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Improving sewage sludge dewaterability with rapid and cost-effective in-situ generation of Fe^{2+} combined with oxidants

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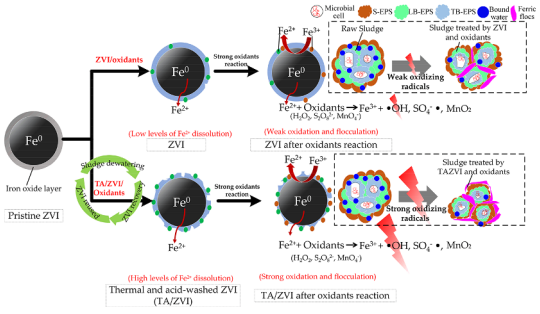
HIGHLIGHTS

- TA/ZVI/oxidants process is a feasible and inexpensive method for sludge dewatering.
- TA/ZVI/oxidants have greater promotion of sludge dewaterability than ZVI/oxidants.
- TA/ZVI/oxidants treatment significantly decreased EPS and bound water.
- Detailed surface structure of pristine and treated ZVI was shown and compared.
- Stable and highly-effective sludge dewaterability was seen after four cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Zero-valent iron (ZVI) combined with oxidants is a promising conditioning strategy for improving sewage sludge dewaterability. However, challenges, such as a low dewatering rate and utilization efficiencies of ZVI, restrict further application of ZVI/oxidant treatments. This study employs, for the first time, rapid and cost-effective in-situ generation of Fe^{2+} combined with common oxidants, namely H_2O_2, $Na_2S_2O_8$, and $KMnO_4$, to effectively improve sludge dewaterability. A comparative investigation of a standalone ZVI/oxidants treatment and when combined with a thermal and acid-wash (TA) pretreatment (TA/ZVI/oxidants) was systematically conducted to determine the sludge dewatering efficiency. Under the optimal operational conditions, the average water content of dewatered cake (Wc) was 18.47% less with the TA/ZVI/oxidants treatment when compared with the ZVI/oxidants treatment. The Wc values decreased to 54.81, 58.06, and 59.32 wt%, after the TA/ZVI/H_2O_2, TA/ZVI/$Na_2S_2O_8$, and TA/ZVI/$KMnO_4$ treatments, respectively. The potential mechanism by which the TA/ZVI/oxidants treatment enhanced dewatering was investigated by determining the characteristics of both the sludge and the ZVI surface structure. Results indicate that the TA/ZVI/oxidants process caused more Fe^{2+} dissolution, more strong oxidizing radicals and more strong flocculating Fe^{3+}. The large amount of strong oxidizing radicals and strong flocculating Fe^{3+} caused cell lysis and disrupted the protein-like and polysaccharide-like materials in the EPS, thereby decreasing the particle size, negative zeta potential, viscosity and colloidal forces, which then released the bound water trapped within the net-like floc and led to improved sludge dewaterability. In the ZVI

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reuse experiment, the TA/ZVI/oxidants treatment remained highly effective for sludge dewatering even after four cycles. Furthermore, economic analysis indicates that the TA/ZVI/H_2O_2 treatment can save approximately 52.32% per year compared with using the traditional polyacrylamide (PAM) treatment.

1. Introduction

With the increase of urbanization, the amount of sewage sludge produced by municipal wastewater treatment plants (WWTPs) is quickly increasing. Thus, sewage sludge production has become a global issue [1]. Sewage sludge with a high moisture content (> 97%) could cause serious environmental and human health problems due to the large amount of organic pollutants and toxic metals [2]. The surface of sludge is covered by a stable gel that makes it difficult to release the free water [3]. Sludge dewatering is a crucial step that decreases the burden of sludge transportation and disposal [4]. Therefore, developing a high-efficiency method to improve the solids content of sludge is urgent.

Further removing extracellular polymeric substances (EPS) [5] and bound water in sludge [6] is still a challenge of sludge dewatering. Various widely used sludge conditioning methods, including microwave treatment [7], ultrasonication and acidification [6], flocculation [8], and advanced oxidation processes (AOPs) [9–11], have been developed to enhance sludge dewaterability. Previous studies illustrate that disintegration of EPS and removal of bound water could efficiently accelerate the sludge dewaterability. Among these conditioning methods, AOPs are commonly used as an effective technology to improve the dewaterability and disintegration of sludge. In our previous studies, Fenton's reagent conditioning is a rapid, feasible and efficient technology to destroy sludge floc, decompose EPS and release bound water through the production of hydroxyl radicals (·OH) [9,12]. Sulfate radical (SO_4^{-}·)-based AOPs, such as Fe^{2+}/persulfate ($S_2O_8^{2-}$) [13–14] and thermal/Fe^{2+}/peroxymonosulfate (HSO_5^{-}) [10], are also effective methods to degrade EPS and improve sludge dewatering. However, the utilization of the Fenton's reagent and Fe^{2+} activated $S_2O_8^{2-}$ is generally limited due to the high operating cost [15], excessive consumption of radicals by Fe^{2+} [16], and large production of iron sludge [17]. To overcome these drawbacks, there is a need to develop a low cost, high efficiency, and eco-friendly technology for sludge dewatering.

Iron is one of the most abundant elements on earth. Compared to Fe^{2+}, zero-valent iron (ZVI) is a more green, inexpensive, stable, and nontoxic material that can be used as a heterogeneous catalyst [18]. Furthermore, ZVI has a greater advantage because it can be recycled by magnetic force [19]. Recently, the application of ZVI in sludge dewatering has been gaining more attention [11,20–22]. For example, Zhou et al. [20,21,23] reported that the capillary suction time (CST) of sludge was reduced by 50% when the sludge was treated by ZVI and oxidants (hydrogen peroxide (H_2O_2), $S_2O_8^{2-}$, and HSO_5^{-}). Li et al. [22] demonstrated that after a combined electrolysis/electrocoagulation and ZVI/$S_2O_8^{2-}$ (EZP) treatment, CST and specific resistance to filtration (SRF) decreased by 49.1% and 87.4%, respectively. Zhen et al. [11] also found that the percentage of removed water remained lower than 60.0% with the addition of ZVI/$S_2O_8^{2-}$. These studies indicate that ZVI/oxidants treatment has the potential to be an effective method for enhancing sludge dewaterability. However, some challenges still remain in the development of ZVI/oxidants treatment, such as improving the ZVI treatment efficiency at a low operational cost and further promoting the ZVI utilization efficiency. Pristine ZVI is covered with a thick passive layer on the surface, which prevents mass transfer and leads to a low treatment efficiency [18]. To further enhance its performance, pretreatment of ZVI is necessary and can include acid washing, thermal pretreatment, ultrasound-pretreatment, and pre-magnetization [24]. Acid washing or thermal pretreatment are considered as rapid, simple, inexpensive, and feasible strategies to remove the passive layer, thereby promoting the reaction efficiency [24]. Acid washing pretreatment can breakdown the passivating oxide layer of ZVI and increase its surface area [25]. Thermal pretreatment can overcome the high activation energy barrier and accelerate mass transport of ZVI [24]. Furthermore, combining the advantages of these two pretreatments may result better effects. Moreover, these ZVI pretreatments have not yet been applied to sludge dewatering. Therefore, a simple, rapid and inexpensive ZVI pretreatment, namely a thermal and acid-washed (TA) pretreatment, combined with an oxidants system, may be a potentially novel and feasible technique to improve sludge dewaterability.

Common oxidants, including H_2O_2, ClO^{-}, MnO_4^{-}, and $S_2O_8^{2-}$, have been coupled with ZVI for removing contaminants [21,26]. In this study, we propose a novel combined TA/ZVI/oxidants method to improve sludge dewatering. Three oxidants were tested, namely H_2O_2, sodium persulfate ($Na_2S_2O_8$) and potassium permanganate ($KMnO_4$). We also considered the impact of ZVI/oxidants on the sludge dewatering performance as a background. Hence, the objectives of this study were to (1) optimize ZVI pretreatment parameters (temperature and reaction time) for subsequent TA/ZVI/oxidants conditioning for sludge dewatering; (2) compare the dewatering efficiency of sludge under ZVI/oxidants and TA/ZVI/oxidants treatments; (3) elucidate the potential mechanisms for the significant enhancement of sludge dewaterability after TA/ZVI/oxidants treatment by exploring the sludge characteristics, including EPS, bound water content, rheological behavior, particle size, zeta potential and oxidation-reduction potential (ORP), and the ZVI surface structure characteristics via scanning electronic microscopy (SEM), Brunauer-Emmett-Teller (BET) analysis and X-ray powder diffraction (XRD); and (4) evaluate the reuse efficiency of ZVI during the TA/ZVI/oxidants process and assess its economic feasibility.

2. Materials and methods

2.1. Sewage sludge and reagents

Sewage sludge was obtained from a secondary sedimentation tank at a WWTP in Guangzhou, China. This WWTP treats 750,000 m^3/d of municipal wastewater by an anaerobic/anoxic/oxic (A/A/O) process. The sludge samples were settled by gravity for approximately 12 h to increase the sample concentration. The thickened samples were stored at 4 °C before use. All tests were completed within 3 days. The solids content of the thickened samples was 2.99 ± 0.03%. The other main sludge characteristics are presented in Table S1 (Supporting Information, (SI)).

All chemicals were of analytical reagent grade. All stock solutions were prepared with deionized water. The ZVI powder (400 mesh diameter) was purchased from Macklin Chemical Reagent Co., Ltd (Shanghai, China). The oxidants (H_2O_2, $Na_2S_2O_8$, and $KMnO_4$) were purchased from Aladdin Chemical Reagent Co., Ltd (Shanghai, China). Sulfuric acid (H_2SO_4) was purchased from Guangzhou Chemical Reagent Co., Ltd, China.

2.2. Experimental procedures

2.2.1. ZVI/oxidants

To determine the optimal operating parameters for sludge dewaterability, a series of single-factor experiments were conducted under different doses of ZVI and oxidants (H_2O_2, $Na_2S_2O_8$, and $KMnO_4$), and initial pH. The dose ranges for ZVI, H_2O_2, $Na_2S_2O_8$ and $KMnO_4$, as well as the pH range, were chosen based on the studies of Guo et al. [26] and Zhen et al. [11]. The single-factor experiments are outlined in Text S1 (SI). After conditioning, the sludge dewatering efficiency was assessed

Nomenclature

AOP	Advanced oxidation process
A/A/O	Anaerobic/anoxic/oxic
BET	Brunauer-Emmett-Teller
CST	Capillary suction time
DS	Dry solid
DSC	Differential scanning calorimetry
D50	Median value of particle size
$ZVI_d\%$	Dissolving rate of iron
EDS	Energy-dispersive spectrometer
EZP	Electrolysis/electrocoagulation and ZVI/$S_2O_8^{2-}$
EPS	Extracellular polymeric substances
FRI	Fluorescence regional integration
$FeCl_3$	Ferric chloride
·OH	Hydroxyl radical
H_2O_2	Hydrogen peroxide
k	Consistency index
LB-EPS	Loosely bound extracellular polymeric substances
n	Flow behavior index
RS	Raw sludge
SEM	Scanning electronic microscopy
$\dot{\gamma}$	Shear rate
H_2SO_4	Sulfuric acid
ORP	Oxidation-reduction potential
PAM	Polyacrylamide
$S_2O_8^{2-}$	Persulfate
HSO_5^-	Peroxymonosulfate
$KMnO_4$	Potassium permanganate
NaOH	Sodium hydroxide
$Na_2S_2O_8$	Sodium persulfate
SB-EPS	Soluble extracellular polymeric substances
SRF	Specific resistance of filtration
SO_4^-·	Sulfate radical
$SWR_{(t)}$	Net percentage sludge water removal at time
H_2SO_4	Sulfuric acid
τ	Shear stress
τ_y	Yield stress
TB-EPS	Tightly bound extracellular polymeric substances
TA	Thermal and acid-washed pretreatment
3D-EEM	Three-dimensional excitation-emission matrix
TOC	Total organic carbon
TSS	Total suspended solids
VSS	Volatile suspended solids
Wc	Water content of dewatered cake
WWTPs	Wastewater treatment plants
XRD	X-ray powder diffraction
ZVI	Zero-valent iron

by determining the water content of dewatered cakes (Wc) using a novel controllable pressure filter press [27]. The details of this filter press are presented in Fig. S1 (SI) and described by Dai et al. [9].

2.2.2. TA/ZVI/oxidants

To improve ZVI performance, ZVI powders were treated with a thermal and acid-washed pretreatment as follows. The ZVI powders were soaked in a 0.1 M H_2SO_4 solution at different temperatures (25, 30, 35, 40, 45, 50, and 55 °C) and reaction times (0, 5, 10, 15, 20, 25, and 30 min). The temperature range and reaction times were chosen based on the studies of Tyrovola et al. [28] and Fu et al. [29]. The mixtures were soaked in a DDHZ-300 thermostatic oscillator (Taicang, China) with a stirring speed of 150 rpm. After soaking, the ZVI powders were collected by filtration and washed three times with deoxygenated deionized water in an anaerobic chamber. The ZVI powders were then freeze-dried under vacuum at −60 °C for 24 h. The TA/ZVI powders were stored in a vacuum desiccator under anaerobic condition before use [24].

For sludge conditioning, 400 mL of sludge was poured to a 500 mL beaker. The initial pH of the samples was then adjusted to the optimal values using 1 M H_2SO_4 with stirring (1 min, 300 rpm). Different doses of TA/ZVI and oxidants were added to the beakers (10 min, 300 rpm). The conditioned sludge samples were pumped to the filter press to assess the dewatering performance by Wc.

2.2.3. Comparison of dewatering efficiency

Based on the results of the single-factor experiments, ZVI/oxidants and TA/ZVI/oxidants treatments were used to compare the sludge deep dewatering efficiency and to analyze the dewatering mechanism. Six types of conditioned sludge samples were investigated: ZVI/H_2O_2, ZVI/$Na_2S_2O_8$, ZVI/$KMnO_4$, TA/ZVI/H_2O_2, TA/ZVI/$Na_2S_2O_8$ and TA/ZVI/$KMnO_4$ (Table 1).

The conditioned sludge samples were analyzed for EPS, bound water, rheological behavior, particle size, zeta potential, ΔORP, and filtrate total organic carbon (TOC). Additionally, the surface structure characteristics of the ZVI samples were analyzed.

2.3. Analytical methods

Sludge dewatering efficiency. The sludge dewatering efficiency was assessed by measuring the net percentage of sludge water removed at time ($SWR_{(t)}$) and the Wc value [30]. The bound water content was measured using a Q2000 differential scanning calorimetry (DSC) analyzer (TA, USA) [31]. The detailed measurement methods of $SWR_{(t)}$ and bound water are outlined in Text S2 (SI) and Text S3 (SI), respectively.

EPS extraction and analysis. A modified heat extraction method was used to extract EPS from the sludge samples [32,33]. The EPS in the sludge was classified as three layers: soluble EPS (S-EPS), loosely bound EPS (LB-EPS), and tightly bound EPS (TB-EPS). The EPS extraction

Table 1
Different conditioning and dewatering procedures of sludge samples.

Sludge methods	Experimental procedures	
	Conditioning process	High pressure filtration process
ZVI/H_2O_2	H_2SO_4 (1 min, 300 rpm) → ZVI of 1.5 mM/g DS and H_2O_2 of 0.6 mM/g DS (10 min, 300 rpm)	Feeding (10 min, 1 MPa) → Compressing (20 min, 6 MPa)
ZVI/$Na_2S_2O_8$	H_2SO_4 (1 min, 300 rpm) → ZVI of 2.5 mM/g DS and $Na_2S_2O_8$ of 0.4 mM/g DS (10 min, 300 rpm)	
ZVI/$KMnO_4$	H_2SO_4 (1 min, 300 rpm) → ZVI of 2.5 mM/g DS and $KMnO_4$ of 0.4 mM/g DS (10 min, 300 rpm)	
TA/ZVI/H_2O_2	Pretreated ZVI powders (20 min, 40 °C) → H_2SO_4 (1 min, 300 rpm) → TA/ZVI of 1.5 mM/g DS and H_2O_2 of 0.6 mM/g DS (10 min, 300 rpm)	
TA/ZVI/$Na_2S_2O_8$	Pretreated ZVI powders (15 min, 45 °C) → H_2SO_4 (1 min, 300 rpm) → TA/ZVI of 2.5 mM/g DS and $Na_2S_2O_8$ of 0.4 mM/g DS (10 min, 300 rpm)	
TA/ZVI/$KMnO_4$	Pretreated ZVI powders (15 min, 45 °C) → H_2SO_4 (1 min, 300 rpm) → TA/ZVI of 2.5 mM/g DS and $KMnO_4$ of 0.4 mM/g DS (10 min, 300 rpm)	

procedures are provided in Text S4 (SI). The EPS was filtered with a 0.45 mm membrane before analysis. The protein and polysaccharide concentrations were measured using the Coomassie Brilliant Blue G-250 [34] and anthrone methods [35], respectively. Organic compounds were measured by three-dimensional excitation-emission matrix (3D-EEM) fluorescence spectroscopy using a Hitachi F-4600 fluorescence spectrophotometer (Hitachi, Japan). The excitation and emission ranges were 200–400 nm and 280–500 nm, respectively. The spectra were recorded at a scan rate of 1,200 nm/min, using excitation and emission slit bandwidths of 5 nm. Table S2 shows the six regions of the EEM spectra [36,37].

Rheological behavior analysis. Rheological behavior was measured using a Physica MCR 300 rheometer (Anton Paar, Austria). A PP 50 plate was used for the tests. The shear rate was increased from 0.01 to 1000 s^{-1} for 5 min and then vice versa to assess the variations [38]. The temperature was maintained at 25 °C. The rheological data in this study was analyzed using the Herschel-Bulkley model (Eq. (1)) [39].

$$\tau = \tau_y + k\dot{\gamma}^n \quad (1)$$

where τ is the shear stress (Pa); $\dot{\gamma}$ is the shear rate (s^{-1}); τ_y is the yield stress (Pa); k is the consistency index (PaÂ·s^n); and n is the flow behavior index.

Physicochemical characteristics analysis. The particle size distribution and zeta potential were determined using a Malvern 3000 mastersizer (Malvern, UK) and a 90Plus PALS zetasizer (Brookhaven, USA), respectively. The filtrate TOC concentration was detected using a TOC-VCPH analyzer (Shimadzu, Japan). The ORP was examined using an ST5000 ORP electrode with an Ag/AgCl reference (OHAUS, USA). ΔORP represents the variation between the ORP values at 0.5 and 0 min [40].

Characterization of ZVI. The surface morphology of the pristine and used ZVI were characterized with an SU8010 SEM (Hitachi, Japan) equipped with an X-ray energy-dispersive spectrometer (EDS). The specific surface area of the ZVI was measured based on BET N_2 adsorption data at 77.0 K using an ASAP2020 surface area analyzer (Micromeritics, USA) [17]. The XRD measurements were recorded using a Smartlab 9 kW X-ray diffractometer (Rigaku, Japan) employing Cu radiation and a scanning rate of 2°/min in the range from 20 to 90°. The detailed measurement method of the iron dissolving rate (ZVI_d%) [20] and dissolved Fe^{2+} in sludge [41] is outline in Text S5 (SI).

3. Results and discussion

3.1. Sludge dewatering efficiency of the ZVI/oxidants

Fig. S2 (SI) shows the variations of the Wc during the ZVI/H_2O_2, ZVI/$Na_2S_2O_8$ and ZVI/$KMnO_4$ treatments. As the ZVI dosages increased from 0 to 3.0 mM/g dry solid (DS), the Wc values first decreased and then slowly increased (Fig. S2a). Specifically, the optimal ZVI dosages for the respective treatments were 1.5 mM/g DS (ZVI/H_2O_2), 2.5 mM/g DS (ZVI/$Na_2S_2O_8$), and 2.5 mM/g DS (ZVI/$KMnO_4$). This indicates that a high ZVI dose is associated with inferior sludge dewaterability. A possible explanation is that an overdose of ZVI could generate excessive Fe^{2+}, leading to decreased ·OH production [19]. When the H_2O_2 addition increased from 0 to 1.0 mM/g DS, the Wc values initially decreased and then gradually increased (Fig. S2b). For the ZVI/$Na_2S_2O_8$ and ZVI/$KMnO_4$ treatments, the trends in Wc values were similar to that of ZVI/H_2O_2. The optimal oxidant dosages for each treatment were 0.6 mM/g DS (ZVI/H_2O_2), 0.4 mM/g DS (ZVI/$Na_2S_2O_8$), and 0.4 mM/g DS (ZVI/$KMnO_4$). At higher doses of oxidants, sludge dewaterability was substantially worse. This may be explained by the slow release of Fe^{2+} caused by slow corrosion on the ZVI surface, as well as the surface mass transfer inhibition [42]. Fig. S2c shows that better sludge dewaterability of the treatments was achieved when the pH was 3.0 (ZVI/H_2O_2), 5.0 (ZVI/$Na_2S_2O_8$), and 2.0 (ZVI/$KMnO_4$). This result implies that acidic conditions can promote ZVI corrosion, accelerate the release of Fe^{2+}, and improve the mass transfer rate, thus enhancing the sludge dewatering performance [43]. In summary, the optimum conditions were as follows for 1) the ZVI/H_2O_2 treatment: a ZVI of 1.5 mM/g DS, H_2O_2 of 0.6 mM/g DS and an initial pH of 3.0; 2) the ZVI/$Na_2S_2O_8$ treatment: a ZVI of 2.5 mM/g DS, $Na_2S_2O_8$ of 0.4 mM/g DS and an initial pH of 5.0; and 3) the ZVI/ $KMnO_4$ treatment: a ZVI of 2.5 mM/g DS, $KMnO_4$ of 0.4 mM/g DS and an initial pH of 2.0.

Under the optimal conditions, the Wc values decreased to 71.33 wt % (ZVI/H_2O_2), 68.07 wt% (ZVI/$Na_2S_2O_8$), and 70.69 wt% (ZVI/$KMnO_4$). These Wc values were higher than those obtained using the electrochemical/Fenton treatment (59.00 wt%) [44] and the electrochemical/ZVI/H_2O_2 treatment (65.37 wt%) [45]. This indicates that the improvement of sludge dewaterability was very limited after the ZVI/oxidants treatment. Similarly, Zhou et al. [20,21,23] reported that compared to the RS, the CST reduction rate of sludge treated by ZVI/oxidants (H_2O_2, $S_2O_8^{2-}$, and HSO_5^-) decreased by approximately 50%. This also indicates a limited dewatering efficiency. Moreover, these studies demonstrate that the large contact surface of the oxidants and ZVI can promote sludge dewaterability. It is difficult to improve the

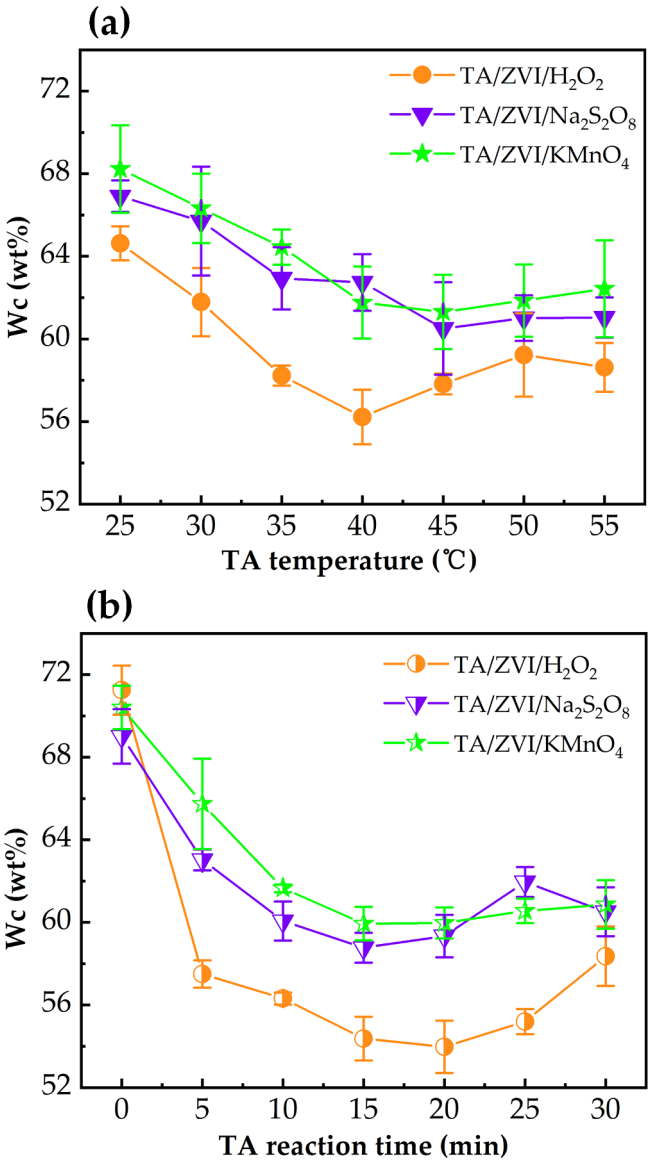

Fig. 1. Effects of TA conditions on sludge dewaterability under TA/ZVI oxidants treatment: (a) TA temperature (Operating parameter: reaction time of 10 min), and (b) TA reaction time (Operating parameters: TA temperature of 40 °C (TA/ZVI/H_2O_2), 45 °C (TA/ZVI/$Na_2S_2O_8$), 45 °C (TA/ZVI/$KMnO_4$)).

dewatering efficiency when the oxidants react with ZVI; thus, the low sludge dewatering efficiency might be due to the passivation layer of the ZVI [17,18], which would restrain electron transfer, thereby inhibiting the reactivity of ZVI [24]. A low concentration of Fe^{2+} was released and the oxidation of EPS was restricted. To enlarge the contact surface of ZVI and accelerate mass transport, ZVI pretreatment is required.

3.2. Sludge dewatering efficiency of TA/ZVI/oxidants

In this study, a TA pretreatment was used to improve the ZVI performance. To evaluate the effects of the TA pretreatment temperature and reaction time on sludge dewaterability under the TA/ZVI/oxidants treatment, two groups of experiments were conducted.

3.2.1. Effect of TA temperature on the sludge dewatering efficiency

The Wc after TA/ZVI/oxidants treatment decreased rapidly and then gradually increased as the temperature rose from 25 to 55 °C (Fig. 1a). The optimal TA temperatures for the TA/ZVI/H_2O_2, TA/ZVI/$Na_2S_2O_8$, and TA/ZVI/$KMnO_4$ treatments were 40, 45, and 45 °C, respectively, and the lowest Wc values decreased to 56.23, 60.50, and 61.31 wt%, respectively. However, the Wc values of the ZVI/oxidants treatment under the optimal conditions were higher than 68.00 wt%. Compared to the ZVI/oxidants treatment, the Wc values of TA/ZVI/oxidants treatment were substantially lower. This difference may arise from the Fe^{2+} concentrations. According to Eqs. (2), (3), and (4), more in-situ Fe^{2+} is produced through iron corrosion due to the large contact surface and rapid mass transport [20,24,25,46]. Fe^{2+} then acts as a catalyst to activate oxidants that produce many strong oxidizing radicals, leading to EPS disruption [47].

$$Fe^0 + H^+ \rightarrow Fe^{2+} + H_2 \quad (2)$$

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \quad (3)$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2 \quad (4)$$

3.2.2. Effect of TA reaction time on the sludge dewatering efficiency

The TA temperature was fixed at the optimal value for each oxidant (as stated above) to examine the impact of the TA reaction time on sludge dewaterability under the TA/ZVI/oxidants treatment. The Wc values of the TA/ZVI/oxidants treatment first decreased and then exhibited an upward trend thereafter (Fig. 1b). These results indicate that exceeding the optimal TA reaction time decreases the sludge dewatering efficiency. This might be explained by excessive iron corrosion. When TA/ZVI was added to the sludge, excessive Fe^{2+} was produced, which subsequently restrained the oxidation process and decreased the generation of strong oxidizing radicals [48]. The optimal TA reaction times were 20 min (TA/ZVI/H_2O_2), 15 min (TA/ZVI/$Na_2S_2O_8$), and 15 min (TA/ZVI/$KMnO_4$). Under these TA reaction times, the lowest Wc values were 53.97, 58.77 and 59.94 wt%, respectively.

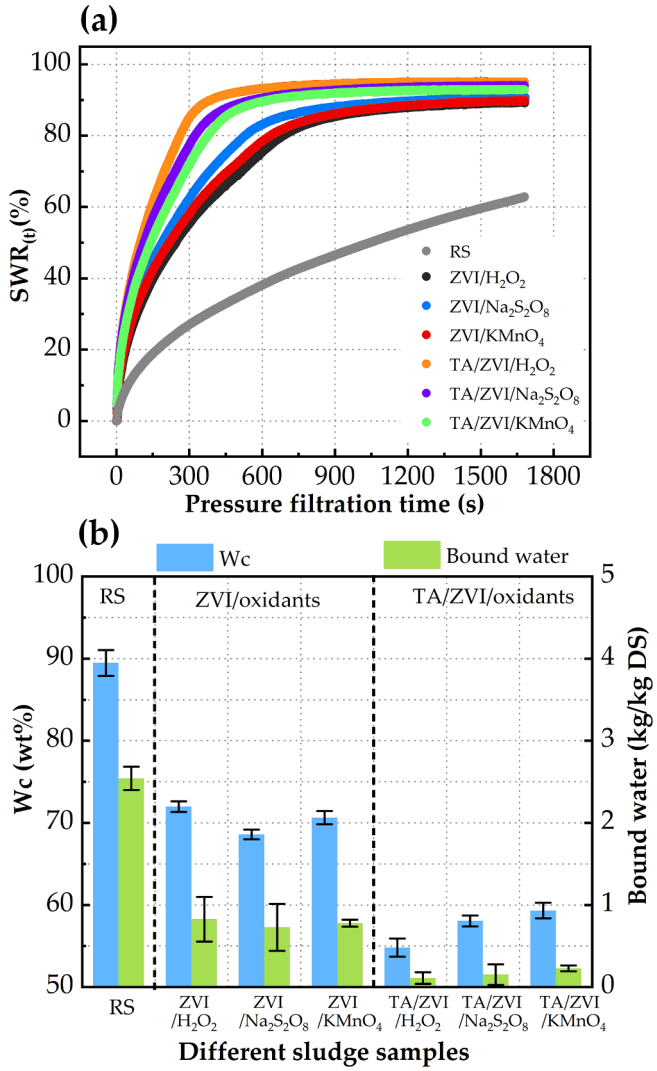

Fig. 2. Sludge dewatering performance of ZVI/oxidants and TA/ZVI/oxidants under optimal conditions: (a) $SWR_{(t)}$, and (b) Wc and bound water.

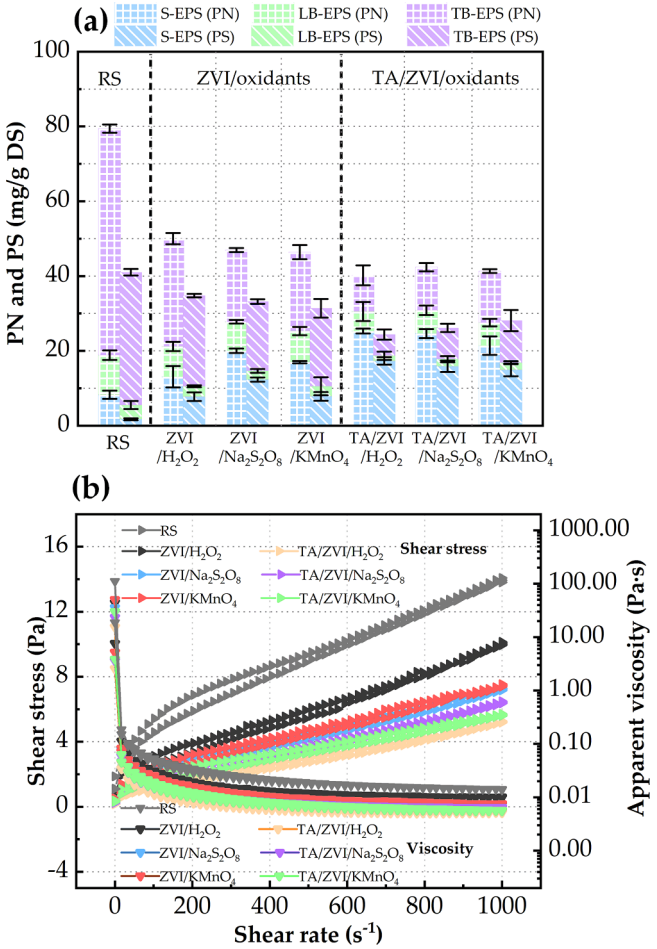

Fig. 3. The EPS concentrations (a), and rheological properties (b) of sludge in various treatments.

3.3. Comparison of TA/ZVI/oxidants and ZVI/oxidants for sludge deep dewatering efficiency

To compare the dewatering efficiency of sludge under the ZVI/oxidants and TA/ZVI/oxidants treatments, experiments were conducted at the above optimal conditions and presented in Table 1.

The sludge dewaterability, as evaluated by determining the $SWR_{(t)}$ and Wc values, exhibited an observable difference under the different treatment conditions (Fig. 2). In comparison to the raw sludge (RS), the $SWR_{(t)}$ values were improved after both ZVI/oxidants and TA/ZVI/oxidants conditioning (Fig. 2a). This might be related to the oxidation process, which can cause the disruption of EPS and, thus, enhance the sludge dewatering efficiency [49]. The $SWR_{(t)}$ values were 89.18% for ZVI/H_2O_2, 90.58% for ZVI/$Na_2S_2O_8$, 89.81% for ZVI/$KMnO_4$, 95.02% for TA/ZVI/H_2O_2, 94.02% for TA/ZVI/$Na_2S_2O_8$, and 92.87% for TA/ZVI/$KMnO_4$. The average $SWR_{(t)}$ values of the TA/ZVI/oxidants treatment were 4.58% higher than the $SWR_{(t)}$ values seen with the ZVI/oxidants treatment. A possible explanation is that TA/ZVI/oxidants treatment had a stronger oxidation capacity to destroy EPS [24].

The Wc values of RS, ZVI/oxidants and TA/ZVI/oxidants (Fig. 2b) were the opposite of those for $SWR_{(t)}$ (Fig. 2a). Compared with the RS, the Wc values of the treated sludge notably decreased. For example, the Wc values decreased from 89.48 wt% (RS) to 71.98, 68.59 and 70.63 wt% after ZVI/H_2O_2, ZVI/$Na_2S_2O_8$ and ZVI/$KMnO_4$ treatment, respectively. Moreover, the average Wc values of the TA/ZVI/oxidants treatment decreased by 18.47% compared with the ZVI/oxidants treatment. The Wc values were 54.81 wt% for TA/ZVI/H_2O_2, 58.06 wt% for TA/ZVI/$Na_2S_2O_8$ and 59.32 wt% for TA/ZVI/$KMnO_4$. Furthermore, as these values were less than 60.00 wt%, they met the landfill standards in China (GB/T 23485-2009). Previous studies showed that the Wc values were 72.90 wt% for the ZVI/HSO_5^- process [19] and 65.37 wt% for the electrochemical/ZVI/H_2O_2 treatment [45]. Compared with these studies, our TA/ZVI/oxidants treatment exhibited a lower Wc value. This indicates that the TA/ZVI/oxidants treatment is a highly efficient method for enhancing sludge dewatering.

The trend in bound water content was similar to that of Wc. Compared with the ZVI/oxidants treatment, the average bound water content of the TA/ZVI/oxidants treatment decreased by 78.90%. Furthermore, the average bound water content of the TA/ZVI/oxidants treatment was 93.55% lower than that of the RS. Cai et al. [45] showed that compared with the RS, the bound water content of sludge after electrochemical/ZVI/H_2O_2 treatment was reduced by 76.14%. Our results indicate that the TA/ZVI/oxidants treatment obtained a higher removal rate of bound water. Thus, these results demonstrate that the TA/ZVI/oxidants treatment is a feasible and efficient strategy to improve the sludge dewatering efficiency and achieve deep dewatering. This treatment showed superiority over ZVI/oxidants treatment. To determine the reason that the sludge dewatering efficiency in the TA/ZVI/oxidants treatment improved more than the ZVI/oxidants treatment, the sludge characteristics and surface structure characteristics of ZVI were investigated.

3.4. The impact of different treatments on sludge characteristics

3.4.1. EPS

Fig. 3a shows the variations of proteins and polysaccharides in S-

Table 2
Fluorescent intensities in three EPS fractions under different treatments (Units: 10^4 RU).

Samples	EPS fractions	Tyrosine/tryptophan amino acid	Tyrosine/tryptophan protein	Polysaccharide	Fulvic acid	Polyaromatic-type humic acid	Polycarboxylate-type humic acid
RS	S-EPS	4.69	4.76	2.23	5.57	3.22	2.32
ZVI/H_2O_2		1.24	3.31	2.46	3.95	18.22	11.42
ZVI/$Na_2S_2O_8$		0.56	1.30	1.41	0.09	4.95	3.82
ZVI/$KMnO_4$		0.68	1.67	5.67	9.21	34.92	31.05
TA/ZVI/H_2O_2		0.09	1.02	0.40	0.01	3.40	2.39
TA/ZVI/$Na_2S_2O_8$		0.20	1.18	0.91	0.41	5.99	3.49
TA/ZVI/$KMnO_4$		0.19	1.13	2.47	4.42	26.53	15.69
RS	LB-EPS	11.17	10.69	7.48	4.57	4.54	4.21
ZVI/H_2O_2		3.80	4.79	3.49	4.77	13.35	6.07
ZVI/$Na_2S_2O_8$		1.49	2.36	2.51	7.44	18.01	11.14
ZVI/$KMnO_4$		2.30	4.06	2.98	5.36	17.05	7.23
TA/ZVI/H_2O_2		0.92	1.56	0.42	2.67	9.82	4.44
TA/ZVI/$Na_2S_2O_8$		1.04	1.83	1.03	3.22	15.26	6.96
TA/ZVI/$KMnO_4$		1.10	2.12	1.33	5.64	19.36	8.95
RS	TB-EPS	15.88	32.55	63.30	0.27	4.64	13.14
ZVI/H_2O_2		9.53	15.56	6.55	3.05	11.48	9.04
ZVI/$Na_2S_2O_8$		5.76	10.14	3.17	7.70	22.95	14.66
ZVI/$KMnO_4$		6.29	13.38	4.57	3.54	11.79	14.08
TA/ZVI/H_2O_2		3.80	6.37	3.68	1.97	11.74	16.84
TA/ZVI/$Na_2S_2O_8$		4.04	7.74	3.90	4.66	15.14	13.24
TA/ZVI/$KMnO_4$		4.87	10.63	4.07	3.05	13.46	13.83

Minimum value — Maximum value

EPS, LB-EPS, and TB-EPS after the different treatments. Compared with the RS, the conditioned sludge contained less proteins in the LB-EPS and TB-EPS but more in the S-EPS. This result is in accordance with other AOP treatments [44,47]. The degradation of proteins in TB-EPS might enhance sludge filterability [50,51]. Compared to ZVI/oxidants treatment, the TA/ZVI/oxidants treatment removed more proteins from the TB-EPS. The highest protein removal rate in the TB-EPS was observed in the TA/ZVI/H_2O_2 treatment (84.01%), followed by the TA/ZVI/$Na_2S_2O_8$ (80.93%) and TA/ZVI/$KMnO_4$ (77.30%) treatments. This might be due to the quantity of oxidizing radicals and ferric hydroxide colloids. The oxidizing radicals could cause cell lysis and EPS disruption [47], whereas ferric hydroxide colloids could have a strong adsorption capacity for proteins in the EPS [52]. This indicates that the TA/ZVI/oxidants treatment induced a higher destruction of protein structure, which lead to excellent dewaterability. A similar trend to the protein variations was found for the polysaccharides in the EPS. Compared to the RS, polysaccharides increased in the S-EPS but decreased in the LB-EPS and TB-EPS after AOP treatment. Moreover, after the TA/ZVI/oxidants treatment, the polysaccharide values in the TB-EPS became lower than that of the ZVI/oxidants treatment. Proteins are easier to remove than polysaccharides. Li et al. [19] found that after electrolysis/electrocoagulation and ZVI activated $S_2O_8^{2-}$ oxidation treatment, the proteins and polysaccharides in TB-EPS decreased by 65.8% and 51.2%, respectively. Our results agree with these findings.

To explore the variations of organic matter in the EPS fractions, the 3D-EEM technique was applied [53]. Table 2 presents the fluorescence regional integration (FRI) of the dominant tyrosine/tryptophan amino acid, tyrosine/tryptophan protein and polysaccharide in the EPS. Zhang et al. [54] found that the FRI of the tyrosine/tryptophan amino acid and tyrosine/tryptophan protein were more abundant than that of the polysaccharide, fulvic acid, polyaromatic-type humic acid, and polycarboxylate-type humic acid; however, our results differ from that study. With respect to the tyrosine/tryptophan amino acid, tyrosine/tryptophan protein, and polysaccharide, intensities of these regions showed a downward trend in the three EPS layers after the ZVI/oxidants and TA/ZVI/oxidants treatments. For example, the average FRI of the tyrosine/tryptophan protein after the TA/ZVI/oxidants treatment decreased for all EPS layers from 4.76×10^4 RU (RS) to 1.11×10^4 RU in S-EPS; from 10.69×10^4 RU (RS) to 1.84×10^4 RU in LB-EPS; and from 32.55×10^4 RU (RS) to 8.25×10^4 RU in TB-EPS. After the TA/ZVI/oxidants treatment, the average FRI of the polysaccharide decreased from 2.23×10^4 RU (RS) to 1.26×10^4 RU in S-EPS; from 7.48×10^4 RU (RS) to 0.93×10^4 RU in LB-EPS; and from 63.30×10^4 RU (RS) to 3.88×10^4 RU in TB-EPS. This result indicates that after treatment, protein-like materials and polysaccharide-like substances were significantly disintegrated. This might be the result of the mineralization effect [47]. Furthermore, the TA/ZVI/oxidants treatment removed more protein-like materials and polysaccharide-like substances in the three EPS layers compared to the ZVI/oxidants. This agrees with the EPS results shown in Fig. 3a. It is possible that strong oxidizing radicals significantly dissolved the protein-like materials and polysaccharide-like substances and the ferric floc easily adsorbed the organic matter. Cai et al. [45] showed that protein-like materials and polysaccharide-like substances play an important role in sludge dewaterability. Thus, the TA/ZVI/oxidants treatment improved sludge dewaterability better than the ZVI/oxidants treatment. Fulvic acids and humic acids are stable high-molecular weight materials [55]. After the AOP treatment, the FRI of the fulvic and humic acids in the three EPS layers slightly increased. This finding agrees with that of Yu et.al. [47].

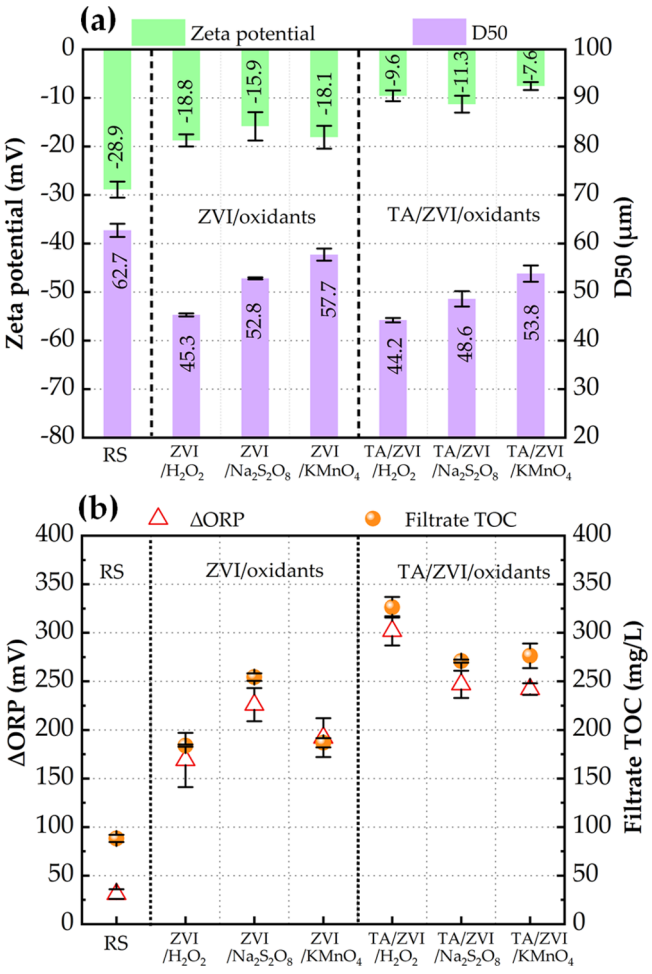

Fig. 4. The particle size and zeta potential (a) of sludge, and ΔORP and filtrate TOC (b) in various treatments.

3.4.2. Rheological behavior

The rheological behavior of sludge reflects the shape of the sludge floc, which is associated with the sludge dewatering performance [54,56]. Thus, changes in the rheological behavior of sludge before and after the ZVI/oxidants and TA/ZVI/oxidants treatments were studied (Fig. 3b). The shear stress in the ascending path was higher than the descending path, resulting in the formation of a hysteresis loop [56]. The thixotropic properties of the sludge were in response to the area of the hysteresis loop [54]. The results show that the area of the hysteresis loop after the TA/ZVI/oxidants conditioning was lower than that of the ZVI/oxidants conditioning. This indicates that the TA/ZVI/oxidants treatment further weakened colloidal forces. Moreover, the trend in the

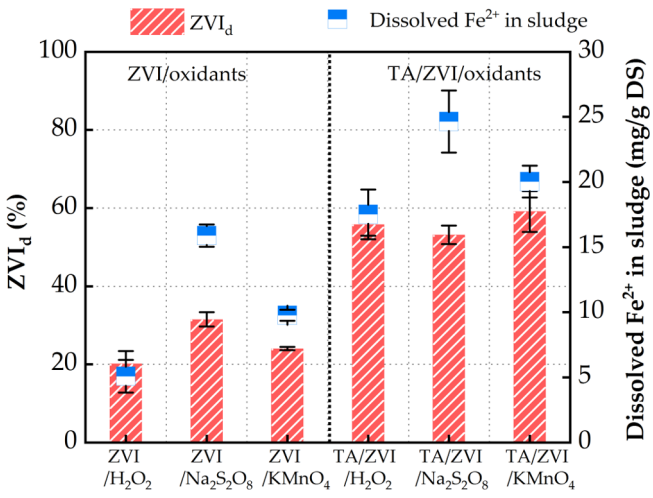

Fig. 5. ZVI_d% and dissolved Fe^{2+} in sludge under various treatments.

viscosity was similar to the area of the hysteresis loops. The results demonstrate that after the TA/ZVI/oxidants treatment, the viscosity of the sludge was lower than that of the sludge treated with ZVI/oxidants. Therefore, the TA/ZVI/oxidants treatment effectively decreased the colloidal forces and viscosity, supporting good sludge dewaterability.

The Herschel-Bulkley model was used to evaluate rheology of the sludge (Eq. (1)). After the TA/ZVI/oxidants conditioning, the yield stress (τ_y) value decreased from 1.8630 Pa (RS) to 0.2530 Pa (TA/ZVI/H_2O_2), 0.3590 Pa (TA/ZVI/$Na_2S_2O_8$), and 0.3827 Pa (TA/ZVI/$KMnO_4$) (Table S3). The consistency index (k) value decreased from 0.2798 PaÂ·s^n for RS to 0.0763, 0.1075, and 0.1458 PaÂ·s^n after TA/ZVI/H_2O_2, TA/ZVI/$Na_2S_2O_8$, and TA/ZVI/$KMnO_4$ treatments, respectively. Moreover, compared with the ZVI/oxidants treatment, the τ_y and k values of the sludge treated by TA/ZVI/oxidants were lower, denoting weaker strength and firmness of the sludge [57]. This suggests that the TA/ZVI/oxidants treatment was better able to weaken the sludge strength and

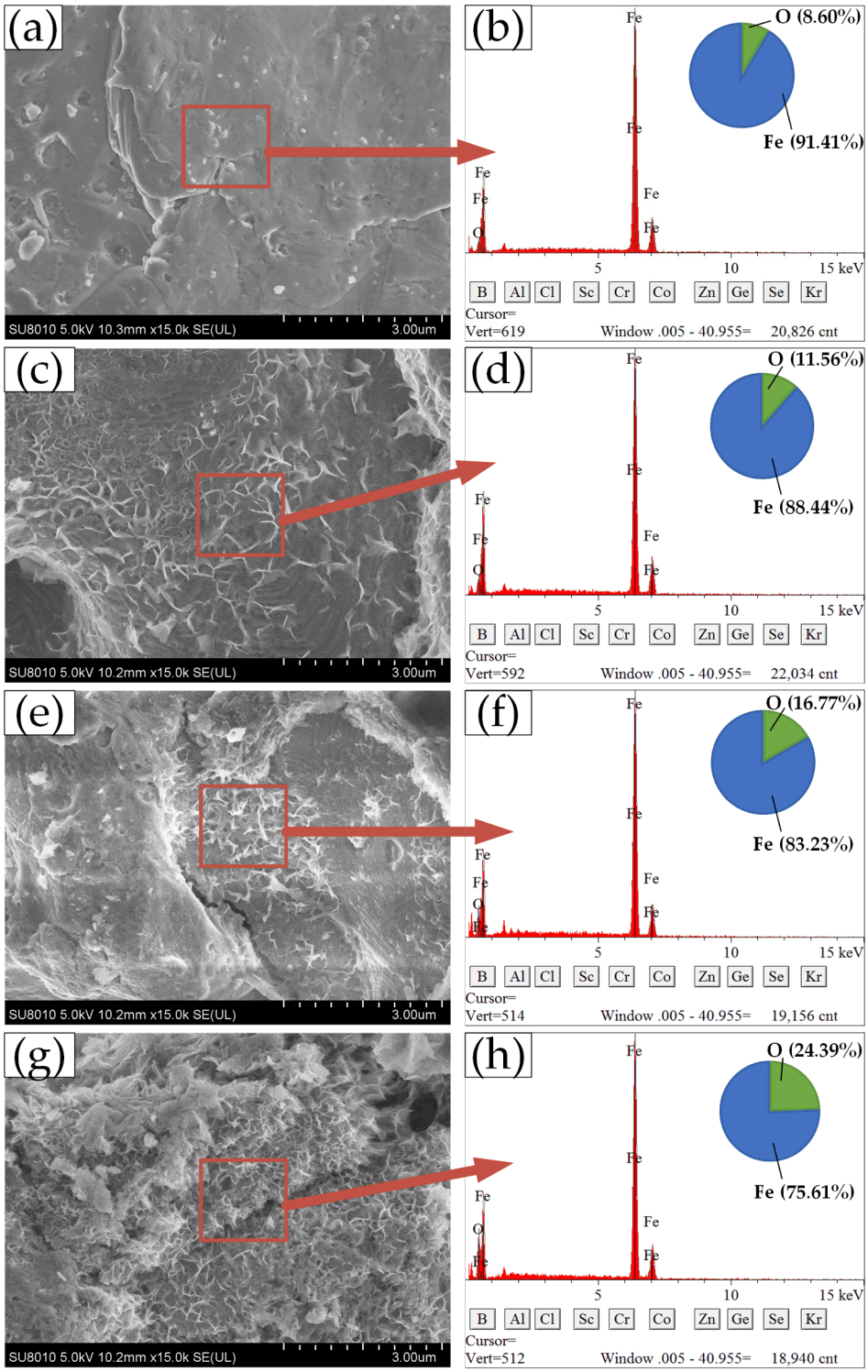

Fig. 6. SEM images of (a) pristine ZVI, (c) TA/ZVI, (e) ZVI after H_2O_2 reaction, and (g) TA/ZVI after H_2O_2 reaction; EDS spectra and normalized element distribution of (b) pristine ZVI, (d) TA/ZVI, (f) ZVI after H_2O_2 reaction, and (h) TA/ZVI after H_2O_2 reaction.

Table 3
BET surface area of the ZVI.

Samples	BET surface area (m^2/g)
Pristine ZVI	0.18
TA/ZVI	4.23
ZVI after H_2O_2 reaction	0.85
ZVI after $Na_2S_2O_8$ reaction	2.13
ZVI after $KMnO_4$ reaction	1.24
TA/ZVI after H_2O_2 reaction	7.02
TA/ZVI after $Na_2S_2O_8$ reaction	5.74
TA/ZVI after $KMnO_4$ reaction	5.52

firmness compared to the ZVI/oxidants treatment. This behavior could account for the strong oxidation effect and ferric hydroxide colloid that destroyed the EPS floc, indicating breakdown of the internal structures [51]. As a result, the lower viscosity and colloidal forces, along with weaker strength and firmness, were found. This result was supported by the EPS analysis (Fig. 3a).

3.4.3. Particle size distribution and zeta potential

Fig. 4a presents the variations in particle size and zeta potential of the sludge before and after the ZVI/oxidants and TA/ZVI/oxidants treatments. The D50 of the RS was 62.7μ m. The ZVI/oxidants and TA/ZVI/oxidants treatments changed the sludge floc into smaller fragments. Moreover, the average D50 of the TA/ZVI/oxidants treatment was 5.91% smaller than that with the ZVI/oxidants treatment. The major reason for the reduction of D50 was the oxidation capacity. Strong oxidizing radicals produced by the AOP reaction destroyed the cell wall and EPS structure of the microorganisms, which was conducive to filter press [9]. The zeta potentials of the treated sludge were higher than −18.8 mV, which is notably higher than the zeta potential of RS (-28.9 mV). Furthermore, the average zeta potential values were 46.71% higher for the TA/ZVI/oxidants treatment than for the ZVI/oxidants treatment. The zeta potentials of the TA/ZVI/oxidants treatment were −9.6 mV (TA/ZVI/H_2O_2), −11.3 mV (TA/ZVI/$Na_2S_2O_8$), and −7.6 mV (TA/ZVI/$KMnO_4$). The zeta potential approached zero, which indicates the formation of massive strong flocculation, resulting in enhanced dewatering [44]. There are two major reasons for the increased zeta potential: destruction of TB-EPS [44] and appearance of $Fe(OH)_n$ [58].

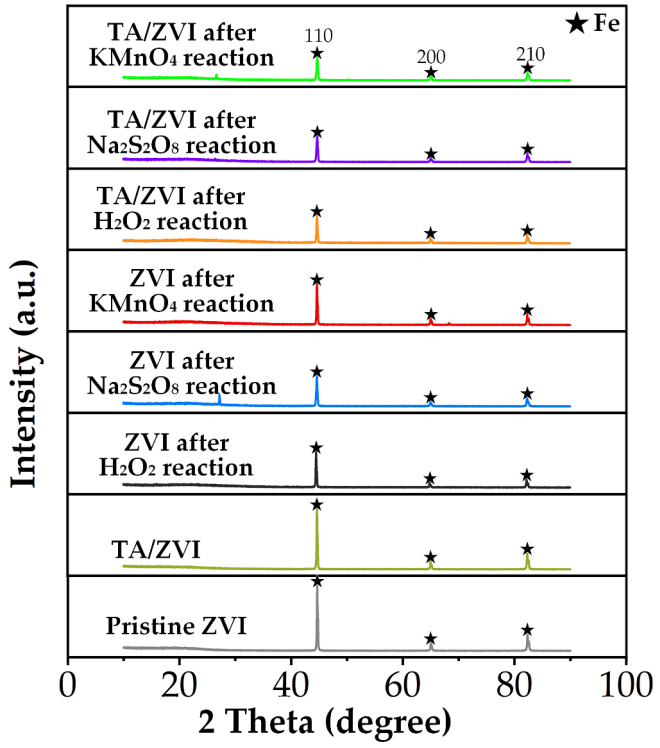

Fig. 7. XRD patterns of ZVI particle under various treatments.

3.4.4. ΔORP and filtrate TOC

ORP is a commonly used parameter to reflect oxidation processes. The ΔORP of the sludge is a rapid evaluation factor affecting the sludge dewaterability [40]. Fig. 4b presents the changes in ΔORP and filtrate TOC values before and after the ZVI/oxidants and TA/ZVI/oxidants treatments. The ΔORP values significantly increased after the ZVI/oxidants and TA/ZVI/oxidants treatments. The ΔORP value of RS was 31 mV, while those of the treated sludge were 169 mV (ZVI/H_2O_2), 226 mV (ZVI/$Na_2S_2O_8$), 192 mV (ZVI/$KMnO_4$), 302 mV (TA/ZVI/H_2O_2), 247 mV (TA/ZVI/$Na_2S_2O_8$), and 242 mV (TA/ZVI/$KMnO_4$). It was observed that the ΔORP values of the TA/ZVI/oxidants treatment were apparently higher than those of the ZVI/oxidants treatment. Lv et al. [40] demonstrated that optimal sludge dewaterability was achieved with a ΔORP value of 387 mV after a combined HSO_5^- pre-oxidation and Fe^{3+} coagulation treatment. The ΔORP values of the TA/ZVI/oxidants were higher than 240 mV. This result indicates that compared with the ZVI/oxidants treatment, the TA/ZVI/oxidants treatment had a more effective oxidation effect, which would generate stronger oxidizing radicals during the sludge conditioning. This confirms the hypothesis mentioned above. Furthermore, the trend of filtrate TOC was consistent with the changes in the ΔORP values. The filtrate TOC after the ZVI/oxidants and TA/ZVI/oxidants treatments were much higher than that of the RS. High filtrate TOC values mean more generation of strong oxidizing radicals [12]. These oxidizing radicals caused the degradation of EPS and converted the bound water into free water. As a result, sludge dewaterability was enhanced.

3.5. The impact of different treatments on surface structure characteristics of ZVI

3.5.1. Iron utilization efficiency

The dissolved iron concentration (mainly Fe^{2+}) from ZVI plays a vital role in AOP catalysis [20,21]. To further confirm the influence of ZVI on the sludge dewatering process, the dissolved Fe^{2+} concentrations and ZVI_d% values under various AOP treatments were analyzed. The ZVI_d% after the ZVI/oxidants treatment (< 31.51%) was not high (Fig. 5). Zhou et al. [23] reported that the ZVI_d% was lower than 20%

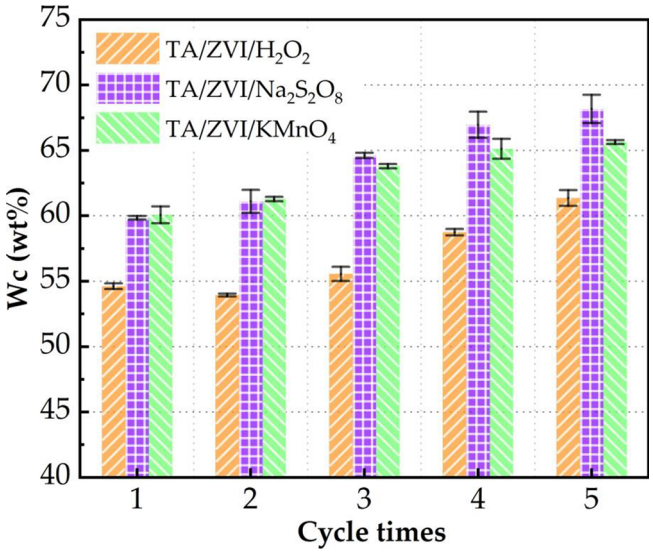

Fig. 8. Sludge deep dewatering after five cycles of the TA/ZVI/oxidants treatment.

when the sludge was conditioned by the ZVI/HSO_5^- treatment. Kang et al. [59] also found a low ZVI_d% after the ZVI/$S_2O_8^{2-}$ treatment. These results are supported by our findings (a low ZVI_d% for the ZVI/oxidants treatment). After the TA/ZVI/oxidants treatment, the ZVI_d% was higher than 53%. Moreover, the dissolved Fe^{2+} concentrations showed the same trend under different AOP treatments. The dissolved Fe^{2+} concentrations increased to 17.52, 24.64, and 20.04 mg/g DS, after the TA/ZVI/H_2O_2, TA/ZVI/$Na_2S_2O_8$, and TA/ZVI/$KMnO_4$ treatments, respectively. The results indicate that after the TA pretreatment, the ZVI_d% significantly increased and the TA/ZVI tended to generate more Fe^{2+}, which then reacted with the oxidants to produce many strong oxidizing radicals and iron hydroxide floc. These oxidation and flocculation could simultaneously react with floc, leading to improved sludge dewatering. This explains the improved oxidation efficiency.

To determine the effect of different AOP treatments on the surface structure characteristics of ZVI, the ZVI powder was characterized by SEM, BET and XRD in the following study.

3.5.2. SEM and EDS

Fig. 6 presents the surface morphology of ZVI under different treatments. Pristine ZVI had a smooth and dense surface (Fig. 6a), which is consistent with the study of Huang et al. [17]. After the TA pretreatment, the surface of TA/ZVI became rough with a large number of small acicular materials (Fig. 6c). These acicular materials may have increased the specific surface area, thereby increasing the contact area for oxidants or pollutants and improving the density of highly reactive sites [24]. Few coarse structures were generated with the ZVI/H_2O_2 reaction (Fig. 6e). Without the TA pretreatment, it was difficult for ZVI to react with H_2O_2. However, the TA pretreatment destroyed the thick layer and deeply corroded the pristine ZVI. As a result, numerous small acicular materials appeared after the TA/ZVI/H_2O_2 reaction (Fig. 6g). These small acicular materials were helpful for reacting with the oxidants and absorbing the EPS. These results demonstrate that the degree of ZVI corrosion reflects the ZVI_d%.

The EDS spectra and normalized element distribution of ZVI are summarized in Fig. 6b, d, f, and h. Without the TA pretreatment, the main element of the pristine ZVI was Fe, accounting for 91.41% (Fig. 6b). After the TA pretreatment, the O element on the ZVI surface increased from 8.60% to 11.56% (Fig. 6d). This indicates obvious oxidation of the ZVI surface. The oxidation products of ZVI could be Fe$(OH)_3$ and FeOOH [17]. Moreover, the Fe element increased and the O element further decreased after the ZVI/H_2O_2 and TA/ZVI/H_2O_2 reactions (Fig. 6f and h). Compared to the ZVI/H_2O_2 reaction, the O element of the TA/ZVI/H_2O_2 reaction was lower. This demonstrates that the oxidation and corrosion degree of the TA/ZVI/H_2O_2 reaction was higher than that of the ZVI/H_2O_2 reaction. These results are supported by the surface morphology of ZVI.

3.5.3. BET surface area

The specific surface area of pristine ZVI was 0.18 m^2/g (Table 3). After the TA pretreatment, the specific surface area of TA/ZVI increased to 4.23 m^2/g, which is over 23.5 times higher than the pristine ZVI. A possible explanation for the higher specific surface area is that under the TA condition, the passivation layer of the ZVI surface was removed and the ZVI was dissolved [24]. Moreover, the average specific surface area of TA/ZVI after the oxidants reaction was 4.3 times greater than that of ZVI after the oxidants reaction. The specific surface area of TA/ZVI after the oxidants reaction were 7.02 m^2/g (TA/ZVI after the H_2O_2 reaction), 5.74 m^2/g (TA/ZVI after the $Na_2S_2O_8$ reaction), and 5.52 m^2/g (TA/ZVI after the $KMnO_4$ reaction). The higher specific surface area of ZVI might offer numerous porous structures to allow contact with oxidants or pollutants, which can improve the efficiency of the oxidation reaction. These results were further confirmed by the SEM of ZVI.

3.5.4. XRD

XRD was used to further investigate the structural variations on the ZVI surface. The results are shown in Fig. 7. The pristine ZVI sample had three distinct characteristic peaks of 110, 200, and 210 crystal planes. This finding is consistent with the results from Huang et al. [17]. After the TA pretreatment, peak intensities of the crystal planes were weakened. This suggests that the TA/ZVI surface was covered by amorphous materials and that TA/ZVI dissolved. This inference is consistent with the results of the morphology images and EDS (Fig. 6c and d). After the ZVI or TA/ZVI reacted with the oxidants, the peak

Table 4
Economic analyses of the recent and traditional processes for the enhancement of sludge dewaterability.

Sludge conditioning methods	Chemical agents	Wc (wt%)	Treatment cost[j] (USD$/year)	Disposal cost[k] (USD$/year)	Total cost[l] (USD$/year)
ZVI/H_2O_2[a]	H_2SO_4; ZVI; H_2O_2	71.98	37,406.7	162,830.1	200,236.8
ZVI/Na_2SO_8[b]	H_2SO_4; ZVI; Na_2SO_8	68.07	97,025.6	142,890.7	239,916.3
ZVI/$KMnO_4$[c]	H_2SO_4; ZVI; $KMnO_4$	70.63	93,046.9	155,345.6	248,392.5
TA/ZVI/H_2O_2[d]	H_2SO_4; ZVI; H_2O_2	58.75	29,228.6	110,606.1	139,834.7
TA/ZVI/Na_2SO_8[e]	H_2SO_4; ZVI; Na_2SO_8	59.85	87,759.8	113,636.4	201,396.2
TA/ZVI/$KMnO_4$[f]	H_2SO_4; ZVI; $KMnO_4$	60.08	84,143.1	114,291.1	198,434.2
PAM[g]	PAM	80.06	64,459.0	228,811.4	293,270.4
Fenton's reagent/lime[h]	H_2SO_4; $FeSO_4$Â·$7H_2O$; H_2O_2; Lime	48.87	58,546.0	89,233.3	147,779.3
EZP[i]	ZVI; $FeSO_4$Â·$7H_2O$; Na_2SO_8	73.16	103,514.0	169,988.8	273,502.8

[a] Dose of ZVI and H_2O_2 were 1.5 and 0.6 mM/g DS.
[b] Dose of ZVI and $Na_2S_2O_8$ were 2.5 and 0.4 mM/g DS.
[c] Dose of ZVI and $KMnO_4$ were 2.5 and 0.4 mM/g DS.
[d] TA temperature, TA reaction time, TA/ZVI dose, and H_2O_2 dose were set as 40 °C, 20 min, 1.5 mM/g DS, and 0.6 mM/g DS, respectively. The ZVI was reused for four cycles.
[e] TA temperature, TA reaction time, TA/ZVI dose, and $Na_2S_2O_8$ dose were set as 45 °C, 15 min, 2.5 mM/g DS, and 0.4 mM/g DS, respectively. The ZVI was reused for one cycle.
[f] TA temperature, TA reaction time, TA/ZVI dose, and $KMnO_4$ dose were set as 45°, 15 min, 2.5 mM/g DS, and 0.4 mM/g DS, respectively. The ZVI was reused for one cycle.
[g] Refer to Liang et al. [52].
[h] Refer to Dai et al. [9].
[i] Refer to Li et al. [22].
[j] Chemical agents were industrial grade. The price of chemical agents was according to http://www.alibaba.com/. Treatment cost was calculated according to Table S4.
[k] The dewatered sludge disposal fee is USD $62.5/ton, which gathered from the local market.
[l] The total annual sludge production of a small scale WWTP with a daily sludge production of 10 ton 80 wt%/day is 3650 ton 80 wt%/year.

Table 5
Comparison of the ZVI/oxidants and Fe^{2+}/oxidants treatment for sludge dewaterability.

Treatment	Operating conditions	Wc (wt%)	The reduction of SRF (%)	The reduction of CST (%)	Reference
Electrochemical/ZVI/H_2O_2	Applied current density of 15 mA/cm^2, pH of 3, ZVI of 140 mg/L, H_2O_2 of 0.4 mg/L	65.37		73.5	Cai et al. [45]
ZVI/$Na_2S_2O_8$	ZVI of 2.0 g/g TSS, $Na_2S_2O_8$ of 0.5 g/g TSS			90.0	Kang et al. [59]
ZVI/$KHSO_5$	ZVI of 0.25 g/g TSS, $KHSO_5$ of 0.1 g/g TSS			50.0	Zhou et al. [23]
Fenton's reagent/lime	pH of 3, Fe^{2+} of 70 mg/g DS, H_2O_2 of 30 mg/g DS, Lime of 50 mg/g DS	44.56	96.5		Liang et al. [12]
Fe^{2+}/$Na_2S_2O_8$	Fe^{2+} of 1.5 mmol/gVSS, $S_2O_8^{2-}$ of 1.2 mmol/gVSS			88.8	Zhen et al. [14]
EDTA/Fe^{2+}/$KHSO_5$	EDTA of 0.4 mmol/gVSS, Fe^{2+} of 1.2 mmol/g VSS, $KHSO_5$ of 1.0 mmol/gVSS		70.6	60.0	Wang et al. [60]
TA/ZVI/H_2O_2 [a]	TA temperature of 40 °C, TA reaction time of 20 min, TA/ZVI of 1.5 mM/g DS, and H_2O_2 of 0.6 mM/g DS	58.75			This study
TA/ZVI/Na_2SO_8 [b]	TA temperature of 45 °C, TA reaction time of 15 min, TA/ZVI of 2.5 mM/g DS, and Na_2SO_8 of 0.4 mM/g DS	59.85			This study
TA/ZVI/$KMnO_4$ [c]	TA temperature of 45 °C, TA reaction time of 15 min, TA/ZVI of 2.5 mM/g DS, and $KMnO_4$ of 0.4 mM/g DS	60.08			This study

Note:
[a] The ZVI was reused for four cycles;
[b] The ZVI was reused for one cycle;
[c] The ZVI was reused for one cycle.

intensities of the crystal planes presented an apparent downward trend. Specifically, after TA/ZVI reacted with oxidants, peak intensities of the crystal planes were lower than that of ZVI/oxidants. This indicates that the ZVI surface was further dissolved and reacted. This inference is consistent with the results of the increased ZVI_d% (Fig. 5).

Using the results of the ZVI surface structure characteristics, we summarized the reason why the TA/ZVI/oxidants treatment exhibited stronger oxidation and flocculation effects, and further became more conducive to dewatering.

4. In-depth discussion

4.1. ZVI reuse and economic analysis

ZVI has proven to be a promising technology for sludge dewaterability [20]. Compared to Fe^{2+}, the biggest advantage of ZVI is its stability and reusability [18]. Based on the above results, the ZVI_d% was lower than 60% after the TA/ZVI/oxidants treatment. This indicates that only part of the TA/ZVI was dissolved while the residual ZVI could be reused. In this study, after sludge conditioning, the residual undissolved TA/ZVI powder was recovered using magnetic force and then reused in the recycling experiments. Fig. 8 shows the results of sludge dewatering efficiency using recycled TA/ZVI/oxidants under optimal conditions. It was found that the TA/ZVI/oxidants treatment effectively maintained the sludge dewatering efficiency. Even after four cycles, the Wc values of the TA/ZVI/H_2O_2, TA/ZVI/$Na_2S_2O_8$, and TA/ZVI/$KMnO_4$ treatments were 58.75, 66.96, and 65.13 wt%, respectively. After five cycles, the dewatering efficiency rapidly decreased; thus, new ZVI is needed to supply each round of the TA/ZVI/oxidants process. By reusing ZVI, the reagent cost can be lowered because the ZVI is more stable, much cheaper and reusable compared to Fe^{2+} salt [19]. In this study, ZVI could be reused four times, which would reduce the ZVI requirement and result in substantial savings. In particular, the dewatering efficiency was consistently effective for the TA/ZVI/H_2O_2 treatment up to five cycles. After five cycles, the Wc value of the TA/ZVI/H_2O_2 treatment approached 60 wt%.

Table S4 presents an economic analysis of sludge treated with ZVI/oxidants, TA/ZVI/oxidants, polyacrylamide (PAM), Fenton's reagent/lime, and EZP. The approximate total treatment cost of the TA/ZVI/oxidants treatments was lower than that of the ZVI/oxidants treatment. The approximate total treatment cost of the TA/ZVI/H_2O_2, TA/ZVI/$Na_2S_2O_8$, and TA/ZVI/$KMnO_4$ treatment was USD $8.01/ton 80 wt%, USD $24.04/ton 80 wt%, and USD $23.05/ton 80 wt%, respectively. Thus, the approximate total treatment cost of the TA/ZVI/H_2O_2 treatment is much lower than for the ZVI/H_2O_2, ZVI/$Na_2S_2O_8$, ZVI/$KMnO_4$, TA/ZVI/$Na_2S_2O_8$, and TA/ZVI/$KMnO_4$, PAM [52], Fenton's reagent/lime [9], and EZP [22] treatments.

The total annual sludge production of a small scale WWTP with a daily sludge production of 10 ton 80 wt%/day is 3,650 ton 80 wt %/year. The total cost, which includes both sludge treatment and disposal, is predominantly made up of the disposal cost [9]. The disposal fee for dewatered sludge is about USD $62.5/ton [27]. Table 4 shows that the total annual cost of our ZVI/oxidants and TA/ZVI/oxidants treatments is much lower than the traditional PAM treatment. Furthermore, the average annual total cost of the TA/ZVI/oxidants treatment is 21.62% lower than with the ZVI/oxidants treatment. The annual total cost of TA/ZVI/H_2O_2 treatment was USD $139,834.7/year, which was the lowest value. The total annual cost of traditional PAM was as high as USD $293,270.4/year. Thus, using the TA/ZVI/H_2O_2 treatment as the sludge conditioning method would save approximately 52.32% per year compared with the traditional PAM treatment; 5.37% per year compared with the Fenton's reagent/lime treatment; and 48.87% per year compared with the EZP treatment. In general, our results demonstrate that the TA/ZVI/H_2O_2 treatment is a more practical and economical technique for achieving deep dewatering of sludge.

4.2. Comparison of ZVI/oxidants and Fe^{2+}/oxidants

Table 5 compares the sludge dewaterability of different ZVI/oxidants and Fe^{2+}/oxidants treatments. Previous studies demonstrated that the Fe^{2+}/oxidants treatment is also a cost-efficient and feasible strategy for improving dewaterability [12,14,60]. Our previous study showed sufficient improvement of the sludge dewaterability with a 96.5% lower SRF and a Wc of 44.56 wt% under the Fenton's reagent/lime treatment. In another study, Zhen et al. [14] used an Fe^{2+}/$Na_2S_2O_8$ treatment to dewater sludge, achieving a better sludge dewaterability with an SRF reduction of 88.8%. Wang et al. [60] also reported that an EDTA/Fe^{2+}/$KHSO_5$ treatment could substantially enhance sludge dewaterability with an SRF reduction of 60.0%. Recently, several attempts have been made to use ZVI as the catalyst in place of Fe^{2+} [23,45,59]. These studies presented good sludge dewaterability after ZVI/oxidants treatment. The CST reduction rate of sludge was 73.5% for the electrochemical/ZVI/H_2O_2 treatment [45], 90.0% for the ZVI/$Na_2S_2O_8$ treatment [59], and 50.0% for the ZVI/$KHSO_5$ [23]. Compared to the Fe^{2+}/oxidants treatment, the sludge dewaterability of the ZVI/oxidants treatment requires further improvement. As a green, cheap, and reusable material, ZVI has some superior features; therefore, ZVI/oxidants has the potential to be a feasible method for enhancing sludge dewaterability. To improve ZVI performance, we used a TA pretreatment. Our results indicate that after the TA/ZVI/oxidants treatment, the sludge dewaterability was greatly improved.

TA/ZVI/oxidants treatment is a feasible, highly efficient and economical technique for achieving deep dewatering of sludge. However, there remains possible drawbacks associated with the use of the TA/ZVI/oxidants treatment. For example, the TA/ZVI/oxidants method for sludge conditioning is still in the beginning stages, further research needs to focus on reactor design and optimization of the operating conditions. Our study provides a technological reference to further develop medium or even large-scale tests for the deep dewatering of sludge. Furthermore, due to its fine particle size, the recovery rate of the ZVI powder is not high, which increases the application cost. Further research should also focus on the development of a device to recover ZVI, as well as on a method to use industrial scrap iron, which is cheaper and has a large particle size. Moreover, the pH adjustment might complicate the sludge conditioning process, thus driving up the cost and restricting further promotion and application of this technology. Further studies are necessarily to avoid an acid and neutralization process.

4.3. Possible mechanism of TA/ZVI/oxidants conditioning process

The underlying mechanism of TA/ZVI/oxidants in improving sludge dewatering is illustrated in Fig. 9. In the ZVI surface layer, after the TA pretreatment, dissolved Fe^{2+} was released from the iron and the oxidation layer became simultaneously rough. During the redox reactions, more Fe^{2+} catalyzed the oxidants (H_2O_2, $Na_2S_2O_8$, and $KMnO_4$) to produce strong oxidizing radicals and strong flocculating Fe^{3+}. Meanwhile, the Fe^{3+} from the reaction was gradually transformed to Fe^{2+}. As a result, iron microcirculation occurred. In the sludge layer, a large amount of strong oxidizing radicals was generated from the oxidants catalyzed by Fe^{2+}. The oxidizing radicals caused cell lysis and the disruption of proteins and polysaccharides in the EPS. Furthermore, Fe^{3+} was formed during the reaction, which caused flocculation through charge neutralization and adsorption. Additionally, the particle size became smaller and the zeta potential became higher after treatment. Moreover, the lower viscosity and colloidal forces, as well as weaker strength and firmness were observed. As a result, the bound water, which was trapped in net-like sludge floc, was released, leading to improved sludge dewatering.

Our results demonstrate that the TA/ZVI/oxidants treatment is superior to that of the ZVI/oxidants. The TA/ZVI/oxidants treatment significantly improved the sludge dewaterability. Furthermore, the total cost of the TA/ZVI/oxidants treatment is much lower than that of the ZVI/oxidants treatment. To explain the observed activity, we

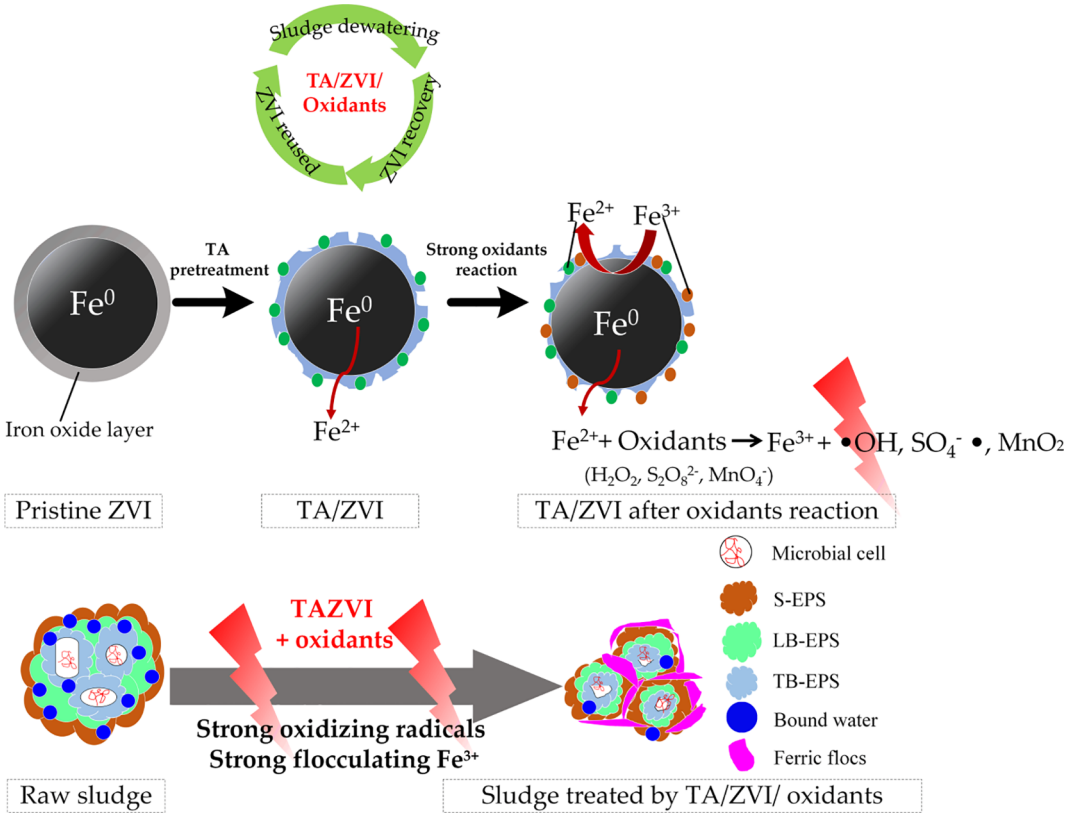

Fig. 9. Mechanisms of improving sludge dewatering in the TA/ZVI/oxidants system.

considered the sludge characteristics and surface structure characteristics of ZVI. Compared to the ZVI/oxidants treatment, the TA/ZVI/oxidants treatment removed more protein-like and polysaccharide-like materials in the LB-EPS and TB-EPS. The viscosity, colloidal forces, strength and firmness of the TA/ZVI/oxidants treatment showed lower values than that of the ZVI/oxidants treatment. The particle size of the TA/ZVI/oxidants treatment was smaller than that of the ZVI/oxidants treatment while the zeta potential was higher for the TA/ZVI/oxidants treatment. The oxidation capacity of the TA/ZVI/oxidants was apparently higher than that of the ZVI/oxidants. Moreover, the ZVI_d%, dissolved Fe^{2+} concentrations and specific surface area of ZVI were higher after the TA/ZVI/oxidants treatment.

5. Conclusions

In this study, rapid and cost-effective in-situ generation of Fe^{2+} was combined with common oxidants, namely H_2O_2, $Na_2S_2O_8$ and $KMnO_4$, to improve sludge dewaterability. The subsequent conclusions are as follows: (1) The TA/ZVI/oxidants treatment achieved deep dewatering of sludge (Wc $<$ 60 wt%) under optimal conditions. Moreover, the TA/ZVI/oxidants treatment decreased the Wc and bound water significantly more than the ZVI/oxidants treatment. (2) Compared to the ZVI/oxidants treatment, the TA/ZVI/oxidants treatment removed more protein-like and polysaccharide-like materials in the LB-EPS and TB-EPS. Furthermore, compared with the ZVI/oxidants treatment, there was a more notable decrease in particle size, negative zeta potential, viscosity and colloidal forces after the TA/ZVI/oxidants treatment. (3) Compared with the ZVI/oxidants treatment, the oxidation capacity, ZVI_d%, dissolved Fe^{2+} concentrations, and specific surface area of ZVI after the TA/ZVI/oxidants treatment were higher. (4) Based on the recycling experiment and economic analysis, the TA/ZVI/oxidants treatment is an efficient, alternative, and inexpensive strategy to achieve deep dewatering of sludge when compared to the ZVI/oxidants, PAM, Fenton's reagent/lime, and EZP treatments.

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Appendix A. Supplementary data

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