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Roles of Fe(III) and Fe(VI) in enhancing dewaterability of sewage sludge based on floc size grading

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ABSTRACT

Ferric chloride and potassium ferrate have been proven to improve the dewaterability of sewage sludge. Flocs are flocculated by forming an $Fe(OH)_3$ colloid under the condition of ferric chloride. Furthermore, potassium ferrate can enhance dewaterability by solubilizing extracellular polymeric substances (EPS) and releasing bound water through oxidation. However, previous studies were all based on raw sludge consisting of a complex matrix, which increases the difficulty of analyzing the mechanism of a treatment. Although studies have shown that the main factors affecting the performance of dewatering are mainly related to EPS, surface charge, and particle size, they did not reveal the changes in the performance of EPS induced by ferric chloride and potassium ferrate. The primary functions of the influencing factors were also not compared. Our pre-experiments have shown that ferric chloride is more effective than potassium ferrate in improving dewaterability. To address these issues, size grading was adopted in the current study to screen raw sludge into samples with different particle sizes (0.5, 0.25, 0.1, and 0.075 mm). These samples were separately added with 4 mg/g of $FeCl_3$ or 0.2 g/L of K_2FeO_4 with pH = 4. All experimental parameters were derived from previous experimental results. Capillary suction time was used to characterize sludge dewatering. Zeta potential, particle-size distribution, Fourier transform infrared spectroscopy, and 3D excitation–emission matrix fluorescence spectroscopy were used to explore the influencing mechanisms. When conditioned by $FeCl_3$, parts of EPS were released due to the oxidability of Fe^{3+}. The floc surface charge was reduced, and the tiny particles formed large particles as a result of the flocculation of ferric iron and the small amount of soluble EPS. For samples conditioned by K_2FeO_4, EPS was dissolved, and a large amount of soluble EPS was released and further degraded. In this process, the floc surface charge decreased, and tiny particles were flocculated due to the presence of small amount of Fe^{3+}. Comparison of the experimental groups with different particle sizes showed that the flocculation of tiny particles in the sludge (<0.075 mm) improved the dewatering performance of the sludge and accounted for the superior effect of ferric chloride compared with that of potassium ferrate.

Keywords: Dewaterability; Iron compound; Particle size; Excitation–emission matrix; Tiny floc

1. Introduction

Sludge treatment and disposal pose problems in most countries. Dewatering is a key process in sludge volume reduction, transport, and ultimate disposal. Various approaches, such as thermal treatment [1], ultrasonication [2], oxidation [3–5], electrodewatering [6], flocculence [7], freezing, and thawing [8], have been developed to improve sludge dewaterability. The performance of these methods implies that solubilization and disruption of flocs improve dewaterability. Previous

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studies have focused on floc particle size, zeta potential, and extracellular polymeric substances (EPS).

Extracellular polymers are essential in the bioflocculation, settling, and dewatering of activated sludge [9,10]. EPS secreted by a multispecies community of microorganisms are the major components of sludge floc matrixes and mainly contain polysaccharide, protein, and DNA [11–13]. Increasing levels of EPS were initially believed to benefit sludge dewaterability by improving the level of sludge flocculation. This process decreases the number of small particles in the sludge, a factor that makes sludge easy to dewater. Further increase in EPS becomes detrimental to sludge dewaterability when a certain level of sludge flocculation has been attained. Sludge with a high EPS content exhibits low shear sensitivity and dispersion degree, which in turn result in improved filterability in terms of low resistance to filtration (sludge resistance filtration (SRF)). The floc-stabilizing role of EPS components is inconsistent with Boris Derjaguin and Lev Landau, Evert Verwey and Theodoor Overbeek (DLVO) theory; that is, the zeta potential increases with increasing EPS content due to the increased EPS charge content [14]. Particle-size distribution is another factor that affects sludge dewaterability. Flocculation changes the particle-size distribution of sludge and sludge dewatering characteristics by binding small particles. The zeta potential is significantly related to extracellular polymers; the decreased negative charge of the sludge reduces the repulsion forces and enhances the compaction of sludge flocs [15]. Zhang et al. [16] revealed a strong correlation between SRF and the zeta potential ($R^2 = 0.99$, $p < 0.01$).

Ferric chloride, a common conditioner with oxidizing reaction (1), has been investigated in previous research [17,18]. Our preliminary study indicated that $FeCl_3$ and steel slag effectively enhance dewaterability [19]. Potassium ferrate (K_2FeO_4), an environmentally friendly oxidant, has been used in water and wastewater treatments. In recent studies, potassium persulfate was investigated as a potential alternative oxidant for improving sludge dewaterability [20–22]. K_2FeO_4 is a strong oxidizing agent based on the reduction potentials of reactions (2) and (3) in acidic and alkaline solutions, respectively [23].

$$Fe^{3+} + e^- \rightarrow Fe^{2+}, \quad E^0 = +0.77V \tag{1}$$

$$FeO_4^{2-} + 8H^+ + 3e^- \leftrightarrow Fe^{3+} + 4H_2O, \quad E^0 = +2.20V \tag{2}$$

$$FeO_4^{2-} + 4H_2O + 3e^- \leftrightarrow Fe^{3+} + 5OH^-, \quad E^0 = +0.72V \tag{3}$$

During the process, ferrate(VI) ions are reduced to Fe(III) ions, and they simultaneously form a coagulant ($Fe(OH)_3$). Organic compounds, such as EPS in activated sludge, are destroyed by pretreatment with K_2FeO_4; ferric-coagulating species are generated simultaneously and may increase the flocculation and dewaterability of the sludge [24]. K_2FeO_4 can oxidize organic and inorganic materials by disrupting colloidal contaminants, such as chlorophenols [25], organosulfur compounds, and antibiotics [26]. Moreover, K_2FeO_4 is a coagulant that can facilitate the removal of heavy metals [27].

In the present study, $FeCl_3$ and K_2FeO_4 were used as flocculant and oxidizing agents, respectively. Raw sludge was pretreated by using sifters with different diameters. This process is rarely found in related literature. This study explored the key factors that enhance dewaterability and elucidated the role of particle size, EPS, and the zeta potential in the dewatering mechanism.

2. Methods

2.1. Materials

The raw sewage sludge used in this study was a mixture of primary and secondary sludge from Sanjintan Sewage Treatment Plant in Wuhan, China. The capacity of this municipal wastewater treatment plant is 3×10^5 m³/d. Raw sludge samples were collected in polypropylene containers and stored at 4°C in a refrigerator for at most 4 d [28]. Prior to the experiment, the raw sludge was removed from the refrigerator and exposed to normal environmental conditions until its temperature reached 20°C.

K_2FeO_4 (≥92%) was used as a source of Fe(VI). The pH of the solution was adjusted with hydrochloric acid (2%). Deionized water was used in all the experiments. For the $FeCl_3$ solution (2 mol/L), $FeCl_3$ (≥97%) was dissolved in deionized water.

2.2. Experimental procedure

The raw sludge was stirred rapidly for 30 min to mix the sludge particles evenly with water. Subsequently, the mixed raw sludge was sieved through 0.5, 0.25, 0.1, and 0.075 mm sieves and were denoted as raw S, S1, S2, S3, and S4, respectively. The characteristics of the sludge samples were examined according to standard methods (US EPA1995), and the results are shown in Tables 1 and 2. The experiment was conducted in a glass reactor equipped with a thermometer and an electric stirrer. In each experiment, 4 mg/g of ferric chloride solution or 0.2 g/L of K_2FeO_4 powder was added to 500 mL of the pretreated sludge (the dosage was calculated by dry solid content). Prior to the K_2FeO_4 experiment, the pH of the sludge samples (500 mL) was adjusted to the required pH with hydrochloric acid. The sludge was conditioned with $FeCl_3$ solution at 270 rpm for 3 min and subsequently at 60 rpm for 5 min. Afterward, the sludge was conditioned with K_2FeO_4 at 270 rpm for 5 min and then at 120 rpm for 25 min. The obtained sample was used for further analysis. The main experimental procedure of this study is illustrated in Fig. 1.

Table 1
Basic characteristics of the sludge sample

Parameter	Value		
	Raw S	S2	S4
Moisture (%)	95.02	95.11	96.50
pH	7.18 ± 0.14	7.20 ± 0.11	7.21 ± 0.10
Organic content (%)	39.10 ± 0.31	36.07 ± 0.25	35.18 ± 0.22
CST(s)	141.9 ± 7.8	148.7 ± 9.3	359.1 ± 9.8

2.3. Analytical methods

2.3.1. EPS extraction procedure

The raw sludge samples were allowed to settle at 5,000 rpm for 10 min, and the supernatant was collected as soluble EPS. The sediment was resuspended to its initial volume with 0.05% NaCl solution. The suspension was transferred and heated for 30 min in a water bath at 60°C. The extracted solution was centrifuged at 5,000 rpm for 10 min and separated as bound EPS. The particulates present in the two EPS fractions were removed with polytetrafluoroethylene membranes with a pore size of 0.45 μm prior to organic analysis [29,30].

2.3.2. 3D excitation–emission matrix

Excitation–emission matrix (EEM) spectra are a collection of a series of emission spectra over a range of excitation wavelengths and can be used to identify fluorescent compounds present in complex mixtures. The peak locations, peak intensities, and ratios of different peaks in the EEM spectra of the EPS samples were not substantially influenced by ionic strength. 3D EEM spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer with an excitation range of 200–400 nm at 5 nm sampling intervals and an emission range of 220–550 nm at 5 nm sampling intervals. The spectra were recorded at a scan rate of 12,000 nm/min using excitation and emission slit bandwidths of 3 nm. Each scan exhibited 67 emission and 41 excitation wavelengths. The software Origin 8.0 (OriginLab Inc., USA) was used to process the EEM data [31].

2.3.3. Analysis of other items

Capillary suction time (CST) was measured with a 304M CST equipment (Triton, UK) at 25°C. A sufficient amount of sludge was poured into a funnel with a 1.8 cm inner diameter, and the time was recorded automatically. The zeta potential was determined with a Malvern Zetasizer Nano ZS (Malvern Instruments Ltd., UK) by collecting the supernatant of sludge after centrifuging at 4,500 rpm for 5 min before the supernatant was collected and mixed with the sludge at a ratio of 9:1. Particle-size distribution was determined with a Mastersizer 2000 laser particle-size analyzer (Malvern, UK) at a stirring rate of 1,000 rpm after dispersing the sludge in an aqueous solution.

3. Results and discussion

3.1. Sludge dewaterability

Tables 1 and 2 show that the inorganic chemical compositions of the sludge samples gradually increased, whereas the organic content presented an opposite trend, which was not evident. In the blank groups, the CST of raw S, S1, S2, S3, and S4 was determined. Fig. 2 illustrates that the decrease in floc particle size exerted a negative effect on the dewaterability of the sludge. In particular, when the particle size was below 0.25 mm, the effect became remarkably significant, and the CST of S4 became more than twice that of raw S. In the experimental groups, the addition of $FeCl_3$ to the sludge samples resulted in a rapid decrease in CST, and the value increased with decreasing particle size. However, Fig. 3 shows that the CST reduction percentage R (%) of S4 was higher than those of the other groups, which indicated the remarkable improvement of $FeCl_3$ in tiny flocs. Similar results were also observed for the Fe(VI) groups, in which the CST value was higher than those of the $FeCl_3$ groups.

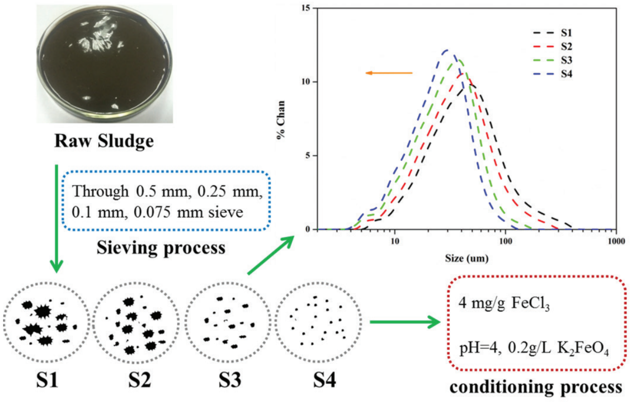

Fig. 1. Main experimental procedure of this study.

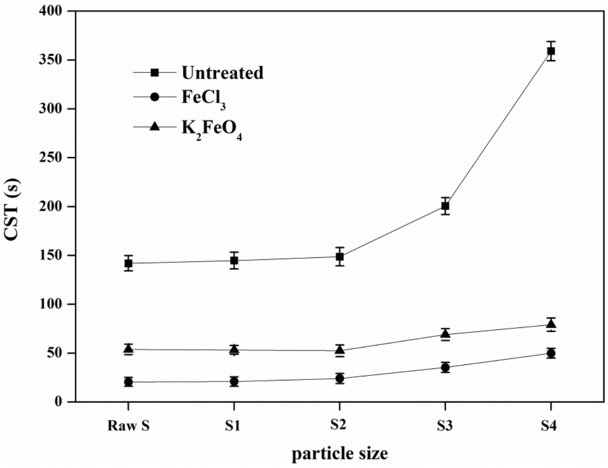

Fig. 2. CST evolution of sludge as a function of particle-size distribution and $FeCl_3$ or K_2FeO_4.

Table 2
Main inorganic chemical compositions of raw sludge sample (wt%)

Constituents	CO_2	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	CaO	K_2O	Fe_2O_3
Raw S	31.50	1.42	11.04	30.73	5.12	1.95	3.62	1.69	10.97
S2	31.40	1.48	10.98	29.93	5.61	1.99	3.78	1.73	10.97
S4	29.50	1.42	11.36	34.29	4.17	1.80	3.74	1.75	9.70

3.2. Variation of zeta potential

Screens with different sizes were used to sieve the raw sludge, and the zeta potential was separately measured (Fig. 4). In the untreated experimental groups, a decreasing trend and poor dewaterability were observed with decreasing particle size, as described in Fig. 2. This finding implied that variation in particle evidently affected the dewaterability of sludge. Comparison of the two bar graphs in Fig. 3 shows that the reduction percentages of CST and zeta potential declined with decreasing particle size (except for group S4) when pretreated with $FeCl_3$. An opposite trend was observed for K_2FeO_4, except for group S4. Furthermore, the addition of K_2FeO_4 reduced the particle surface charge ranging from 44.6% to 63.3%, which was higher than the surface charge of $FeCl_3$. These observations suggested that sludge dewaterability was related to the zeta potential. In addition, given that decreasing surface charge was related to increasing zeta potential, the sludge aggregates settled down rapidly and dewatered easily. However, different $FeCl_3$ and K_2FeO_4 mechanisms could not be illustrated by only using the zeta potential. The zeta potential evolution of the flocs may be altered through the degradation of EPS or charge neutralization of ferric and ferrous irons. Consequently, further investigations should be performed to evaluate these relations. The current findings show that floc size is an important controlling factor with respect to sludge dewatering, especially when the floc size is less than 0.075 mm.

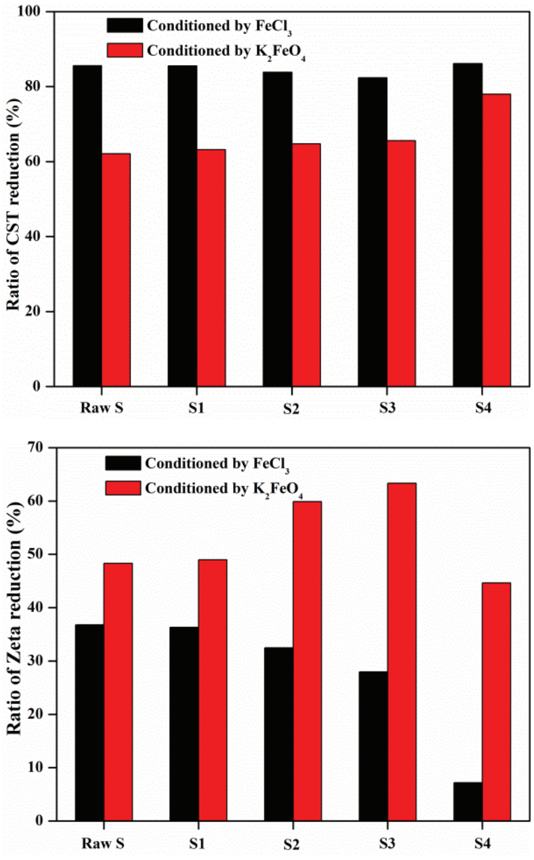

Fig. 3. CST/zeta potential reduction percentage after conditioned.

The enhancement of $FeCl_3$/Fe(VI) dewaterability was assessed through the CST/zeta potential reduction percentage *R* (%), which was calculated as follows:

$$R_C(\%) = \frac{\mathrm{CST}_0 - \mathrm{CST}_e}{\mathrm{CST}_0} \times 100\% \tag{4}$$

$$R_Z(\%) = \frac{\mathrm{Zeta}_0 - \mathrm{Zeta}_e}{\mathrm{Zeta}_0} \times 100\% \tag{5}$$

where CST_0 is the CST of a raw sludge sample (s), CST_e is the CST of the sample after conditioning (s), Zeta_0 is the zeta potential of the raw sludge sample (mV), and Zeta_e is the zeta potential of the sample after conditioning (mV).

3.3. Fourier transform infrared analysis

The Fourier transform infrared (FTIR) analysis of dried sludge is illustrated in Fig. 5. The band at 3,400 cm^{-1} corresponds to the O–H stretching vibration [32]. The band at 2,920 cm^{-1} accounts for the asymmetric vibration of CH_2 of

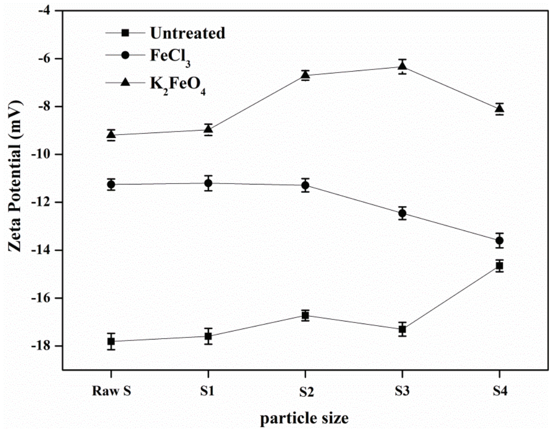

Fig. 4. Zeta potential evolution of sludge as a function of particle-size distribution and $FeCl_3$ or K_2FeO_4.

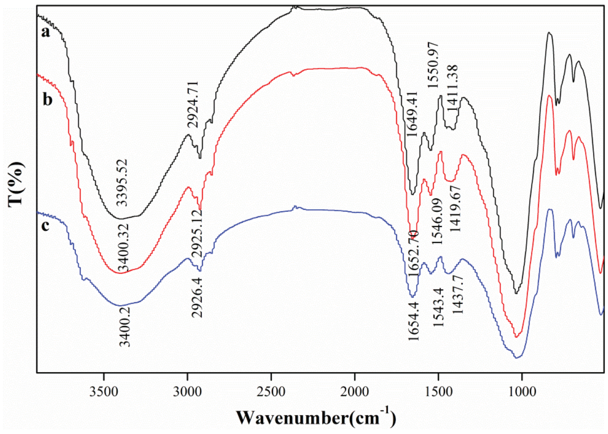

Fig. 5. FTIR spectra of the sludge with and without conditioned (a, raw sludge; b, conditioned by $FeCl_3$; and c, conditioned by K_2FeO_4), all the samples without sieved.

the aliphatic structures and lipids [33]. The two broad bands at 1,540 and 1,654 cm^{-1} are of protein origin (amides II and I, respectively) [34]. The band at 1,437 cm^{-1} corresponds to the C=C band of aromatic rings polarized by oxygen atoms bound near one of the C atoms. This band suggests the presence of basic oxygen-containing functionalities, such as chromene structures, diketones or quinone groups, and pyrone-like groups [35]. The bands at 1,443 and 1,423 cm^{-1} correspond to phenolic O–H plane variable-angle vibration and C–O stretching vibration, respectively. The band at 1,426 cm^{-1} is the phenolic O–H and C–O stretching [36]. As shown in Fig. 5, several band transformations occurred in the test groups. More band shifts were observed in Group C than in Group B. Additionally, the relative intensities of bands at 1,654 and 1,543 cm^{-1} in Group C indicated the degradation and removal of protein-like substances, which provided spectral information on the chemical structure changes of the components in the EPS samples.

3.4. EEM fluorescence analysis

3D EEM fluorescence spectroscopy is a rapid and sensitive technique for determining fluorescence compounds in EPS and exploring the possible mechanisms of improved sludge dewaterability. Typical EEM fluorescence spectra of EPS and their corresponding fractions for the control groups and sludge samples treated with $FeCl_3$ or K_2FeO_4 are depicted in Fig. 6. The main peak, which is located at the excitation/emission wavelengths (Ex/Em) of 370–390/440–470 nm (Peak A) in the EEM spectra, could be identified from the fluorescence spectra of EPS in the control groups. Peak A is associated with humic acid-like organics [37,38].

After $FeCl_3$ treatment, three peaks were identified at Ex/Em wavelengths of 340–350/435–445 nm (Peak B), 280/350–360 nm (Peak C), and 245/450 nm (Peak D). Peak B is associated with visible humic acid-like fluorescence. Similar fluorescence signals have also been reported for naturally dissolved organic matter [39] and extracellular substances of waste-activated sludge [40,41]. The third peak (Peak C), located at an Ex/Em wavelength of 280/350–360 nm, is a tryptophan protein-like substance [42], and Peak D represents fulvic acid-like substances [43]. The Peak B locations showed a blue shift, and Peaks C and D were new peaks. The changes in the humic acid-like and tryptophan protein-like contents in soluble extracellular polymeric substances (SEPS) showed a similar pattern with decreasing floc size, but the fulvic acid-like substances presented the opposite trend. Four main peaks (Peaks A, B, C, and D) were observed after K_2FeO_4 treatment. The fluorescence intensities in Peak A were considerably lower than those in the control groups. Fluorescence intensities, except for those with sizes less than 0.075 mm, were reduced with decreasing floc size.

The fluorescence parameters of EEM spectra, including peak locations and fluorescence intensity, generally indicated the oxidation of fluorescing materials. When pretreated with $FeCl_3$, new peaks were observed, and the intensity ratio of the humic acid-like substances increased. These observations suggested that the EPS structure was destroyed, and parts of bound EPS were solubilized and converted into soluble EPS. In the experimental groups, the intensities of Peaks B and C increased with decreasing floc size in soluble EPS; the increase in soluble EPS often results in increased surface charge and poor dewaterability [44]. Therefore, the zeta potential evolution of the flocs may be mainly altered by charge neutralization of ferric in groups conditioned by $FeCl_3$. The relative intensities of the bands gradually decreased after K_2FeO_4 oxidation, thereby indicating the degradation and removal of fluorescence components present in sludge EPS, which could explain the zeta potential results. These results indicated that the different mechanisms in EPS were weak oxidation, which is the release of EPS for $FeCl_3$, and strong oxidation, which is the release of EPS and degradation for K_2FeO_4.

3.5. Variation in particle-size distribution

The particle-size distributions of the sludge samples before and after treatment were determined to investigate the status of the particles and obtain insights into the responsible dewatering mechanisms (Table 3). When conditioned with $FeCl_3$, the average median particle sizes of all sludge samples (S3 and S4) increased. The particles aggregated and formed large flocs, especially in the group of tiny flocs (S4). The particle size increased in group S4 after K_2FeO_4 treatment.

For the S1 and S2 groups, the conditioned sludge exhibited smaller flocs than those of untreated sludge, which may be attributed to the oxidation effect. For the S4 group, the sludge conditioned with $FeCl_3$ showed larger flocs than the sludge conditioned with K_2FeO_4. Floc particles (S3 and S4) conditioned with $FeCl_3$ increased significantly and formed larger flocs than those conditioned with K_2FeO_4. For the groups conditioned with $FeCl_3$, flocculation of tiny flocs was mainly caused by the release of intracellular and extracellular substances and the coagulation effects of ferric. Increasing the levels of ECP was initially believed to aid sludge dewaterability by improving the level of sludge flocculation. This step decreases the number of small particles present in the sludge [45]. For the groups conditioned with K_2FeO_4, the reduction percentage of CST increase was accompanied with increased d50 of floc size in the S4 group. These findings reveal that floc size is an important controlling factor in sludge dewatering. Generally, a large particle size denotes good settleability and dewaterability. Higgins and Novak [46] observed that supracolloidal flocs in the range of 1–100 μm exert the most adverse influence on sludge dewaterability, and dewaterability decreases with increasing quantities of flocs in this size range. The high reduction percentage of CST conditioned with $FeCl_3$ was mainly due to the increase in the amount of tiny flocs.

4. Conclusions

Different dewatering processes in sewage sludge conditioning were proposed based on the abovementioned results and analysis (Fig. 7). When conditioned by $FeCl_3$, parts of EPS were released due to the oxidability of Fe^{3+}. The floc surface charge was reduced, and the tiny particles formed large particles as a result of the flocculation of ferric iron and the small amount of SEPS. For the samples conditioned by K_2FeO_4, EPS was dissolved, and a large amount of SEPS was released and further degraded. In this process, the floc surface charge decreased, and the tiny particles were flocculated because of the presence of a small amount of Fe^{3+}. During treatment with $FeCl_3$ and K_2FeO_4, the dissolution of EPS and the reduction in surface charge were the preconditions needed to improve the

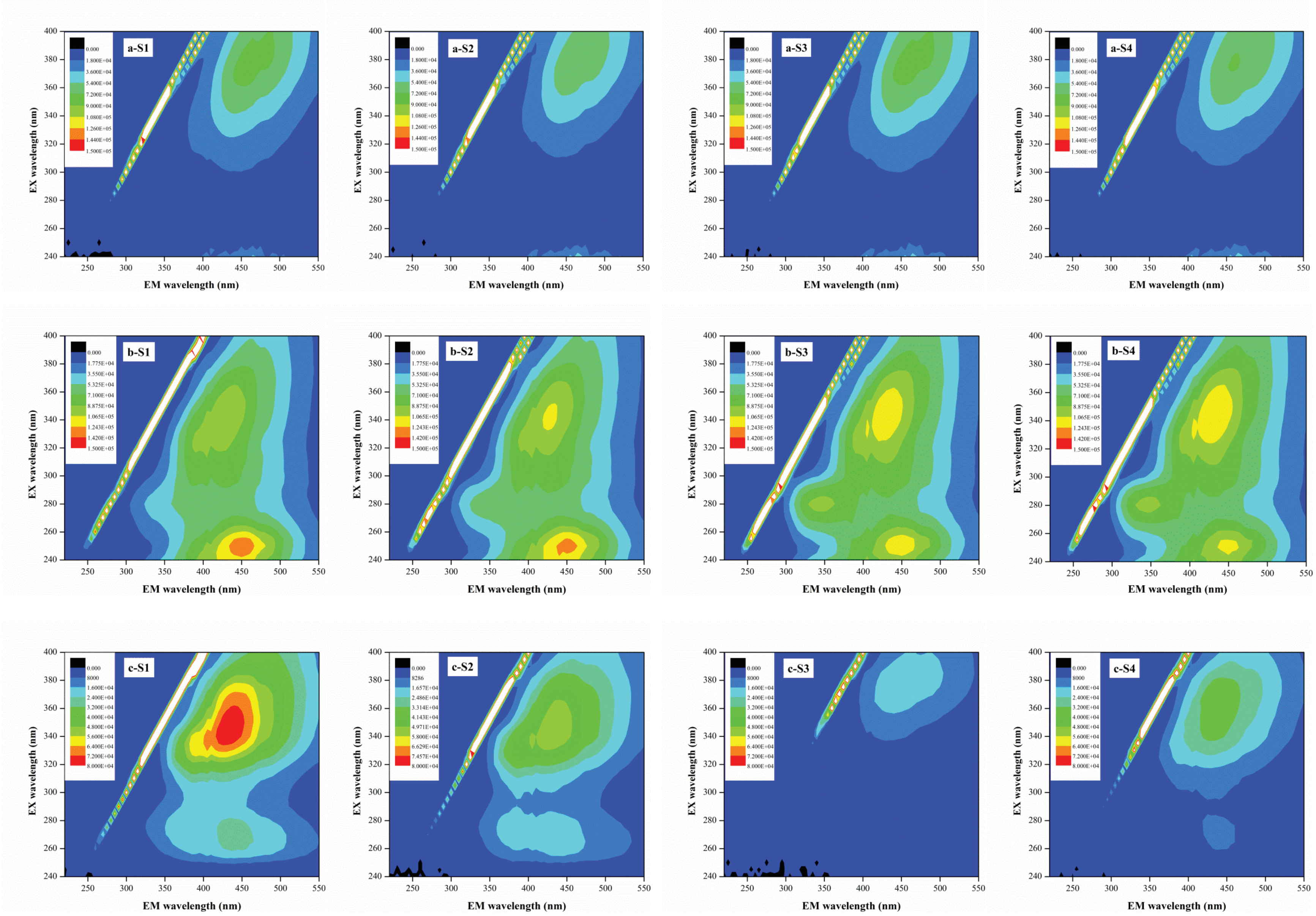

Fig. 6. EEM fluorescence spectra of the soluble EPS fractions before (a) and after treatment by $FeCl_3$ (b) or K_2FeO_4 (c) with different particle-size distribution (S1, S2, S3, and S4).

Table 3
Floc-size distribution (d_{10}, d_{50}, and d_{90}) of sludge samples before and after treatment

	Untreated (μm)			Conditioned by $FeCl_3$ (μm)			Conditioned by K_2FeO_4 (μm)		
	d_{10}	d_{50}	d_{90}	d_{10}	d_{50}	d_{90}	d_{10}	d_{50}	d_{90}
S1	15.20	39.23	97.96	14.00	35.30	83.05	14.30	36.50	82.16
S2	15.55	39.83	90.56	14.04	35.09	80.78	14.61	36.74	82.00
S3	12.97	32.66	64.19	15.15	34.37	66.52	13.88	32.42	63.31
S4	11.63	28.40	53.58	16.30	37.30	73.87	12.73	29.14	52.20

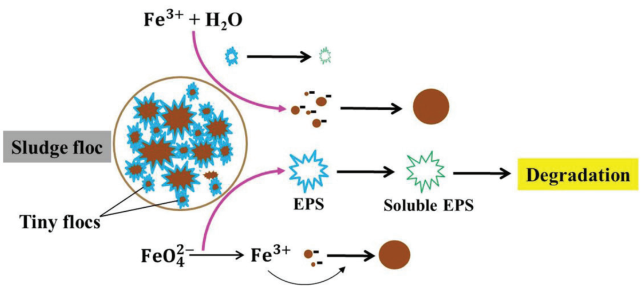

Fig. 7. Graphical illustration of mechanism in enhancing dewaterability.

dewaterability of the sludge. The particle sizes in group S4, especially for $FeCl_3$, were all enhanced. Improving the particle size of the tiny particles further promoted sludge dewatering.

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