}, D_{50}, and D_{90} can be seen in Table 2, where D_{10} of raw sludge was 9.18 μm, D_{50} was 31.15 μm, and D_{90} was 68.96 μm. The sludge after conditioning under the optimal conditions had a D_{10} of 8.73 μm, D_{50} of 29.67 μm, and D_{90} of 66.22 μm, and the average particle size of the sludge decreased in the sludge distribution curve to the left of the original sludge. This may be due to the generation of free radicals (• OH) oxidising the hydrophilic components (e.g. proteins, polysaccharides) in the extracellular polymers (EPS), destroying the floc skeleton structure, and its degradation leading to loss of floc support and release of small particles from the larger

floc, resulting in a reduction of sludge particle size[39].

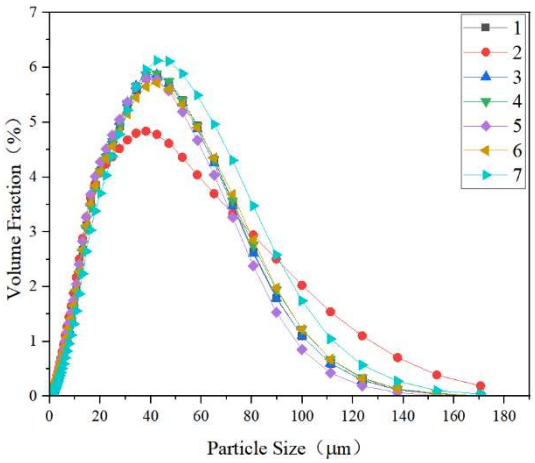


Fig. 5 Particle size distribution of sludge

Table 3 D_{10}, D_{50} and D_{90} of the sludge

Groups	D_{10}/μm	D_{50}/μm	D_{90}/μm
1	9.18	31.15	68.96
2	8.07	29.88	81.07
3	9.33	31.07	68.79
4	9.57	31.70	70.20
5	8.73	29.67	66.22
6	9.08	31.11	70.41
7	11.11	35.27	76.20

3.5 3D-EEM analysis

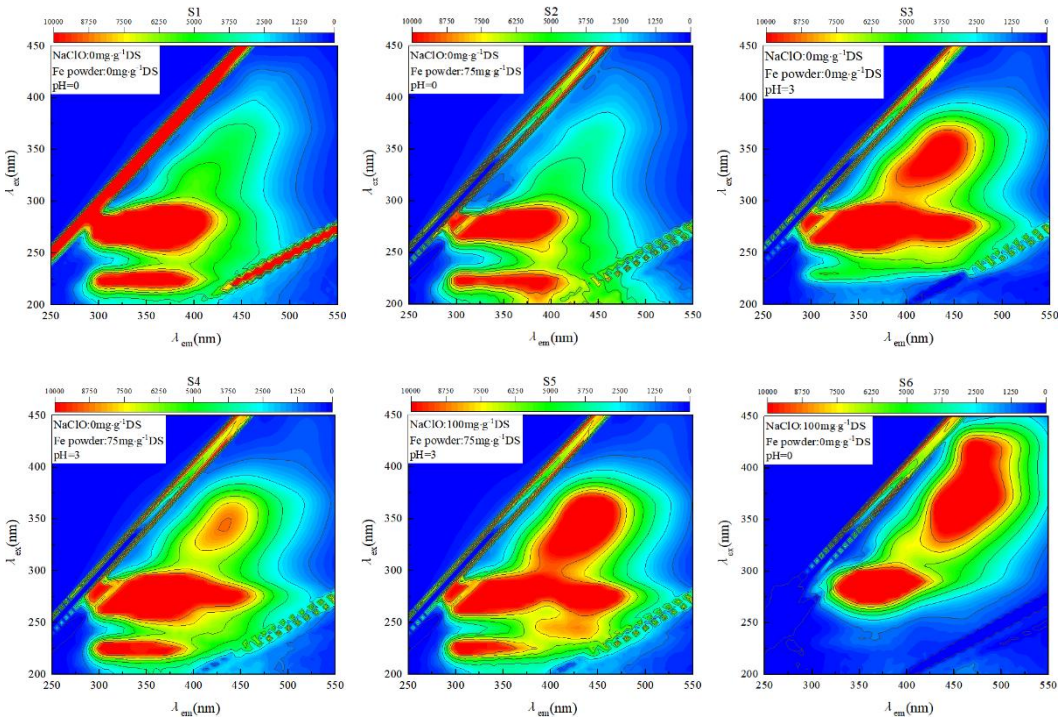
The changes of substances in the EPS of the above sludge samples were analysed by 3D-EEM maps. The fluorescent substances in the 3D-EEM analysis maps were divided into

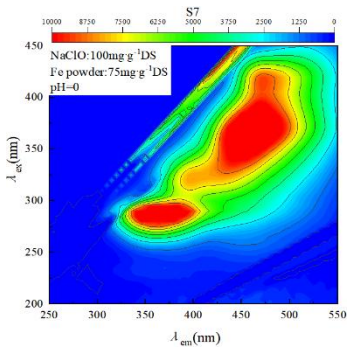
five regions, and the fluorescent substances represented by each region are shown in Table 3.

Table 4: 3D-EEM fluorescence region substance table

Region	Ex/Em (mm)	Fluorescent substance
A	200-250/300-330	Tyrosine
B	200-250/330-380	Tryptophan
C	200-250/380-500	Glutamic acid
D	250-400/300-380	Soluble microbial by-products
E	250-400/380-500	Humic acid-like

The 3D-EEM profiles of S-EPS with different NaClO and ZVI dosages are shown in Fig. 6.

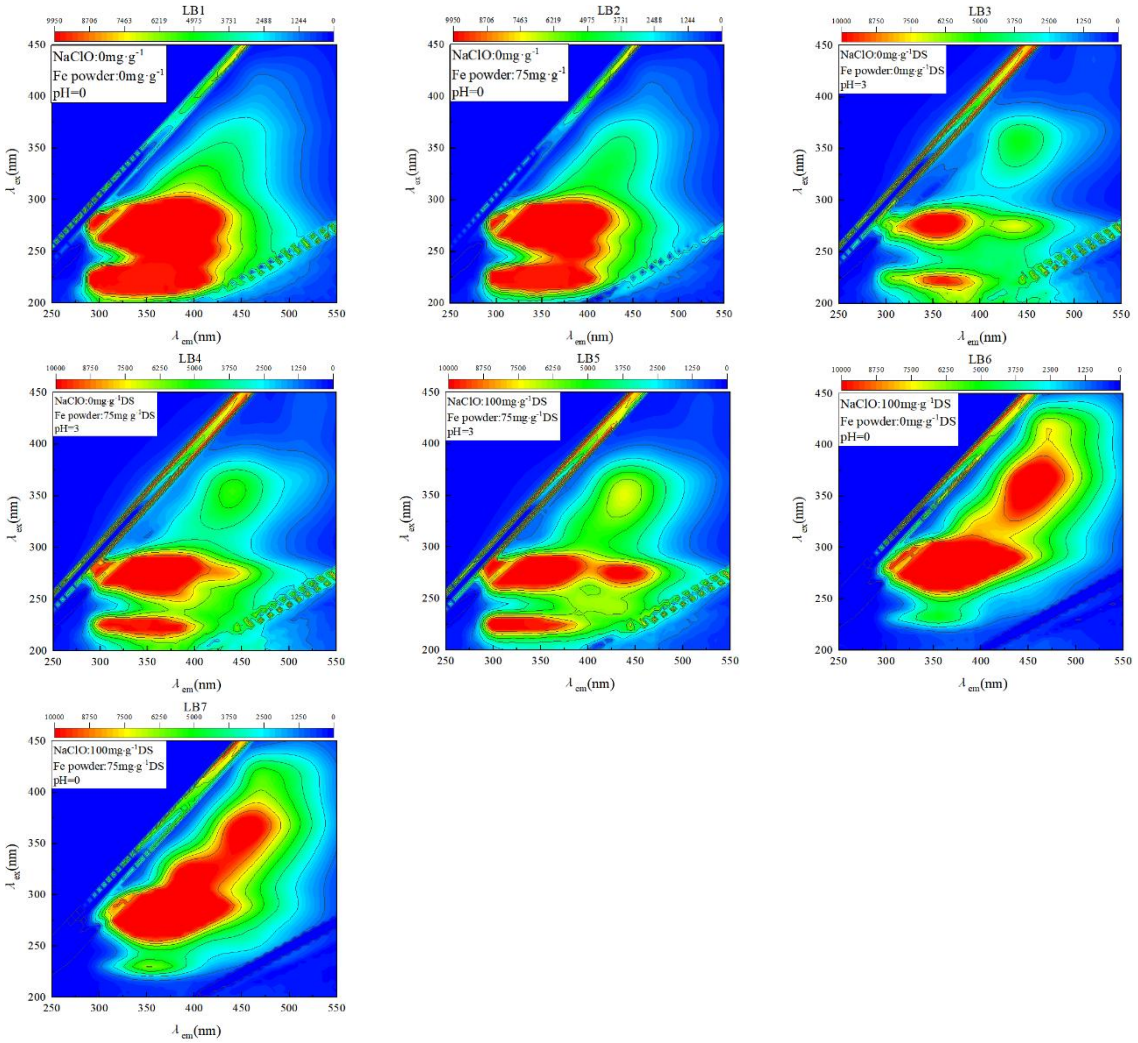




293 **Fig. 6 Three-dimensional fluorescence profiles of S-EPS under different treatments**

294 The main peaks of soluble microbial by-products and tryptophan in the supernatant
295 of raw mud are more obvious and more abundant, while tyrosines, humic acids, and
296 glutamates are less abundant. In the group of iron powder alone, it can be seen that the
297 content is consistent with that in the original mud. In the group of pH=3, it can be seen that
298 tyrosines and tryptophan-like substances are weakened, and humic acid-like substances are
299 enhanced. The fluorescence peaks of humic acids in the supernatant of the iron powder
300 group at pH=3 were not obvious. In the group with sodium hypochlorite and the group with
301 sodium hypochlorite and iron powder, the trend of substance change was basically the
302 same; tryptophan and tyrosine substances obviously showed a decreasing trend, humic acid
303 substances obviously increased, and soluble microbial by-products also showed a
304 decreasing trend compared with the original mud. In the sludge treated with iron powder
305 and sodium hypochlorite at pH=3, humic acids increased significantly in S-EPS, and
306 glutamates and tryptophan decreased significantly.

307 The 3D-EEM patterns of LB-EPS under different NaClO and ZVI dosages are shown
308 in Fig. 7.



309 **Fig. 7 3D fluorescence spectra of LB-EPS under different treatments**

310 Soluble microbial by-products and tryptophan-like proteins were more abundant in
311 the raw mud LB-EPS, while tyrosine, glutamate, and humic acid-like substances were less
312 abundant in comparison. The content of all substances increased when iron powder was
313 added alone. Humic acid-like substances, glutamic acid-like substances, and tyrosine-like
314 substances decreased significantly when acid was added alone. The changes in the group
315 with sodium hypochlorite and the group with sodium hypochlorite and iron powder were
316 more or less the same. Tyrosines, tryptophan, and glutamates were significantly decreased,
317 while humic acids were significantly increased. At pH=3, the sludge treated with iron

powder and sodium hypochlorite group showed a significant decrease in glutamates and an increase in humic acids in the LB-EPS compared to the original sludge.

The 3D-EEM patterns of TB-EPS under different NaClO and ZVI dosages are shown in Fig. 8.

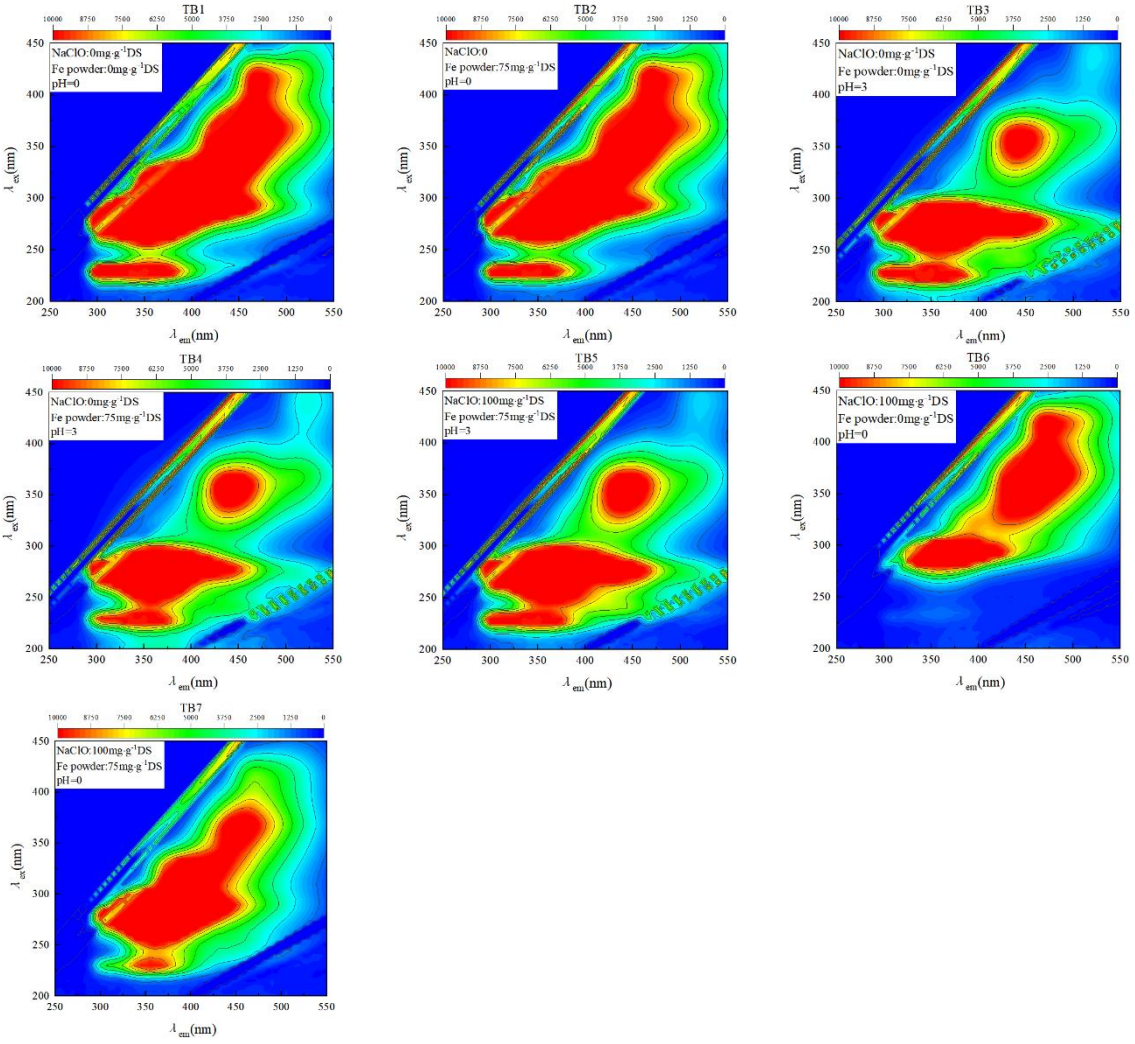


Figure 8: 3D fluorescence spectra of TB-EPS under different treatments.

Soluble microbial by-products, humic acids, tyrosines, and tryptophan were present in the raw mud TB-EPS. The content of iron powder alone was basically the same as that in the original mud, and the changes in the pH=3 group, the group with iron powder at pH=3 and the group with iron powder and sodium hypochlorite at pH=3 were the same, and the content

of humic acids was significantly reduced compared with that in the original mud. The tyrosine and tryptophan contents were significantly reduced in the group with sodium hypochlorite and the group with iron powder and sodium hypochlorite.

The EPS of different layers extracted from the sludge samples was analysed, and it was found that the ZVI-NaClO system could reduce the glutamates and humic acids in the sludge EPS after treatment of the sludge. It is also consistent with the shortest CST as well as changes in polysaccharide and protein content. Adequate decomposition of the TB-EPS matrix is essential for the removal of bound water held in the EPS. [22]confirmed that acidified ZVI-activated sodium hypochlorite degraded hydrophilic organics by generating free radicals (hydroxyl radicals and chlorine radicals) pathway. Through oxidative degradation, the macromolecules in the extracellular polymers were not only decomposed into soluble components released into the supernatant, but also may be further converted into small-molecule products with no fluorescence properties. This process significantly reduced the water-holding capacity of EPS and weakened its binding effect with water molecules, thus promoting the mud-water separation efficiency and effectively enhancing the sludge dewatering performance.

3. 6 Mechanistic analysis of acid/ZVI-activated NaClO conditioning system

The ESR profile of ZVI-activated NaClO under acidic conditions is shown in Fig. 9. The characteristic peaks of 1:2:2:1 indicate the DMPO-OH complexes[40]. The results show that hydroxyl radicals are generated through equations (Eqs. 1, 2), and the free radicals

generated after activation destroy the sludge structure[17]. Because a large amount of organic matter was released into the outer layer, some fine particles were also formed, which accompanied the destruction of sludge floc, the degradation of EPS, and the oxidative treatment released bound water and became free water[26]. In summary, sodium hypochlorite activated by acidified ZVI enhanced the sludge dewatering performance.

$$ClO^- + H_2O \rightarrow HClO + OH^- \quad (3)$$

$$HClO + Fe^{2+} \rightarrow Fe^{3+} + \text{-}OH + Cl^- \quad (4)$$

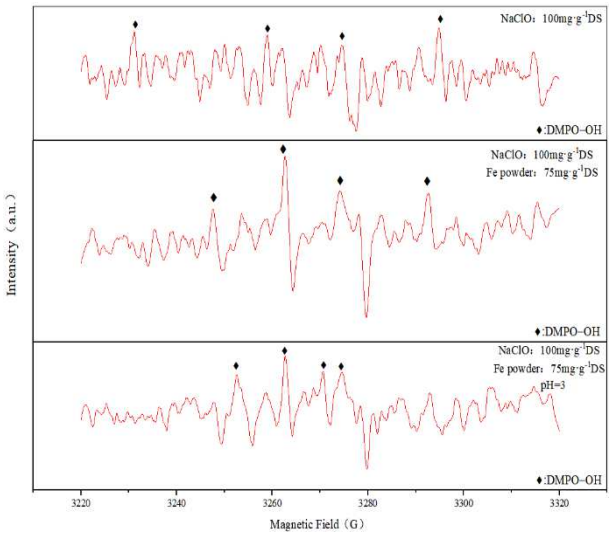


Fig. 9 ESR profiles under different treatments

4. Conclusions

In this paper, we explored the relationship between sludge cracking and organic matter migration and transformation and dewatering performance in the ZVI-NaClO conditioning system, revealed the mechanism of conditioning action, determined the optimal experimental conditions, detected and analysed the content of each component in the EPS, the sludge filtration time, etc. and obtained the following conclusions:

(1) The action of the acidified ZVI-NaClO system significantly improved the sludge dewatering performance. At pH=3, Fe^0 dosing of 75 mg/gDS and NaClO dosing of 100 mg/gDS, the sludge CST significantly decreased from 192.7 s in the original sludge to 51.3 s.

(2) In the acidified ZVI-NaClO group, both protein and polysaccharide levels in the supernatant increased. Protein levels rose from 94.0 mg/L in the original sludge to 209.0 mg/L, while polysaccharide levels increased from 12.8 mg/L to 43.3 mg/L.

(3) The ZVI-NaClO system can oxidise and degrade organic matter in sludge, reducing glutamic acid and humic acid compounds in the sludge.

Declarations

Ethical Approval

Not applicable. This study does not involve human or animal subjects, and thus no ethical approval is required.

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Availability of data and materials

The datasets used and/or analysed during the current study available from the corresponding author on reasonable request.

References

[1] MEYER T, BARQUIN A, GIONEST P, et al. Multivariate data analysis of full-scale sludge dewatering [J]. Journal of Environmental Chemical Engineering, 2020, 8(2): 103648.

[2] GUO J Y, GAO Q F, CHEN Y H, et al. Insight into sludge dewatering by advanced oxidation using persulfate as oxidant and Fe2+as activator: Performance, mechanism and extracellular polymers and heavy metals behaviors [J]. Journal of Environmental Management, 2021, 288: 112476.

[3] RAO B Q, WANG G Q, XU P. Recent advances in sludge dewatering and drying technology [J]. Drying Technology, 2022, 40(15): 3049-3063.

[4] WANG Y H, LI H, FANG W H, et al. Persistence evaluation of fecal pollution indicators in dewatered sludge and dewatering filtrate of municipal sewage sludge: The impacts of ambient temperature and conditioning treatments [J]. Water Research, 2025, 268: 122641.

[5] LIN W, LIU X, DING A, et al. Advanced oxidation processes (AOPs)-based sludge conditioning for enhanced sludge dewatering and micropollutants removal: A critical review [J]. Journal of Water Process Engineering, 2022, 45: 102468.

[6] WONG J W C, MURUGESAN K, SELVAM A, et al. Dewatering of saline sewage sludge using iron-oxidizing bacteria: Effect of substrate concentration [J].

Bioresource Technology, 2016, 213: 31-38.

[7] YU Y, LI P P, ZHU B X, et al. The application of sulfate radical-based advanced oxidation processes in hydrothermal treatment of activated sludge at different stages: A comparative study [J]. Environmental Science and Pollution Research, 2022, 29(39): 59456-59465.

[8] AI J, WANG Z Y, DIONYSIOU D D, et al. Understanding synergistic mechanisms of ferrous iron activated sulfite oxidation and organic polymer flocculation for enhancing wastewater sludge dewaterability [J]. Water Research, 2021, 189: 116652.

[9] LIU J B, WEI Y S, LI K, et al. Microwave-acid pretreatment: A potential process for sludge dewaterability [J]. Water Research, 2016, 90: 225-234.

[10] CAI M Q, HU J Q, WELLS G, et al. Understanding Mechanisms of Synergy between Acidification and Ultrasound Treatments for Activated Sludge Dewatering: From Bench to Pilot-Scale Investigation (vol 52, pg 4313, 2018) [J]. Environmental Science & Technology, 2018, 52(10): 6077-6077.

[11] DAI Y K, HUANG S S, LIANG J L, et al. Role of organic compounds from different EPS fractions and their effect on sludge dewaterability by combining anaerobically mesophilic digestion pre-treatment and Fenton's reagent/lime [J]. Chemical Engineering Journal, 2017, 321: 123-138.

[12] CHEN Y S, CHEN H P, LI J, et al. Rapid and efficient activated sludge treatment by electro-Fenton oxidation [J]. Water Research, 2019, 152: 181-190.

[13] XU L L, ZHOU X X, DU J X, et al. The dewatering performance and mechanism of streptomycin mycelial residue based on Fenton oxidation [J]. Process Safety and Environmental Protection, 2025, 195: 106784.

[14] GUO S D, WU Y H, WANG Z Y, et al. Effect of electrolytic zero-valent iron activated sodium hypochlorite on sludge dewatering performance [J]. Water Science and Technology, 2024, 89(4): 989-1002.

[15] CHENG X S, WANG S N, HUANG W X, et al. Current status of hypochlorite technology on the wastewater treatment and sludge disposal: Performance, principals and prospects [J]. Science of the Total Environment, 2022, 803: 150085.

[16] YANG P, LI D D, ZHANG W J, et al. Study of sludge conditioning using organic acids chelated ferrous ion catalyzed NaClO oxidation: Evolution of extracellular polymeric substances and floc structure [J]. Journal of Environmental Management, 2021, 280: 111757.

[17] GUO X Z, CHEN S J, LIU Z Z, et al. Catalytic oxidation of methylene blue by using Ni-Fe bimetallic catalyst/NaClO system: Performance, kinetics, mechanism, and DFT calculations [J]. Separation and Purification Technology, 2023, 306: 122612.

[18] XIAO K K, SEOW W Y, CHEN Y, et al. Effects of thermal-Fe (II) activated oxone treatment on sludge dewaterability [J]. Chemical Engineering Journal, 2017, 322: 463-471.

[19] LIANG J L, HUANG J J, ZHANG L, et al. High-level waste activated

442 sludge dewaterability using Fenton-like process based on pretreated zero valent scrap
443 iron as an in-situ cycle iron donator [J]. Journal of Hazardous Materials, 2020, 391:
444 122219.
445 [20] LIANG J L, HUANG J J, ZHANG S W, et al. A highly efficient
446 conditioning process to improve sludge dewaterability by combining calcium
447 hypochlorite oxidation, ferric coagulant re-flocculation, and walnut shell skeleton
448 construction [J]. Chemical Engineering Journal, 2019, 361: 1462-1478.
449 [21] BEHIN J, AKBARI A, MAHMOUDI M, et al. Sodium hypochlorite as an
450 alternative to hydrogen peroxide in Fenton process for industrial scale [J]. Water
451 Research, 2017, 121: 120-128.
452 [22] LU Y, ZHENG G Y, WU W Z, et al. Significances of deflocculated sludge
453 flocs as well as extracellular polymeric substances in influencing the compression
454 dewatering of chemically acidified sludge [J]. Separation and Purification Technology,
455 2017, 176: 243-251.
456 [23] RAYNAUD M, VAXELAIRE J, OLIVIER J, et al. Compression
457 dewatering of municipal activated sludge: Effects of salt and pH [J]. Water Research,
458 2012, 46(14): 4448-4456.
459 [24] CHEN Z, ZHANG W J, WANG D S, et al. Enhancement of activated sludge
460 dewatering performance by combined composite enzymatic lysis and chemical re-
461 flocculation with inorganic coagulants: Kinetics of enzymatic reaction and re-
462 flocculation morphology [J]. Water Research, 2015, 83: 367-376.

[25] WEI H, TANG Y N, SHOEIB T, et al. Evaluating the effects of the preoxidation of H_2O_2, NaClO, and $KMnO_4$ and reflocculation on the dewaterability of sewage sludge [J]. Chemosphere, 2019, 234: 942-952.

[26] YU W B, WEN Q Q, YANG J K, et al. Unraveling oxidation behaviors for intracellular and extracellular from different oxidants (HOCl vs. H_2O_2) catalyzed by ferrous iron in waste activated sludge dewatering [J]. Water Research, 2019, 148: 60-69.

[27] TAO S Y, YANG J K, HOU H J, et al. Enhanced sludge dewatering via homogeneous and heterogeneous Fenton reactions initiated by Fe-rich biochar derived from sludge [J]. Chemical Engineering Journal, 2019, 372: 966-977.

[28] LI A M, HUANG C, FENG X, et al. Upgradation of sludge deep dewatering conditioners through persulfate activated by ferrous: Compatibility with sludge incineration, dewatering mechanism, ecological risks elimination and carbon emission performance [J]. Environmental Research, 2022, 211: 113024.

[29] AI L X, DENG F, HU X P, et al. Study on anaerobic digestion effect of waste iron scrapand reduced iron powder on residual sludge [J]. Industrial Water Treatment, 2019, 39(08): 69-73.

[30] YUAN J, CHEN Y, LI Q, et al. Impact of pH on Release of Nitrogen and Phosphorus from Excess Sludge [J]. CHINA WATER AND WASTE WATER, 2010, 26(01): 96-98.

[31] YAO X Z, WANG D S, DONG W Y, et al. Fenton oxidation conditioning

484 improves the dewatering performanceof residual sludge and its mechanism of action
485 [J]. CHINESE JOURNAL OF ENVIRONMENTAL ENGINEERING, 2025, 19(04):
486 805-814.
487 [32] GUO S D, YIN X, HUANG Y X, et al. Comparison of the effects of
488 electrolytic activation of sodium hypochlorite andsodium persulfate on sludge
489 dewatering [J]. Acta Scientiae Circumstantiae, 2024, 44(05): 112-119.
490 [33] ZHU X F, YANG Q, LI X M, et al. Enhanced dewaterability of waste
491 activated sludge with Fe(II)-activated hypochlorite treatment [J]. Environmental
492 Science and Pollution Research, 2018, 25(27): 27628-27638.
493 [34] CATALYSIS G K L E, POLLUTION CONTROL G K L O E C, HEALTH
494 RISK CONTROL S O E S, et al. Mechanism of zero valent iron and anaerobic
495 mesophilic digestion combined with hydrogen peroxide pretreatment to enhance
496 sludge dewaterability: Relationship between soluble EPS and rheological behavior
497 [J]. Chemosphere, 2020, 247: 125859.
498 [35] LIU J, YANG Q, WANG D B, et al. Enhanced dewaterability of waste
499 activated sludge by Fe(II)-activated peroxymonosulfate oxidation [J]. Bioresource
500 Technology, 2016, 206: 134-140.
501 [36] RAN B, LIU L Y, HUA C. Comprehensive investigation and mechanisms
502 of drilling waste sludge dewaterability by Fe(II)/persulfate pretreatment [J]. Journal
503 of Environmental Chemical Engineering, 2021, 9(6): 106751.
504 [37] LIANG J L, ZHANG L, YE M Y, et al. Evaluation of the dewaterability,

heavy metal toxicity and phytotoxicity of sewage sludge in different advanced oxidation processes [J]. Journal of Cleaner Production, 2020, 265: 121839.

[38] ZHANG W J, CHEN Z, CAO B D, et al. Improvement of wastewater sludge dewatering performance using titanium salt coagulants (TSCs) in combination with magnetic nano-particles: Significance of titanium speciation [J]. Water Research, 2017, 110: 102-111.

[39] ZHANG Y P, PEI J H, ZHENG S C, et al. Improving Dewaterability of Waste Activated Sludge by Combinationof Sludge Biochar Loaded Fe^{2+} Activated Persulfate and PAM [J]. Environmental Science and Technology, 2021, 44(12): 113-119.

[40] GAO C Q, YU W, ZHU Y C, et al. Preparation of porous silicate supported micro-nano zero-valent iron from copper slag and used as persulfate activator for removing organic contaminants [J]. Science of the Total Environment, 2021, 754: 142131.