



## Improvement of settleability and dewaterability of sludge by newly prepared alkaline ferrate solution



Yulei Liu<sup>a</sup>, Lu Wang<sup>b</sup>, Jun Ma<sup>a,\*</sup>, Xiaodan Zhao<sup>a</sup>, Zhuangsong Huang<sup>a</sup>, Gurumurthy Dummi Mahadevan<sup>b</sup>, Jingyao Qi<sup>a,\*</sup>

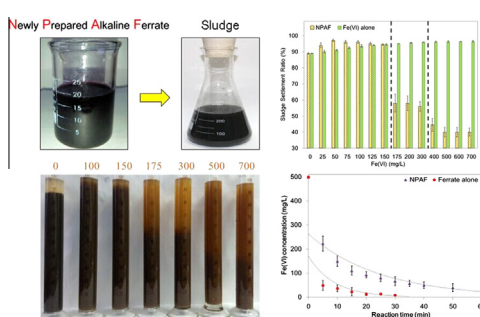
<sup>a</sup>State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China

<sup>b</sup>Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

### HIGHLIGHTS

- NPAF enhanced sludge disintegration and improved the settling and dewatering property of sludge.
- The increase of ferrate stability led to the better performance of NPAF.
- The flocculation of ferric in situ formed also contributed to the sludge settling.
- The improvements of settleability and dewaterability attributed to the degradation polymeric matters.
- The effect of single Fe(VI) or alkali on sludge reduction was feeble.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Dewatering and settleability by alkaline hydrolysis and oxidation (e.g. ferrate) has been a key issue in waste activated sludge treatment. This study demonstrated that, the newly prepared alkaline ferrate (NPAF), containing Fe(VI) and KOH, could effectively disrupt sludge structure and simultaneously improved the dewaterability. It was determined that, at 500 mg/l of NPAF dosage range, the sludge settleability and dewaterability were improved to 55.1% and 7%, respectively. At low dosage of NPAF (i.e. <150 mg/l), the dissolved organic matter in the medium was increased whereas, in higher concentration (i.e. 200–700 mg/l) free water content of sludge floc was released by degrading polymeric substances and other biological macromolecules. The disintegration and structural damages of sludge floc treated with different NPAF concentration and extent to which complete damage (400 mg/l) were determined by scanning electron microscope. Owing to the presence of alkali-KOH in NPAF, the stability of Fe (VI) was significantly improved by 4–6 times, which may resulted on the excellent performances of NPAF for the degradation of the macromolecules.

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### 1. Introduction

Sludge (including sludge floc and biofilm) treatment is always a core issue for any sewage disposal practice, due to its higher cost

expenses. It was estimated that, the sludge treatment and disposal may account for up to 60% of the total operation cost in the waste water treatment plant [1]. In practice, a typical treatment method usually followed in five steps: thickening, stabilization, conditioning, dewatering, and disposal, where dewatering was considered as a critical step in the process. The sludge dewatering process is always affected by its physicochemical characteristic such as thickness, odor, organic pollutants and heavy metals contamination.

\* Corresponding authors. Tel./fax: +86 451 86283010 (J. Ma). Tel./fax: +86 451 86413167 (J. Qi).

E-mail addresses: [majun@hit.edu.cn](mailto:majun@hit.edu.cn) (J. Ma), [qjy\\_hit@hotmail.com](mailto:qjy_hit@hotmail.com) (J. Qi).

Since the higher ( $\geq 99\%$  for secondary sludge) water and organic solids of sludge, its dehydration by chemical conditioning (flocculation, acid or alkali) was widely adopted [2]. These chemicals denaturants will increase the flocculation ability of sludge, thereby disrupt the floc structure and facilitate the release of bound water and organic matters [3]. Although, many physical methods such as ultrasound, microwave, thermal, and high pressure homogenization were also combined with the chemical methods to further improve sludge disintegration. Most of the previous studies exhibited the increase of dissolved organic matter concentrations after alkaline treatment, but sludge dewatering ability could be deteriorated because of disruption of sludge flocs and cells. It was noted that, during the treatment process, extreme pH of the environment, the protein denaturation, saponification of lipids and hydrolysis of RNA were the common factors to affect the dewatering process. Furthermore, extensive swelling and solubilization of the gels in strong alkali ( $-\text{OH} \rightarrow -\text{O}^-$ ) ionization condition, lead to the polymers forms of gels containing a large amount of water, and yield poor dewaterability in the process [4].

Recently, the use of strong oxidizing agents with ecofriendly by-products such as Fe(VI) in the treatment process has tremendously increased. Fe(VI), being strong oxidizing agent [5–8], also can be applied in sludge conditioning, disinfection, emerging pollutants and heavy metals removal [9]. Some studies on Fe(VI) treatment revealed that, devitalization of bacteria and viruses in sludge was achieved within ten minutes [10–12] and selective reaction of Fe(VI) with the amino acids, organic sulphides and nitrogenous compounds wane the odor of sludge [13–16]. However, the use of Fe(VI) in the sludge treatment has some disadvantages, i.e. it has limited effect on sludge dehydration. During the removal of suspended solids from the sludge, Jiang et al. compared the performance of Fe(VI) with ferric sulfate and aluminum sulfate, and pointed that Fe(VI) produced less wet sludge only by 10% than ferric sulfate and aluminum sulfate for the equivalent doses compared [17]. Ye et al. also noted that the performance of Fe(VI) on sludge reduction was slightly improved, where the dewaterability was enhanced by 2.5%, in neutral conditions [18], while the potassium ferrate in acidic environment (pH = 3) decreased the moisture content in the sludge by 6.8% [19]. The stability of Fe(VI) is relatively low in acidic or neutral environment and complicated constituent nature of sludge may cause Fe(VI) in feeble role and pointless consumption during treatment. Furthermore, Fe(VI) required tedious purification for the acquisition of solid ferrate, which was considered as the critical limiting factor during process. However, newly prepared ferrate solution contains high concentration of alkali, which may also play an important role in the action of NPAF on sludge by exerting an additional effect of hydrolysis on floc. And, most importantly, the stability of Fe(VI) could be improved due to the alkaline environment [8], and more ferric hydroxide formed in the alkaline condition would able enhance the flocculation of sludge. All these considerations suggested the possibility for removing the purification step during the Fe(VI) preparation and improving the sludge reduction effect, which triggered our interest to study the effect of newly prepared ferrate solution (NPAF) on sludge reduction.

Our focus in this study was based on the performance of NPAF on the settleability and dewaterability of the sludge during the treatment process. We also emphasized the changes in the sludge

characteristics, such as soluble chemical oxygen demand (SCOD), total phosphorus (TP), total organic carbon (TOC) and total nitrogen (TN) during NPAF treatment. Any structural changes on sludge microbial cells was analyzed by scanning electron microscope (SEM) and the chemical compositions and structures of treated sludge were determined by excitation–emission matrix (EEM) fluorescence spectroscopy and molecular weight (MW) distribution analysis. In addition, contrast effects on the changes in sludge properties among NPAF, Fe(VI) and alkali lone groups were also determined.

## 2. Materials and methods

### 2.1. Activated sludge samples

Sludge samples were collected from aerated basin of Wenchang Municipal Wastewater Treatment Plant (WWTP), Harbin, China. P. R. The samples were brought back to the laboratory in an ice packed plastic container, and were then stored at 4 °C until further use. The initial sample characteristics such as pH, total suspended solids, COD and SCOD was determined and for reliable data. All the following experiments were completed within three days of sampling (see Table 1).

### 2.2. Preparation of NPAF

Wet synthesis of NPAF and pure potassium Fe(VI) was prepared according to the previously described method by Thompson et al [20]. The final product and solid potassium Fe(VI) were collected and stored in a vacuum desiccator prior to use.

### 2.3. Oxidation treatment of sludge with NPAF

The prepared NPAF was an alkaline solution containing approximately 90–100 mM of Fe(VI) concentration. The amount of NPAF dosed into sludge was determined by the concentration of Fe(VI). In brief, the sludge samples (~200 ml) were mixed with different dose of NPAF (25–700 mg/l) and stirred at a rough speed of 400 rpm for an hour. The alkali contents of sludge solutions with different dosage of NPAF (25–700 mg/l) were shown in Table 2. For control experiments, the Fe(VI) (0–700 mg/l) and alkali-KOH (0.05–0.4 M) concentration were taken into consideration throughout the experiment. All the tests were carried out at ambient temperature (25 °C) and significance of each value was based on the triplicate experiments.

### 2.4. Analytical methods

Absorption measurement for Fe(VI) concentration was determined at 510 nm ( $\epsilon_{510} = 1150 \text{ M}^{-1} \text{ cm}^{-1}$ ) on a UV–Visible spectrophotometry. For fluorescence EEM analysis, the sludge solutions was diluted 40 times (UV<sub>254</sub> of all sample after dilution <0.05) and analyzed using Hitachi F-7000 fluorescence excitation–emission matrix spectroscopy (Hitachi corporation, Japan). The molecular weight distribution analysis of the sludge was determined by the diluted solution (100 times) and applied on to a high pressure size exclusive chromatography (HPSEC) (LC-10A,

**Table 1**  
Characteristics of excess activated sludge collected from municipal WWTP of Wenchang.

	TSS (g/l)	VSS (g/l)	pH	COD (mg/l)	SCOD (mg/l)
Sludge sample	12.57 ± 0.15	7.14 ± 0.21	6.90	17,881 ± 221	1178 ± 117

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