

Performance and mechanism of sludge dewaterability enhanced by potassium ferrate pretreatment and calcium chloride addition

Yali Liu, Xiaorong Kang, Xin Li, Zheng Wang and Zhaoqian Jing

ABSTRACT

The potential benefits and mechanisms of potassium ferrate pretreatment and calcium chloride addition on sludge dewaterability were investigated in this study. The capillary suction time (CST) was used to evaluate sludge dewaterability. Results indicated that potassium ferrate of 0.1 g/g total solids (TS) and calcium chloride of 0.4 g/g TS were optimal parameters, and corresponding CST reached 43.7 s. Soluble organics in extracellular polymeric substances (EPS) were determined by three-dimensional excitation-emission matrix fluorescence spectroscopy, which was used to explain the mechanism of sludge dewaterability. The fluorescence intensities of protein-like and humic-like substances in EPS had a negative relationship with the CST. Scanning electron microscopy images indicated that calcium chloride neutralized the surface charge of particles, making the soluble protein-like substances agglomerate and form bigger flocs, consequently enhancing sludge dewaterability.

Key words | calcium chloride, CST, excitation-emission matrix, sludge potassium ferrate, waste activated sludge

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INTRODUCTION

A large quantities of waste activated sludge (WAS) is produced in biological treatment of wastewater, and the water content of WAS is generally greater than 95%. Therefore, dewatering is the major issue in treatment and disposal of WAS. Now, studies about sludge dewatering still focus primarily on sludge volume reduction and handling properties improvement. Together with more stringent treatment and disposal regulations, the demand for more efficient sludge-conditioning methods need to be improved.

In order to enhance sludge dewaterability, various potential pretreatment technologies have been investigated, such as the addition of calcined aluminum salts (Zhen *et al.* 2011) acids and surfactants (Yuan *et al.* 2011), seawater and brine

(Liu *et al.* 2011), Fenton reagent pretreatment (Buyukkamaci 2004), fungal treatment (Fakhru'l-Razi & Molla 2007), ultrasonication (de La Rochebrochard *et al.* 2013), microwave irradiation (Yu *et al.* 2009), and explosive explosion shockwave pretreatment (Chen & Yang 2012). Recently, potassium ferrate has been demonstrated to be a strong oxidant reagent that can disintegrate flocs structure of WAS by oxidizing organic compounds in extracellular polymeric substances (EPS) efficiently (Zhang *et al.* 2012). At the same time, the potassium ferrate kills the bacteria and viruses in sludge within ten minutes, reacts selectively with organics, and removes the odor of sludge (Ye *et al.* 2012). Most of these pretreatment technologies improved sludge dewatering characteristics by disrupting EPS. This is because the EPS can bind cells and particulate matter together, and the main components of EPS have a strong affinity for water (Bala Subramanian *et al.* 2010; Dvořák *et al.* 2011). Thus, elucidating the role of EPS in sludge dewatering phenomena will be important in addressing sludge-liquid

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separation problems. Until now, many investigations on the role of EPS in bioflocculation, sludge settleability and dewaterability have been carried out, and the results indicated that the dewatering mechanism was based on partial oxidation and rearrangement of the surface components of sludge flocs (Jin *et al.* 2003; Badireddy *et al.* 2010). However, the responsible mechanism of potassium ferrate pretreatment on sludge dewaterability has not been fully understood.

As we know, metal salts play an important role in sludge flocculation, settling and dewatering. The cations can compress the double layer of sludge colloids (Pevere *et al.* 2007), especially, as the divalent cations can bridge negatively charged surfaces of adjacent cells promoting floc formation (Nguyen *et al.* 2007). However, monovalent cations may cause a deterioration in floc properties by displacing divalent cations within the flocs (Novak *et al.* 1988). Some studies indicated that the calcium ion showed a more marked effect than other cations in improving sludge dewaterability (Novak *et al.* 1988).

Therefore, the aim of this study is to explore the possibility of potassium ferrate pretreatment and calcium chloride in increasing dewatering efficiency of WAS. The capillary suction time (CST) was selected as the index to investigate sludge dewatering characteristics. The pretreatment performances of potassium ferrate on WAS were analyzed by particle size and soluble chemical oxygen demand (SCOD). Simultaneously, the mechanism for sludge dewatering was explained by three-dimensional excitation-emission matrix (3D-EEM) and scanning electron microscopy (SEM).

MATERIALS AND METHODS

Experimental materials

WAS used in this study was taken from a secondary sediment tank in a wastewater treatment plant, Harbin, China. Sludge was initially concentrated by settling for 12 h at 4 °C with supernatant discharged. The characteristics of WAS are summarized in Table 1.

Experimental procedure

WAS samples were treated with different dosages of potassium ferrate and calcium chloride to identify the optimal

Table 1 | The characteristics of WAS

Item	Value
Total suspended solids (mg/L)	20,000 ± 500
Volatile suspended solids (mg/L)	10,400 ± 200
Total chemical oxygen demand (mg/L)	11,300 ± 200
SCOD (mg/L)	72
EPS _{SCOD} (SCOD in EPS) (mg/L)	2,215
pH	7.1

conditions for sludge dewaterability. Firstly, WAS samples (300 ml) in 500 ml plexiglas reactors were mechanically stirred with dosages of potassium ferrate (0, 0.05, 0.1, 0.2, 0.3 and 0.4 g/g TS) at 150 rpm for 2 h. Then, calcium chloride in the range of 0–1.6 g/g total solids (TS) were added into pretreated sludge with potassium ferrate of 0.1, 0.2 and 0.4 g/g TS, and the untreated sludge was set as control. The CST, SCOD, average particle size, SEM, and soluble organics in EPS were investigated. Each test was conducted in triplicate with average and standard deviation reported.

Analytical methods

The sludge samples first were centrifuged at 8,000 rpm for 5 min, and then filtrated by 0.45 µm filters before measurement of SCOD and 3D-EEM. The TS, volatile solids (VS), SCOD were analyzed by *Standard Methods* (APHA 1976). The pH was measured using a digital pH-meter (pHS-3C). The CST was measured using a standard CST apparatus (Model 304M, Triton, UK) equipped with an 18-mm diameter funnel and Whatman No. 17 chromatography-grade paper. The particle size was determined by a Malvern Mastersizer 2000 which enables the measurement of particles in the range of 0.02–2,000 µm. The average size of the flocs was given as the mean based on the volume equivalent diameter.

3D-EEM analysis of soluble organics

3D-EEM spectra of soluble organic matters at different dosages of calcium chloride with potassium ferrate of 0.1 g/g TS were measured using a molecule fluorescence spectrometer (FP-6500, Jasco, Japan). Scanning emission spectra from 220 to 550 nm at 1 nm increments was

obtained by varying the excitation wavelength from 220 to 450 nm at 5 nm increments. The excitation and emission slits were maintained at 5 and 3 nm, respectively, and the scanning speed was set at 2,000 nm/min for all samples. The influence of the Raman and Rayleigh scattering was decreased by subtracting the EEM spectra from the EEMs of all samples examined which were obtained from the deionised water (He *et al.* 2011). Origin 8.0 software was employed to process EEM data.

SEM analysis

Sludge surface morphology at different dosages of calcium chloride was observed using an electron microscope (QUANTA 200, FEI, USA). The samples were washed three times with phosphate buffer saline (PBS) and fixed with 2.5% glutaraldehyde (pH 7.2–7.4) overnight at 4 °C, then washed with PBS (pH 6.8) 3 times and 15 min per session before dehydrating by successively passing through 50, 70, 80, 90 and 100% ethanol. Next, sludge samples were further washed by ethanol-isoamyl acetate (1:1) and isoamyl acetate, respectively, followed by drying with a freeze drier (BT2KXL, VIRTIS, USA) and platinizing with an ion coater (SCD 005, BAL-TEC, Switzerland).

RESULT AND DISCUSSION

Effect of potassium ferrate on sludge pretreatment

It is well known that CST was one of the most important indexes for sludge dewaterability, and the shorter the CST is, the better sludge dewaterability becomes. So, the effects

of potassium ferrate conditioning on sludge dewaterability were evaluated by CST. As shown in Figure 1(a), no obvious change of CST was observed at potassium ferrate less than 0.1 g/g TS, while the CST value rose rapidly to 1,114.5 s when the potassium ferrate was 0.4 g/g TS. Compared with untreated sludge, the CST increased almost 16.9 times. It can be seen from Figure 1(b), sludge disintegration degree enhanced with the increase of potassium ferrate. As potassium ferrate dosages increased from 0 to 0.4 g/g TS, the SCOD increased from 197.3 to 3,484.2 mg/L, corresponding average particle size decreased from 126.1 to 104.5 μm . The similar changes were observed in a previous study (Eskicioğlu *et al.* 2006), where sludge flocs structure was disrupted effectively at potassium ferrate of 0.4 g/g TS, and the extracellular and intracellular organics, such as proteins and carbohydrates, were released into the soluble phase. The degeneration of sludge dewaterability was attributed to two aspects. For one thing, the smaller flocs increased with the breakdown of sludge structure, which migrated and might be driven into pores that were previously used for the passage of filtrate (Novak *et al.* 1988). For another, an abundance of negative charges in the flocs interior might be exposed to the disintegrated sludge surfaces after potassium ferrate pretreatment, resulting in the increase of CST (Wojciechowska 2005).

Effect of calcium chloride condition on sludge dewaterability

The co-conditioning of potassium ferrate and calcium chloride on sludge dewaterability is shown in Figure 2. It was obvious that the CST decreased with an increase of calcium

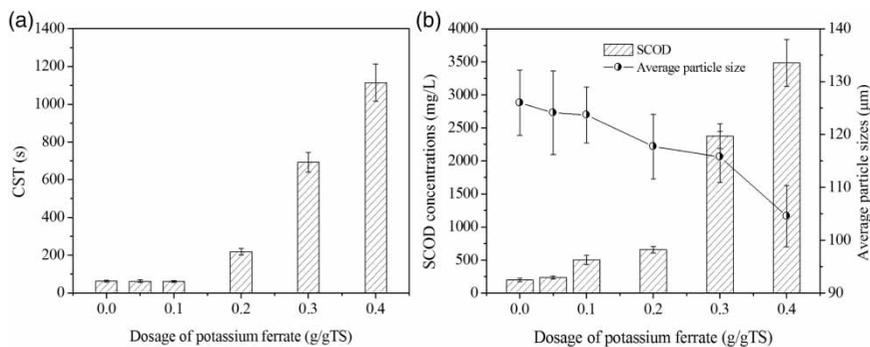


Figure 1 | Effect of potassium ferrate on (a) CST and (b) SCOD and particle size.

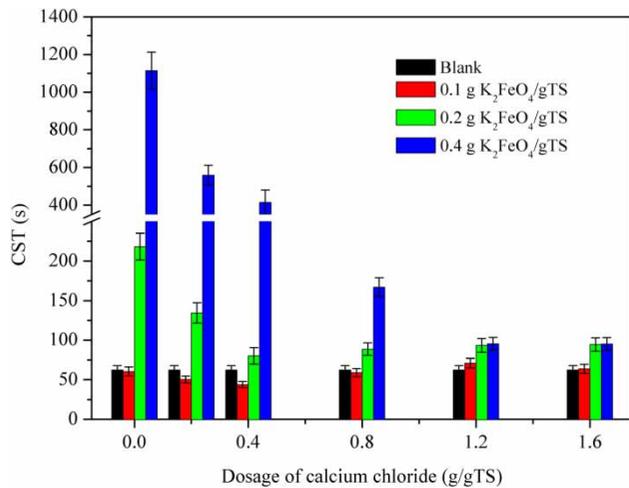


Figure 2 | Effect of calcium chloride dosage on CST at potassium ferrate of 0.1 g/g TS.

chloride at any dosage of potassium ferrate. Take potassium ferrate of 0.4 g/g TS for example, the CST rapidly decreased from 1,114.5 to 95.1 s when calcium chloride dosage increased from 0 to 1.2 g/g TS. The results demonstrated that calcium chloride has potential in enhancing sludge dewaterability. The calcium chloride function is as a physical conditioner in the sludge dewatering process, which acts by a sequence of hydrolysis, adsorption and precipitation reactions in the sludge mixture. Firstly, the adsorption of calcium ion onto sludge surfaces could be attributed to the electrostatic attractive force, which results in particle surface charges being neutralized (Sørensen *et al.* 1997). Then, the electrostatic repulsive force among the sludge particles is reduced, and the colloidal particles agglomerate and form bigger flocs (Figure 3), thus facilitating water removal.

It was a remarkable fact that the CST first decreased and then increased with increase of potassium ferrate. For example,

at calcium chloride of 0.4 g/g TS, the CST decreased from 62.3 to 47.7 s when the potassium ferrate increased from 0 to 0.1 g/g TS. Subsequently, the CST increased to 415.4 s as potassium ferrate continually increased to 0.4 g/g TS. The major reason for sludge dewaterability was that sludge pretreated at a high dosage of potassium ferrate led to smaller particles and more soluble organics were released, which were difficult to be reflocculated.

Change of soluble organics after calcium chloride condition

In order to analyze the mechanism for enhanced dewaterability, Figure 4 shows the 3D-EEM spectra of soluble substances after calcium chloride addition. Two main peaks are identified from EEM fluorescence spectra of soluble organic matters with calcium chloride of 0, 0.4, 0.6, 0.8 and 1.2 g/g TS. The first main peak (Peak A) appeared in all reactors and occurred at excitation/emission wavelengths (Ex/Em) (278–282)/(340–347) nm, which was reported as protein-like substances (Henderson *et al.* 2009). Also, the changes of fluorescence intensity in all reactors were quite different to each other, and the minimum fluorescence intensities of peak A appeared at calcium chloride of 0.4 g/g TS. Peak B located at the center of Ex/Em of 339/442 nm, representing the visible fluorescence of humic-like substances (Coble 1996). Although the intensity of Peak B was much weaker than that of peak A, its change trend was similar to Peak A. From comprehensive analysis of Figures 2 and 4, high CST values corresponded to high soluble protein-like and humic-like substances. A similar result was concluded in sludge dewaterability by mild thermal treatment in calcium chloride solution, where calcium could bridge with the

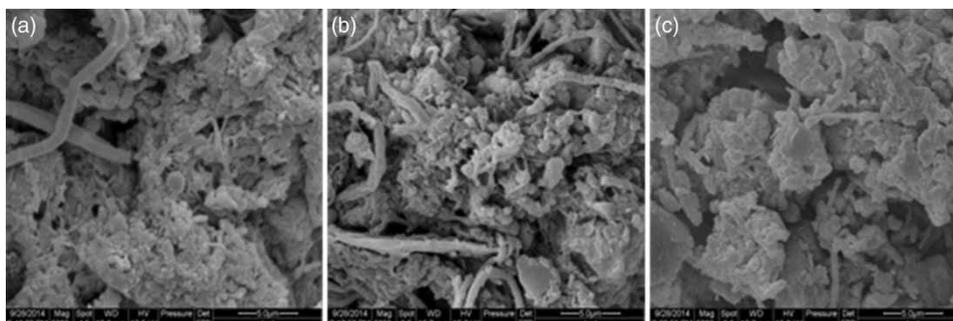


Figure 3 | SEM images of (a) untreated sludge, (b) potassium ferrate of 0.1 g/g TS, and (c) calcium chloride of 0.4 g/g TS.

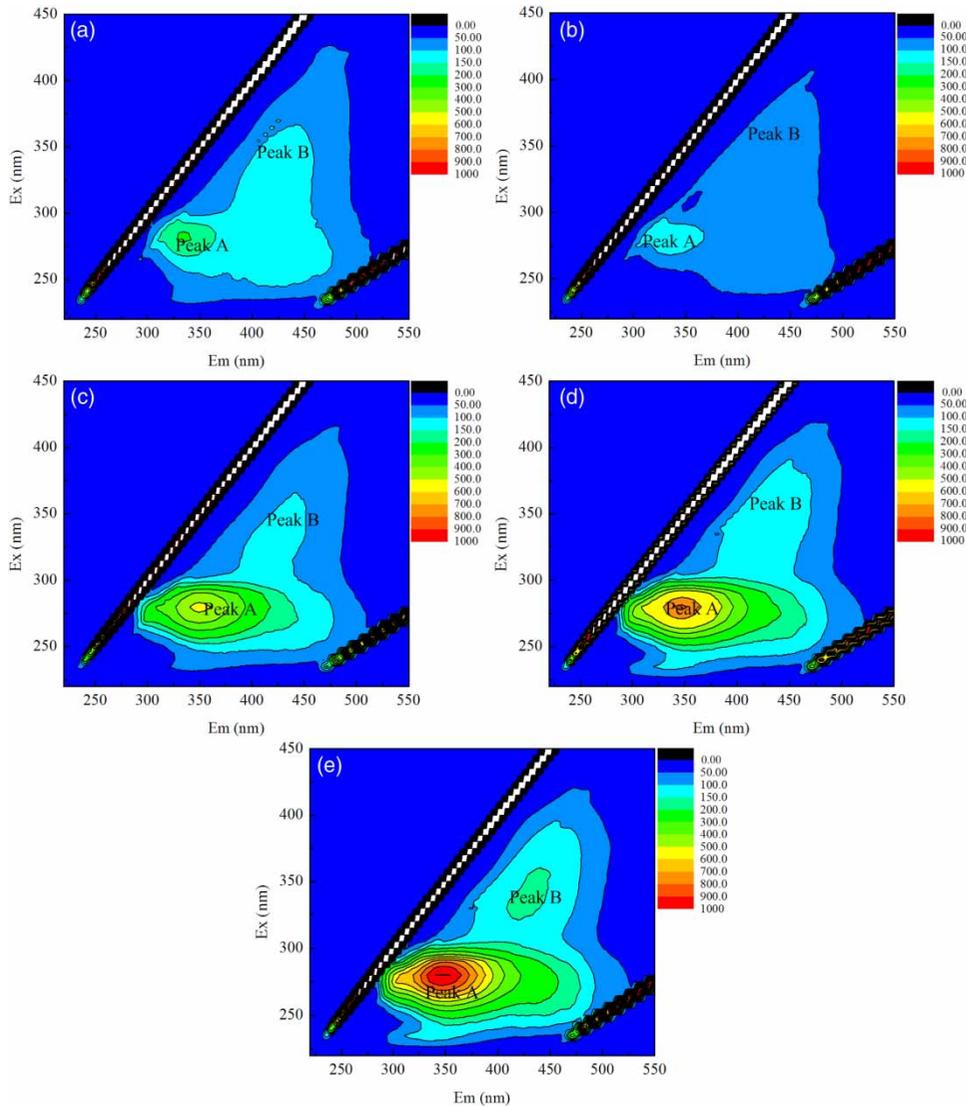


Figure 4 | Typical 3D-EEM spectroscopy in EPS with different calcium chloride addition.

functional groups of soluble protein and carbohydrates to diminish the surface charge of flocs, but when the calcium chloride dosage exceeded a certain point, the protein released again (Guan *et al.* 2012).

CONCLUSION

Potassium ferrate pretreatment significantly disintegrated sludge flocs, and the negative correlation between CST

and disintegration degree was observed. Sludge dewaterability of potassium ferrate pretreated sludge was enhanced efficiently with the aid of calcium chloride. The optimal condition for sludge dewatering was determined to be potassium ferrate of 0.1 g/g TS and calcium chloride of 0.4 g/g TS. Simultaneously, 3D-EEM images indicated that calcium chloride reduced protein-like and humic-like substances in EPS, which should be responsible for improving sludge dewaterability.

ACKNOWLEDGEMENTS

This work was financially supported by the National High Technology Research and Development Program of China (863 Program) (No. 2012AA063503-02).

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