Article

Improved Dewaterability of Waste Activated Sludge by Fe(II)-Activated Potassium Periodate Oxidation

Hong Xiao *,†, Qing Liu †, Yingjun Wang, Ying Zhu, Dexin Fang, G anxue Wu, Zhenxing Zeng and Hong Peng *

College of Environmental Sciences, Sichuan Agricultural University, Chengdu 611130, China
* Correspondence: xiaohong@sicau.edu.cn (H.X.); penghong@sicau.edu.cn (H.P.)
† These authors contributed equally to this work.

Abstract: Fe(II)-activated potassium periodate (KIO₄) oxidation was used to improve the dewaterability of waste-activated sludge for the first time. Compared with those of raw sludge, the capillary suction time (CST), specific resistance filtration (SRF), and water content of filter cake (Wc) of sludge treated using the Fe(II)/KIO₄ process under the optimal conditions (i.e., the initial pH = 6.8, KIO₄ dose = 1.4 mmol/g volatile suspended solids, Fe(II)/KIO₄ molar ratio = 1.2) decreased by 64.34%, 84.13%, and 6.69%, respectively. For conditioned sludge flocs, the Zeta potential and particle size were increased, and hydrophilic proteins in extracellular polymeric substances (EPS) were partly degraded, accompanied by the transformation of tightly bound EPS into soluble EPS and the conversion of dense sludge flocs into loose and porous ones. During Fe(II)/KIO₄ oxidation, Fe(IV) and the accompanying •OH were determined as the predominant reactive species and the underlying mechanism of sludge EPS degradation was proposed. This work provides a prospective method for conditioning the sludge dewaterability.

Keywords: sludge dewaterability; ferrous ion; potassium periodate; extracellular polymeric substances

1. Introduction

Wastewater treatment plants produce massive waste activated sludge (WAS) with moisture content higher than 99%. Sludge dewatering is an imperative procedure to reduce the sludge volume and subsequently to save on the cost of sludge transportation and disposal. The efficiency of sludge dewatering is largely dependent on the extracellular polymeric substances (EPS) [1–6]. Destroying the EPS was deemed to be capable of improving the sludge dewatering performance. Herein, advanced oxidation processes (AOPs) have received much attention due to their efficiency in degrading EPS [7].

Traditional AOPs, such as Fenton [8] and Fenton-like [9] AOPs, have proven to be able to destroy the EPS due to the generation of hydroxyl radicals (•OH). Sulfate radical (SO₄•⁻)-based AOPs seem to perform better due to SO₄•⁻ having a higher redox potential (2.5–3.1 V) than •OH (1.8–2.7 V) [10,11]. More recently, periodate-based AOPs have attracted increasing attentions for the degradation of aqueous contaminants [12–24]. Notably, Zong et al. [17] reported that KIO₄ is readily activated by Fe(II) under acidic conditions, resulting in the enhanced abatement of organic contaminants, with the decay ratios of the selected pollutants even exceeding those in the Fe(II)/peroxymonosulfate (PMS) and Fe(II)/peroxydisulfate (PDS) processes under identical conditions. Thus, we are inspired to use Fe(II)-activated KIO₄ oxidation to degrade EPS in this work, aiming to improve the dewaterability of WAS. To our best knowledge, Fe(II)-activated KIO₄ oxidation with regards to EPS degradation has not yet been reported.

As a new strategy to improve sludge dewaterability, there are two reasons for requiring an in-depth and systematic study. One point is the optimal operational conditions of the Fe(II)/KIO₄ oxidation system. Operational conditions influence the oxidation extent of the EPS, which is directly related to sludge dewatering performance. It is known that
increasing oxidation capability promotes the degradation of the EPS. However, it is a misconception that the more the EPS degrades, the better the sludge dehydration performs. For instance, Yu et al. [6] has corroborated that hydroxylamine enhanced the Fenton (Fenton-HA) system which elevated the oxidation capability, whereas it also deteriorated sludge dewaterability. Thus, determining the optimal operational condition is of great significance. The other reason is the underlying mechanism responsible for EPS degradation in a Fe(II)/KIO₄ oxidation matrix. From the literatures, reactive species, such as iodyl (•IO₃), •OH, superoxide anion (•O₂⁻), singlet oxygen (¹O₂), and Fe(IV), may be generated during KIO₄ oxidation. Lee et al. [25] attributed KIO₄ oxidation on sludge EPS to •IO₃ and •OH. Differently, •IO₃ was excluded as a reactive species in the Fe(II)/KIO₄ process by Zong et al. [17]. Bokare and Choi [26] declared the generation of ¹O₂ in an alkaline KIO₄ solution and monitored the reactivity of ¹O₂ in furfuryl alcohol degradation. Wang et al. [16] reported that ¹O₂ is the dominant free radical in the treatment of bisphenol AF by the FeS activated KIO₄ system. However, the role of ¹O₂ in organic degradation is still quite controversial [27,28]. Noteworthily, Zong et al. [17] demonstrated that high-spin Fe(IV) and its accompanying •OH accounted for the rapid removal of emerging contaminants in Fe(II)/KIO₄ system. Altogether, it can be concluded that the reactive species and their roles vary under different circumstances. An in-depth understanding of the reactive species involved can provide implications for optimizing the reaction conditions. Furthermore, the underlying mechanism of Fe(II)-activated KIO₄ oxidation for sludge dewaterability improvement needs to be clarified.

It is worth noting that although both this study and the research by Zong et al. [17] adopted Fe(II)-activated KIO₄ oxidation to degrade organic matters, their application circumstances are different, i.e., one is for abatement of organic contaminants in acidic solutions, and the other is for degradation of EPS in sludge matrices. Reaction performance and mechanisms under different circumstances may be different. Moreover, achieving the highest degradation efficiency of organic matters may not mean an ideal outcome in this study. Therefore, the objectives of this study focused on (1) determining the optimal conditions (i.e., the initial pH, molar ratio of Fe(II) to KIO₄, and KIO₄ concentration) for sludge dewatering enhancement in an Fe(II)/KIO₄ system, and (2) elucidating the underlying mechanism by which WAS dewaterability is improved.

2. Materials and Methods

2.1. Materials

The raw sludge was obtained from a thickening tank of a sewage treatment plant located at Wenjiang district, Chengdu city, China. The raw sludge samples were stored at 4 °C before usage, and all batch experiments were completed within one week. The main properties of raw sludge are listed in Table 1.

Table 1. Characteristics of raw sludge.

| Parameter                        | Value                       |
|----------------------------------|-----------------------------|
| pH                               | 6.8 ± 0.2                   |
| Water content of filter cake (Wc, %) | 83.75 ± 0.21               |
| Total suspended solids (TSS, g/L) | 21.25 ± 0.3                 |
| Volatile suspended solid (VSS, g/L) | 8.14 ± 0.1                 |
| Specific resistance filtration (SRF) (10¹² m/kg) | 6.24 ± 0.4               |
| Zeta potential (mV)              | −10.60 ± 0.4                |
| Capillary suction time (CST) (s) | 133.35 ± 2                  |

Ferrous sulfate heptahydrate (FeSO₄·7H₂O), sodium hydroxide (NaOH), potassium sodium tartrate tetrahydrate (C₄H₄KNaO₆·4H₂O), anhydrous sodium carbonate (Na₂CO₃), copper sulfate pentahydrate (CuSO₄·5H₂O), potassium bromide (KBr), sulfuric acid (H₂SO₄), glucose (C₆H₁₂O₆), tert-butyl alcohol (TBA), phenol, and sodium acetate (CH₃COONa) were purchased from Chengdu Kelong Chemical Reagent Co., Ltd. (Sichuan, China). Potas-
sium periodate (KIO₄), bovine albumin (BSA), Folin–phenol reagent, ascorbic acid (AA), L-histidine, nitro blue tetrazolium chloride (NBT), phenol, and methanol (MeOH) were obtained from Shanghai Aladdin Biological Technology Co., Ltd. (Shanghai, China). All chemicals were analytically pure and used without further purification.

2.2. Experimental Design

Fe(II)/KIO₄ oxidation was designed to improve the dewaterability of WAS. A series of batch tests were carried out in 300 mL beakers. The beaker was continuously stirred in a thermostatic magnetic stirrer at 25 °C and 150 rpm. CST, SRF, and W_C were selected as representative indicators for sludge dewatering performance. To explore the effect of the initial pH on the sludge dewatering performance, the initial pH was adjusted to 3.0, 4.0, 5.0, 6.8, 8.0, and 9.0 while keeping the KIO₄ dose (at 1.4 mmol/g VSS) and Fe(II)/KIO₄ molar ratio (1.2) unchanged. Similarly, with the Fe(II)/KIO₄ molar ratio fixed at 1.2 and the initial pH maintained at 6.8, the effect of KIO₄ dose (0.6, 0.8 1.0, 1.2, 1.4, 1.6, and 1.8 mmol/g VSS) on the sludge dewatering performance was investigated. To determine the effect of Fe(II)/KIO₄ molar ratio on the sludge dewaterability, the Fe(II)/KIO₄ molar ratio was set as 0.0, 0.3, 0.6, 0.9, 1.2, 1.5, and 1.8 under the conditions of a KIO₄ dose of 1.4 mmol/g VSS and an initial pH of 6.8. For all experiments, the reaction time lasted for 20 min. All experiments were repeated three times.

2.3. Analyses

2.3.1. Determination of Sludge Dewaterability

SRF and CST are both evaluation indexes of sludge filtration and dewatering performance, while W_C is an index reflecting the effectiveness of sludge dewatering. The smaller the values of SRF, CST and W_C, the better the dewatering and filtration performance of the sludge. The CST of sludge was measured by CST instrument (DP-MT) equipment. The SRF was measured by the vacuum filtration method: the Buchner funnel was filled with the sludge suspension of 100 mL, and a constant pressure of 0.06 MPa was applied using a vacuum pump. First, start the stopwatch then, when the filtration starts, the corresponding filtration volume in the measuring cylinder is recorded every 10 s. As the filtration speed slows down, the interval time of the record is increased, and the filter volume is recorded every 1 min. The filtration was stopped when there was no filter drop. The vacuum valve needs to be continuously adjusted throughout the experiment to ensure that the experimental pressure is constant. The SRF (m/kg) of the sludge was calculated by Equation (1) [29]:

\[
SRF = \frac{2PA^2b}{(\mu\omega)}
\]  

where \(P\) (kg/m²) is the pressure applied; \(A\) (m²) is the filter area; \(\mu\) (kg·s/m²) is the KV, \(\omega\) (kg/m³) denotes dry solid weight per unit volume sludge on the filtrate media; and \(b\) is the time-to-filtration ratio, which is the slope of the curve that is obtained by plotting the ratio of the time of filtration to the volume of filtrate (\(t/V\)) versus the filtrate volume (\(V\)).

W_C obtained during SRF test was determined by standard methods [30].

2.3.2. Sludge Properties

The pH value was measured with a pH meter (pHs-3C). Particle size and particle size distribution were determined by a laser particle size analyzer (Malvern Master size 2000). The Zeta potential of the sludge supernatant was measured using a Malvern potential analyzer (Malvern Zeta sizer Nano ZS90). In addition, the physical surface morphology changes of sludge flocs samples were observed by a scanning electron microscope (SEM) (ZEISS Sigma 300). The surface functional groups of sludge flocs were determined by Fourier transform infrared spectroscopy (FT-IR) (Nicolet IS5, Thermo Fisher Scientific, Waltham, MA, USA).

EPS extraction was conducted according to a thermal extraction method [31]. A concise description is as follows: A 15 mL sludge sample was centrifuged at 4000 × g at 4 °C for 15 min. The supernatant was collected and denoted SB-EPS. The pellet was resuspended
in 15 mL of 0.05% NaCl using a vortex mixer, heated at 70 °C for 1 min, and subsequently centrifuged at 4000 × g at 4 °C for 10 min. The collected supernatant was considered LB-EPS. The residual pellet was resuspended in a 0.05% NaCl solution to its original volume, incubated at 60 °C in a water bath for 30 min, and centrifuged at 4000 × g at 4 °C for 15 min to collect TB-EPS. The protein and polysaccharide concentration in EPS were determined using the Lowry method or the phenol-sulfuric acid method [32].

3. Results and Discussion
3.1. Optimization of Sludge Dewatering Conditions
3.1.1. Effects of Initial pH on Sludge Dewaterability

The initial pH value always plays a key role in AOPs, which will affect the sludge dewaterability adjustment by Fe(II) activated KIO₄ oxidation. Figure 1 depicts the effects of the initial pH on the performance indices of sludge dewatering.

![Figure 1](image-url)

**Figure 1. Cont.**
which increase the viscosity of sludge and affect its filtration ability. As a result, sludge (Figure 1b), and 83.75% (Figure 1c), respectively. Interestingly, as the initial pH decreased from 6.8 to 3.0, the CST, SRF, and $W_C$ increased to 101.65 s, $4.05 \times 10^{12} \text{ m/kg}$, and 84.47%, respectively, which signified deterioration in the sludge dewaterability. As it is known that a lower pH in AOPs always results in a higher production of active species, and, consequently, a higher degradation of organic contaminants. During recent decades, EPS has been reckoned as a key factor in hampering sludge dewatering. Many studies endeavored to degrade EPS as much as possible so as to improve sludge dewaterability. However, in this study, more degradation of EPS at an initial pH lower than 6.8 exhibited negative effects on sludge dewaterability. A plausible explanation is the layered structure of EPS and its hydrophilic/hydrophobic characteristics. As Yu et al. [6] reported, EPS were degraded layer by layer in sludge oxidation, and different EPS layers showed quite different hydrophilic/hydrophobic organic distributions. The surface EPS layer possesses a relatively higher hydrophobicity, whereas the inner EPS layer has a relatively higher hydrophilicity. Excessive destruction of the surface hydrophobic EPS and exposure of the inner hydrophilic EPS elevated the energy barrier among sludge flocs, which increased the bound water content of the sludge and resultantly deteriorated the sludge dewaterability [6,33,34]. While increasing the initial pH from 6.8 to 9.0, the sludge dewatering performance also showed a downward trend. The CST, SRF, and $W_C$ increased to 107.25 s, $3.61 \times 10^{12} \text{ m/kg}$, and 84.25%, respectively. This can be explained as follows: In alkaline conditions, Fe(II) easily reacts with OH$^-$ and reduces the amount of effective activator in the reaction system. Moreover, Fe$^{2+}$ and Fe$^{3+}$ react easily with OH$^-$ to form Fe(OH)$_2$ and Fe(OH)$_3$ colloids, which increase the viscosity of sludge and affect its filtration ability. As a result, sludge dewatering becomes more difficult [32]. To sum up, an initial pH that is too low or too high is not conducive to improving the sludge dewaterability, and the initial pH of 6.8 is optimal. This result implied that there is no need to adjust the initial pH during sludge conditioning by Fe(II)/KIO$_4$ oxidation.

### 3.1.2. Effects of KIO$_4$ Dose on Sludge Dewaterability

Figure 2 shows the effects of KIO$_4$ dose pH on performance indices of sludge dewatering.

**Figure 1.** Effect of initial pH on performance indices ((a) CST, (b) SRF, and (c) $W_C$) of sludge dewatering. Conditions: KIO$_4$ dose = 1.4 mmol/g VSS; Fe(II)/KIO$_4$ molar ratio = 1.2.
Figure 2. Effect of KIO₄ dose on performance indices of sludge dewatering. (a) CST, (b) SRF, and (c) WC. Conditions: Initial pH = 6.8; Fe(II)/KIO₄ molar ratio = 1.2.

With the KIO₄ dose increased from 0.6 to 1.4 mmol/g VSS, the CST, SRF, and WC obviously decreased from 88.95 s, 4.14 × 10¹² m/kg and 87.43%, to 47.55 s, 0.99 × 10¹² m/kg and 86.98%.
With the KIO$_4$ dose increased from 0.6 to 1.4 mmol/g VSS, the CST, SRF, and $W_C$ obviously decreased from 88.95 s, $4.14 \times 10^{12} \text{ m/kg}$ and 87.43%, to 47.55 s, $0.99 \times 10^{12} \text{ m/kg}$ and 83.75%, respectively. This implied that more reactive species were generated with the increase in KIO$_4$ dose, which led to an enhanced oxidation of sludge flocs [13]. As the KIO$_4$ dose further increased to 1.8 mmol/g VSS, CST and SRF increased instead; meanwhile, $W_C$ maintained stable. On the one hand, an excess of IO$_4^-$ will react with reactive free radicals (Equation (2)) [35]. On the other hand, due to the decrease in flocculation activity of overoxidized sludge, the sludge filterability is reduced and the dehydration is deteriorated [36].

$$\text{IO}_4^- + \cdot\text{OH} \rightarrow \text{OH}^- + \cdot\text{IO}_4^-$$  \hspace{1cm} (2)

### 3.1.3. Effects of Fe(II)/KIO$_4$ Molar Ratio on Sludge Dewaterability

Figure 3 describes the effects of Fe(II)/KIO$_4$ molar ratio on performance indices of sludge dewatering.

![Figure 3](image-url).
which boosted the coagulation of sludge flocs and significantly improved the dewatering performance of sludge. The increase in Zeta potential may be ascribed to the decomposition of negatively charged organic matter in sludge EPS and neutralization of negative charges by positive-charged iron ions.

As the Fe(II)/KIO₄ molar ratio increased from 0 to 1.2, the CST, SRF, and Wc obviously decreased from 133.35 s, 6.24 × 10¹² m/kg and 89.75%, to 47.55 s, 0.99 × 10¹² m/kg and 83.75%, respectively. The reason for the improvement of sludge dewatering performance is that Fe²⁺, as an initiator, activates IO₄⁻ to generate free radicals, which accelerates the disintegration of sludge flocs. When the Fe(II)/KIO₄ molar ratio was lower than 1.2, insufficient ferrous ions were not capable of forming enough reactive species and, therefore, the oxidation of sludge flocs was greatly limited [37]. Whereas Fe(II)/KIO₄ molar ratio exceeded 1.2, the dewatering performance of the sludge became poor, which was mainly due to the fact that the excess ferrous consumed the reactive species produced. For instance, excessive Fe(II) would result in a competitive consumption of Fe(IV) \( k_{(Fe(IV)+Fe(II))} = 1.4 × 10^5 \text{ M}^{-1} \text{ s}^{-1} \) [17].

3.2. Effects of Fe(II)/KIO₄ Process on Sludge Properties

3.2.1. Zeta Potential and Particle Size Distribution

Zeta potential can reflect the stability of the sludge colloid matrix to a certain extent and, therefore, is listed as one of the key indicators to evaluate the dewatering performance of sludge [38].

As shown in Figure 4a, the Zeta potential of raw sludge was −10.60 mV, which was due to the existence of carboxylic acid and phosphate groups in the EPS [39]. As a comparison, the Zeta potential of the sludge treated by KIO₄ alone changed to −11.92 mV, which brought about an increased electrostatic repulsion and, hence, was detrimental to the improvement of dewatering performance. After treatment with ferrous iron alone, the Zeta potential increased to −7.91 mV, which may be caused by the neutralization of negative charges incurred by Fe²⁺ and its oxidation product (Fe³⁺). Meanwhile, the Zeta potential of the sludge treated by the Fe(II)/KIO₄ oxidation system increased to −1.87 mV, which boosted the coagulation of sludge flocs and significantly improved the dewatering performance of sludge. The increase in Zeta potential may be ascribed to the decomposition of negatively charged organic matter in sludge EPS and neutralization of negative charges by positive-charged iron ions.

The particle size is usually considered another key factor affecting sludge dewatering. As displayed in Figure 4b, the medium value of particle size \( D_{50} \) of sludge flocs was reduced from 52.85 to 51.08 μm after treatment by KIO₄ alone. The reduction in \( D_{50} \) can be explained by the release of some hydrophilic groups in the sludge EPS subjected to
Int. J. Environ. Res. Public Health 2022, 19, x FOR PEER REVIEW 9 of 18

... of N-H and C-N on amide II in the protein is related to the peak near 1533 cm−1. The peaks near 1401 cm−1, 1235 cm−1, 1170 cm−1 and 3164 cm−1 are related to the symmetric and asymmetric stretching vibrations of CH3 in lipids. The amide I band at 1657 cm−1 is mainly related to C=O and C-N stretching associated with proteins. The swelling vibration of N-H and C-N on amide II in the protein is related to the peak near 1533 cm−1. The peaks near 1401 cm−1, 1235 cm−1, and 1035 cm−1, corresponds to the bending vibration and C-O stretching vibration in the face of phenolic O-H, the asymmetric stretching vibration of C-O-C in ester, and the stretching vibration of C-O in polysaccharide, respectively [41]. As presented in Figure 5b, after treatment by Fe(II)/KIO4, the peak at 1235 cm−1 almost disappeared, suggesting the

3.2.2. FT-IR Spectra and SEM Analyses

To further understand the impact of Fe(II)/KIO4 oxidation on sludge dewaterability, the changes in functional groups on sludge flocs were analyzed by FT-IR spectra.

As exhibited in Figure 5a, the peaks around 3415 cm−1 and 3164 cm−1, correspond to O-H stretching vibrations (mainly present in polysaccharides and phenols [40]). The peaks around 2926 cm−1 and 2852 cm−1, are related to the symmetric and asymmetric stretching vibrations of CH3 in lipids. The amide I band at 1657 cm−1 is mainly related to C=O and C-N stretching associated with proteins. The swelling vibration of N-H and C-N on amide II in the protein is related to the peak near 1533 cm−1. The peaks near 1401 cm−1, 1235 cm−1, and 1035 cm−1, corresponds to the bending vibration and C-O stretching vibration in the face of phenolic O-H, the asymmetric stretching vibration of C-O-C in ester, and the stretching vibration of C-O in polysaccharide, respectively [41]. As presented in Figure 5b, after treatment by Fe(II)/KIO4, the peak at 1235 cm−1 almost disappeared, suggesting the

Figure 4. Variations of (a) Zeta potential and (b) particle size distribution of sludge flocs after treatment by different processes. Conditions: Initial pH = 6.8; KIO4 dose = 1.4 mmol/g VSS, Fe(II) dose = 1.68 mmol/g VSS.

![Figure 4](https://example.com/figure4.png)
decomposition of the corresponding organic matter. Meanwhile, the relative intensities of typical peaks located around 1657 cm\(^{-1}\), 1533 cm\(^{-1}\), and 1035 cm\(^{-1}\), decreased, indicating that proteins and polysaccharides on the surface of sludge flocs were partly degraded.

![Figure 5. FT-IR spectra of (a) raw sludge and (b) sludge treated by Fe(II)/KIO\(_4\) process. Conditions: Initial pH = 6.8, KIO\(_4\) dose = 1.4 mmol/g VSS, Fe(II)/KIO\(_4\) molar ratio = 1.2.](image)

To intuitively analyze the influence of sludge treatment on the structure of sludge flocs, SEM analyses were conducted. As shown in Figure 6a, the raw sludge flocs were dense with few pores. This structural characteristic was embodied with low porosity and few filter channels. As a result, water is difficult to separate from the sludge [42]. Therefore, the SRF and CST of raw sludge were maintained at a high level. After treatment by the Fe(II)/KIO\(_4\) process, the dense structure of the sludge flocs transformed to become loose and porous (Figure 6b). The sludge drainage passages for more water permeation were thus reconstructed, which was in favor of promotion of sludge filterability [39,43].

![Figure 6. SEM of (a) raw sludge and (b) treated sludge. Conditions: Initial pH = 6.8, KIO\(_4\) = 1.4 mmol/g VSS, Fe(II)/KIO\(_4\) molar ratio = 1.2.](image)
3.2.3. Polysaccharide and Protein in EPS

EPS consists of high hydrophilic substances, and those substances mainly include proteins and polysaccharides [6]. EPS is highly charged polymers that interact with water molecules to form gels, which can be divided into three parts from outside to inside, namely, the soluble EPS (S-EPS), the loosely bound EPS (LB-EPS), and the tightly bound EPS (TB-EPS) [44]. The S-EPS is weakly bound to cells or dissolved in solutions. The LB-EPS is a loose slime layer without an obvious end. The TB-EPS is bound to the cell surface tightly and stably [45].

As shown in Figure 7, for raw sludge, the proteins concentrations in S-EPS, LB-EPS, and TB-EPS were 53.85, 161.21, and 690.56 mg/L, respectively. In regard to the treated sludge, the proteins concentration in S-EPS greatly increased to 158.85 mg/L, whereas the protein concentration in TB-EPS sharply decreased to 395.26 mg/L. This result indicated that LB-EPS was transformed into S-EPS. Similarly, it has been reported that the oxidative dissolution of EPS leads to the gradual transformation of TB-EPS to LB-EPS and subsequently to S-EPS, and the increased protein content in SB-EPS improved sludge dewatering [46,47]. As a whole, the concentration of proteins in EPS of treated sludge showed a 21.5% decline in comparison to that of raw sludge. In this study, along with the degradation of proteins, the CST and SRF decreased. This result was parallel to the finding by Wang et al. [48], who reported that proteins (including aromatic protein substances and tryptophan protein substances) are negatively correlated with sludge dewaterability. Moreover, the degradation of protein-like substances has been proven to be the key organics benefitting the improvement in sludge dewaterability [49,50].

In addition, the concentration of polysaccharides in the EPS of treated sludge exhibited a slight increase instead of decrease, which is in accordance with Liu et al. [32], who concluded that polysaccharides showed little influence on sludge dewaterability in comparison with proteins while pretreating WAS by Fe(II)-activated PMS oxidation. Similarly, Wu et al. [51] reported that high hydrophilic proteins played a more important role in sludge dewaterability than polysaccharides.
3.3. Reactive Species

The identification of reactive species is of great importance to understand the underlying mechanism of the Fe(II)/KIO₄ process. The possible reactive species include •OH, singlet oxygen (¹O₂), superoxide anion radical (•O₂⁻), iodate radical (•IO₃), and Fe(IV) [12,17]. It has been reported that ascorbic acid (AA) has the ability of non-selective scavenging free radicals, which can be used to preliminarily test whether radical species were generated in the reaction system [52]. Moreover, TBA [53], L-histidine [54], NBT, and phenol [19] have been proven to possess strong scavenging ability on •OH, ¹O₂, •O₂⁻, and •IO₃, respectively. Therefore, AA, TBA, L-histidine, NBT, and phenol were used in this study to identify and differentiate free radicals. Significantly, Zong et al. [17] have provided conclusive evidence for the generation of high-valent iron oxo species (Fe(IV)) in the Fe(II)/KIO₄ process. In more detail, Fe(H₂O)⁶²⁺ first reacts with IO₄(H₂O)⁻ to generate a hydrogen bonding complex Fe(H₂O)⁶²⁺IO₄(H₂O)⁻ (INT1) (Equation (3)); then, one of the six H₂O molecules that are originally coordinated with Fe²⁺ is exchanged by IO₄⁻ to form an inner shell complex Fe(H₂O)⁶²⁺–IO₃(H₂O)⁻ (INT2) (Equation (4)); and thereafter INT2 undergoes an oxygen atom transfer step to consequently produce Fe=O(H₂O)⁴²⁺IO₃(H₂O)⁻ (i.e., Fe(IV) and IO₃⁻) (Equation (5)). Note that Fe(IV) undergoes self-decay and subsequently generates H₂O₂ and Fe(III) (Equation (6)) [55]; thus, •OH can be considered to be indirectly triggered by the self-decomposition of Fe(IV) and the subsequent Fenton reaction (Equation (7)). In addition, it is inferred that •O₂⁻ was generated according to Equation (8). As depicted in Figure 8, the values of three indices (i.e., CST, SRF, and W_C) increased with the addition of AA, indicating that radical species were involved in this system. After the addition of TBA, the values of the three indices also greatly increased, suggesting that scavenging of •OH produced in the Fe(II)/KIO₄ process worsened the sludge dewaterability. It was noteworthy that the additions of NBT and phenol had a slight impact on sludge dewatering performance, indicating that •O₂⁻ and •IO₃ played a small role. In fact, the redox potential of •O₂⁻ is only −0.28 V [56,57], and its oxidative contribution to the degradation of sludge EPS was thus expected to be negligible [58]. Moreover, •IO₃ was excluded as a reactive species in the Fe(II)/KIO₄ process [17]. The seemingly quenching effect that arose from the addition of phenol may be ascribed to the adverse impact of phenol on other reactive species. In regards to the addition of L-histidine, its effect on sludge dewaterability was slightly more obvious compared to the additions of NBT and phenol. However, ¹O₂ was excluded as a reactive species in the Fe(II)/KIO₄ process based on irreputable proofs [17]. Herein, whether L-histidine will react with Fe(IV) or KIO₄ and resultantly poses negative influence on the oxidizing power of Fe(IV) or the generation of •OH merits further investigations.

In summary, the mechanism of sludge EPS degradation by Fe(II)/KIO₄ oxidation under optimal conditions was proposed to consist of the reactions shown in Equations (3)–(11) [17]:

\[
\begin{align*}
\text{Fe(H}_2\text{O)}_6^{2+} + \text{IO}_4(\text{H}_2\text{O})^- &\rightarrow \text{Fe(H}_2\text{O)}_6^{2+}\text{IO}_4(\text{H}_2\text{O})^- \quad \text{(3)} \\
\text{Fe(H}_2\text{O)}_6^{2+}\text{IO}_4(\text{H}_2\text{O})^- &\rightarrow \text{Fe(H}_2\text{O)}_5^{2+}\text{–IO}_3(\text{H}_2\text{O})^- \quad \text{(4)} \\
\text{Fe(H}_2\text{O)}_5^{2+}\text{–IO}_3(\text{H}_2\text{O})^- &\rightarrow \text{Fe(IV)} + \text{IO}_3^- \quad \text{(5)} \\
2\text{Fe(IV)} &\rightarrow 1/3\text{H}_2\text{O}_2 + 2\text{Fe(III)} + 1/3\text{O}_2 \quad \text{(6)} \\
\text{Fe(II)} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe(III)} + \cdot\text{OH} + \text{OH}^- \quad \text{(7)} \\
\text{Fe(II)} + \text{IO}_4^- + \text{H}_2\text{O} &\rightarrow \text{Fe(III)} + \text{IO}_3^- + \cdot\text{O}_2^- + 2\text{H}^+ \quad \text{(8)} \\
\text{Fe(IV)} + \text{EPS} &\rightarrow \text{degradation products} + \text{Fe(III)} \quad \text{(9)} \\
\cdot\text{OH} + \text{EPS} &\rightarrow \text{degradation products} \quad \text{(10)}
\end{align*}
\]
Taking the effects of initial pH, KIO₄ dose, and Fe(II)/KIO₄ molar ratio on sludge dewaterability into comprehensive considerations, the optimal conditions are as follows: the initial pH = 6.8, the KIO₄ dose = 1.4 mmol/g VSS, and the Fe(II)/KIO₄ molar ratio = 1.2. Compared to those of the untreated raw sludge, the CST (47.55 s) decreased by 64.34%, SRF (0.99 × 10¹² m/kg) decreased by 84.13%, and Wc (83.75%) decreased by 6.69% under the optimal conditions. It can be concluded that the dewaterability of WAS can be effectively improved by Fe(II)/KIO₄ oxidation. As for the underlying mechanism, the role of Fe(IV) as a reaction intermediate needs to be emphasized. Although the reactivity of Fe(IV) toward organics is generally weaker than that of radical species (i.e., •OH and SO₄•−), the steady-state concentration of Fe(IV) (∼10⁻⁷ M) could be several orders of magnitude higher than those of •OH and SO₄•− (∼10⁻¹² M). By in situ generating the high-spin Fe(IV) species and accompanying •OH, the Fe(II)/KIO₄ process could achieve a better performance on the degradation of representative pollutants in comparison with the Fe(II)/PMS and Fe(II)/PDS processes [17]. In this work, no comparisons in terms of EPS degradation degree between Fe(II)/KIO₄ and Fe(II)/PMS or Fe(II)/PDS were conducted; hence, we cannot claim that Fe(II)/KIO₄ has a higher oxidizing capacity towards EPS. Additionally, excessive degradation of EPS may instead deteriorate the sludge dewatering performance [6]. It can be inferred that the Fe(II)/KIO₄ process achieved a moderate degree of oxidation towards sludge EPS under the optimal conditions. Apart from the effectiveness in improving sludge dewatering performance, the Fe(II)/KIO₄ process has other attractive advantages. Compared with liquid-form oxidants (e.g., H₂O₂, hypochlorous acid, and peracetic acid), KIO₄, as a solid-form oxidant, is relatively stable and carries less risk during transport and storage. More importantly, there is no requirement for regulation of the initial pH, which can reduce the consumption of agents and simplify the operation. Attributed to the abovementioned advantages, Fe(II)-activated KIO₄ oxidation has great prospect and practical value in sludge conditioning for dewatering.

![Figure 8. CST, SRF, and Wc under the cases of using different quenchers. Optimal conditions: Initial pH = 6.8, KIO₄ dose = 1.4 mmol/g VSS, Fe(II)/KIO₄ molar ratio = 1.2. Radical scavenger usages: 50 mM ascorbic acid, 50 mM L-histidine, 60 mM TBA, 70 mM phenol, and 12 mM NBT, respectively.](image-url)
4. Conclusions

In this study, Fe(II)-activated KIO₄ oxidation was successfully applied to improve the sludge dewatering performance, which is closely relevant to the evolution of sludge properties. Under the optimal conditions, the CST can decrease by 64.34%, SRF can be reduced by 84.13%, and W_C can be lowered by 6.69%. A moderate degree of oxidation towards sludge EPS is crucial for enhancing sludge dewaterability. Herein, regulation of the initial pH of raw sludge is not essential, contributing to less consumption of agents and a simpler operation. High hydrophilic proteins played a major role, whereas polysaccharides played a negligible part in sludge conditioning. In situ generated Fe(IV) should receive special attention, not only due to its own oxidation capacity, but also due to its self-decay that can trigger the generation of •OH. Fe(IV) and accompanying •OH are predominant reactive species responsible for the oxidation of EPS. This work proposes a facile strategy to improve the sludge dewaterability.

Author Contributions: Conceptualization, H.X. and H.P.; methodology, Y.W. and H.P.; software, D.F. and G.W.; validation, Y.Z. and H.P.; formal analysis, H.X., Y.W. and Z.Z.; investigation, Q.L. and Y.Z.; resources, Y.W.; data curation, Y.W.; writing—original draft preparation, Q.L.; writing—review and editing, H.X.; visualization, G.W. and Q.L.; supervision, Y.W.; project administration, Z.Z.; funding acquisition, Z.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the National Natural Science Foundation of China (22106063).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare that they have no known competing financial interest or personal relationships that could have influenced the work reported in this paper.

References

1. Cao, B.; Zhang, W.; Du, Y.; Wang, R.; Usher, S.P.; Scales, P.J.; Wang, D. Compartmentalization of extracellular polymeric substances (EPS) solubilization and cake microstructure in relation to wastewater sludge dewatering behavior assisted by horizontal electric field: Effect of operating conditions. *Water Res.* 2018, 130, 363–375. [CrossRef] [PubMed]

2. Lin, F.; Zhu, X.; Li, J.; Yu, P.; Luo, Y.; Liu, M. Effect of extracellular polymeric substances (EPS) conditioned by combined lysozyme and cationic polyacrylamide on the dewatering performance of activated sludge. *Chemosphere* 2019, 235, 679–689. [CrossRef] [PubMed]

3. Lan, B.; Jin, R.; Liu, G.; Dong, B.; Zhou, J.; Xing, D. Improving waste activated sludge dewaterability with sodium periodate pre-oxidation on extracellular polymeric substances. *Water Environ. Res.* 2021, 93, 1680–1689. [CrossRef] [PubMed]

4. Liu, Y.; Fang, H.H.P. Influences of extracellular polymeric substances (EPS) on flocculation, settling, and dewatering of activated sludge. *Crit. Rev. Environ. Sci. Technol.* 2003, 33, 237–273. [CrossRef]

5. Guo, J.; Gao, Q.; Chen, Y.; He, Q.; Chen, W. 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. Environ. Manag.* 2021, 288, 112476. [CrossRef]

6. Yu, W.; Wen, Q.; Yang, J.; Xiao, K.; Zhu, Y.; Tao, S.; Liang, S.; Hu, S.; Wu, Q.; Hou, H.; et al. Novel insights into extracellular polymeric substance degradation, hydrophilic/hydrophobic characteristics, and dewaterability of waste activated sludge pretreated by hydroxylamine enhanced Fenton oxidation. *ACS EST Eng.* 2021, 1, 385–392. [CrossRef]

7. Shi, Y.; Yang, J.; Yu, W.; Zhang, S.; Liang, S.; Song, J.; Xu, Q.; Ye, N.; He, S.; Yang, C.; et al. Synergetic conditioning of sewage sludge via Fe²⁺/persulfate and skeleton builder: Effect on sludge characteristics and dewaterability. *Chem. Eng. J.* 2015, 270, 572–581. [CrossRef]

8. Ismail, L.; Ferronato, C.; Fine, L.; Jaber, F.; Chovelon, J.-M. Elimination of sulfacetazine from water with SO₄•− radicals: Evaluation of different persulfate activation methods. *Appl. Catal. B Environ.* 2017, 201, 579–581. [CrossRef]

9. Wei, X.; Gao, N.; Li, C.; Deng, Y.; Zhou, S.; Li, L. Zero-valent iron (ZVI) activation of persulfate (PS) for oxidation of bentazon in water. *Chem. Eng. J.* 2016, 285, 660–670. [CrossRef]

10. Ahmed, M.M.; Barbati, S.; Doumeng, P.; Chiron, S. Sulfate radical anion oxidation of diclofenac and sulfamethoxazole for water decontamination. *Chem. Eng. J.* 2012, 197, 440–447. [CrossRef]

11. Liang, H.-y.; Zhang, Y.-q.; Huang, S.-b.; Hussain, I. Oxidative degradation of p-chloroaniline by copper oxide activated persulfate. *Chem. Eng. J.* 2013, 218, 384–391. [CrossRef]
12. Djaballah, M.L.; Merouani, S.; Bendjama, H.; Hamdaoui, O. Development of a free radical-based kinetics model for the oxidative degradation of chlorazol black in aqueous solution using periodate photovolatized process. *J. Photochem. Photobiol. A Chem.* 2020, 408, 113102. [CrossRef]

13. Du, J.; Xiao, G.; Xi, Y.; Zhu, X.; Su, F.; Kim, S.H. Periodate activation with manganese oxides for sulfanilamide degradation. *Water Res.* 2020, 169, 115278. [CrossRef] [PubMed]

14. Sun, H.; He, F.; Choi, W. Production of reactive oxygen species by the reaction of periodate and hydroxylamine for rapid removal of organic pollutants and waterborne bacteria. *Environ. Sci. Technol.* 2020, 54, 6427–6437. [CrossRef]

15. He, L.; Lv, L.; Pillai, S.C.; Wang, H.; Yang, L. Efficient degradation of diclofenac sodium by periodate activation using Fe/cu bimetallic modified sewage sludge biochar/UV system. *Sci. Total Environ.* 2021, 783, 146974. [CrossRef]

16. Wang, Q.; Zeng, H.; Liang, Y.; Cao, Y.; Xiao, Y.; Ma, J. Degradation of bisphenol AF in water by periodate activation with FeS (mackinawite) and the role of sulfur species in the generation of sulfate radicals. *Chem. Eng. J.* 2021, 407, 126738. [CrossRef]

17. Zong, Y.; Shao, Y.; Zeng, Y.; Shao, B.; Xu, L.; Zhao, Z.; Liu, W.; Wu, D. Enhanced oxidation of organic contaminants by iron(II)-activated periodate: The significance of high-valent iron-oxo species. *Environ. Sci. Technol.* 2021, 55, 7634–7642. [CrossRef]

18. Guo, D.; Yao, Y.; You, S.; Jin, L.; Lu, P.; Liu, Y. Ultrastable degradation of micropollutants in water via electro-periodate activation catalyzed by nanoflakes Fe₃O₄. *Appl. Catal. B Environ.* 2022, 309, 121289. [CrossRef]

19. He, L.; Shi, Y.; Chen, Y.; Shen, S.; Xue, J.; Ma, Y.; Zheng, L.; Wu, L.; Zhang, Z.; Yang, L. Iron-manganese oxide loaded sludge biochar as a novel periodate activator for thiocloripid efficient degradation over a wide pH range. *Sep. Purif. Technol.* 2022, 288, 120703. [CrossRef]

20. He, L.; Yang, C.; Ding, J.; Lu, M.-Y.; Chen, C.-X.; Wang, G.-Y.; Jiang, J.-Q.; Ding, L.; Liu, G.-S.; Ren, N.-Q.; et al. Fe, N-doped carbonaceous catalyst activating periodate for micropollutant removal: Significant role of electron transfer. *Appl. Catal. B: Environ.* 2022, 303, 120880. [CrossRef]

21. He, L.; Yang, S.; Shen, S.; Ma, Y.; Chen, Y.; Xue, J.; Wang, J.; Zheng, L.; Wu, L.; Zhang, Z.; et al. Novel insights into the mechanism of periodate activation by heterogeneous ultrasonic-enhanced sludge biochar: Relevance for efficient degradation of levofloxacin. *J. Hazard. Mater.* 2022, 434, 128860. [CrossRef]

22. Li, R.; Wang, J.; Wu, H.; Zhu, Z.; Guo, H. Periodate activation for degradation of organic contaminants: Processes, performance and mechanism. *Sep. Purif. Technol.* 2022, 292, 120928. [CrossRef]

23. Ling, C.; Wu, S.; Han, J.; Dong, T.; Zhu, C.; Li, X.; Xu, L.; Zhang, Y.; Zhou, M.; Pan, Y. Sulfide-modified zero-valent iron activated periodate for sulfadiazine removal: Performance and dominant routine of reactive species production. *Water Res.* 2022, 220, 118676. [CrossRef] [PubMed]

24. Yang, L.; He, L.; Ma, Y.; Wu, L.; Zheng, L.; Wang, J.; Chen, Y.; Li, Y.; Zhang, Z. Periodate-based oxidation focusing on activation, multivariate-controlled performance and mechanisms for water treatment and purification. *Sep. Purif. Technol.* 2022, 289, 120746. [CrossRef]

25. Lee, H.; Yoo, H.-Y.; Choi, J.; Nam, I.-H.; Lee, S.; Lee, S.; Kim, J.-H.; Lee, C.; Lee, J. Oxidizing Capacity of Periodate Activated with Iron-Based Bimetallic Nanoparticles. *Environ. Sci. Technol.* 2014, 48, 8086–8093. [CrossRef] [PubMed]

26. Bokare, A.D.; Choi, W. Singlet-oxygen generation in alkaline periodate solution. *Environ. Sci. Technol.* 2015, 49, 14392–14400. [CrossRef] [PubMed]

27. Lu, X.; Qu, W.; Ma, J.; Xu, H.; Wang, D.; Cheng, H.; Zhang, W.; He, X. The overestimated role of singlet oxygen for pollutants degradation in some non-photocatalytic systems. *Chem. Eng. J.* 2020, 401, 126128. [CrossRef]

28. Lee, J.; von Gunten, U.; Kim, J.-H. Persulfate-Based Advanced Oxidation: Critical Assessment of Opportunities and Roadblocks. *Environ. Sci. Technol.* 2020, 54, 3064–3081. [CrossRef] [PubMed]

29. Lu, M.C.; Lin, C.J.; Liao, C.H.; Huang, R.Y.; Ting, W.P.; Dewatering of activated sludge by Fenton’s reagent. *Adv. Environ. Res.* 2003, 7, 667–670. [CrossRef]

30. APHA. *Standard Methods for the Examination of Water and Wastewater*, 20th ed.; American Public Health Association: Washington, DC, USA, 1998.

31. Zhou, X.; Jiang, G.; Zhang, T.; Wang, Q.; Xie, G.J.; Yuan, Z. Role of extracellular polymeric substances in improvement of sludge dewaterability through peroxidation. *Bioresour. Technol.* 2015, 192, 817–820. [CrossRef]

32. Liu, J.; Qi, Y.; Wang, D.; Li, X.; Yu, Z.; Xin, L.; Deng, Y.; Wang, L.; Yi, K.; Zeng, G. Enhanced dewaterability of waste activated sludge by Fe(II)-activated persymoxonosulfate oxidation. *Bioresour. Technol.* 2016, 206, 134–140. [CrossRef] [PubMed]

33. Kim, M.S.; Lee, K.-M.; Kim, H.-E.; Lee, H.-J.; Lee, C.; Lee, C. Disintegration of Waste Activated Sludge by Thermally-Activated Persulfates for Enhanced Dewaterability. *Environ. Sci. Technol.* 2016, 50, 7106–7115. [CrossRef] [PubMed]

34. Yu, W.; Yang, J.; Tao, S.; Shi, Y.; Yu, J.; Lv, Y.; Liang, S.; Xiao, K.; Liu, B.; Hou, H.; et al. A comparatively optimization of dosages of oxidation agents based on volatile solids and dry solids content in dewatering of sewage sludge. *Water Res.* 2017, 126, 342–350. [CrossRef] [PubMed]

35. Li, X.; Liu, X.; Qi, C.; Lin, C. Activation of periodate by granular activated carbon for acid orange 7 decolorization. *J. Taiwan Inst. Chem. Eng.* 2016, 68, 211–217. [CrossRef]

36. Yang, P.; Li, D.; Zhang, W.; Ai, J.; Peng, S.; Wang, D.; Cui, F. Study of sludge conditioning using organic acids chelated ferrous ion catalyzed NaClO oxidation: Evolution of extracellular polymeric substances and floc structure. *J. Environ. Manag.* 2021, 280, 111757. [CrossRef]
