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Variations in distribution and composition of extracellular polymeric substances (EPS) of biological sludge under potassium ferrate conditioning: Effects of pH and ferrate dosage

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ABSTRACT

The effect of pH on chemical conditioning with potassium ferrate (K_2FeO_4) for improving sludge filtration dewatering performance has been studied. The variation of extracellular polymeric substances (EPS) in conditioning process was investigated in detail to unravel the reaction mechanism. The results indicated that sludge dewaterability was improved by decreasing solution pH in terms of filtration rate and cake solids content. At acid conditions, protonation of EPS resulted in reduction of negative charge and densification of sludge floc. Sludge conditioning efficiency was improved with decrease in pH. Ferrate can solubilize EPS through oxidation process and also remove a portion of soluble EPS (SEPS) by charge neutralization and interfacial adsorption of hydrolyzed ferric ions, consequently compressing EPS and decreasing total extractable EPS content. In addition, when pH and potassium ferrate were 3 and 0.1 g/gTSS, the sludge filtration dewatering rate and extent reached the maximum. Deterioration of sludge dewaterability was observed as the ferrate was overdosed (>0.2 g/gTSS). This could be attributed to the release of a large amount of bound EPS (BEPS) as a result of ferrate oxidation, consequently increasing the sludge filtration resistance.

1. Introduction

The management of wastewater sludge, now often referred to as biosolids, accounts for a major portion of the cost of the wastewater treatment process and represents significant technical challenges. High-performance dewatering has been proven to be an efficient method to reduce sludge volume, cutting transportation and disposal cost [1]. Generally, the moisture in activated sludge can be classified into free water (about 70%), interfacial water (about 20%) and bound water (about 10%) [2]. Except for the sludge characteristics, the dewatering efficiency was mainly dependent on the selection of device and chemical conditioning process.

Many studies suggested that the sludge composition was the major factor affecting sludge dewatering performance. The extracellular polymeric substances (EPS) accounted for 60-80% of sludge biomass [3]. The distribution and chemical compostion of EPS had significant effect on sludge dewatering property [4,5]. Houghton found that the there existed a certain EPS mass at which the sludge dewaterability reach the maximum [6]. Again, EPS content also greatly affected the charge property and floc stability [4]. Higgins and Novak demonstrated that the sludge dewaterability was mainly affected by the ratio of protein and polysaccharide. Proteins exhibited the more significant influence on sludge dewaterability than polysaccharide, high protein/polysaccharide was detrimental to dewatering process [7]. This observation was in agreement with Murtgy and Novak's findings [8].

Prior to dewatering sludges are always conditioned with chemicals in order to improve operating performance of sludge dewatering devices. Addition of traditional chemical conditioners (inorganic salt coagulants and organic polymers) can agglomerate fine sludge colloids to form large flocs through charge

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Table 1
Characteristics of waste activated sludge.

Indicator	Moisture content (%)	pH	VSS/TSS	CST (s)	$d_{0.5}$ (μm)	Zeta potential (mV)	SCOD (mg/L)
Value	98.3	7.5	0.75	320	62	−15.2	130

neutralization and bridging, which can be more easily separated from the water [9,10]. Considering the high water binding properties of EPS, the traditional chemical conditioners are ineffective to remove the bound and intercellular water in sludge flocs. Therefore, many advanced sludge conditioning processes (ASCP) have been developed to improve sludge dewatering performance and to facilitate handling and ultimate disposal. ASCP can destroy the floc structure and solubilize EPS components, consequently converting the bound water into free water, consequently reducing the cake moisture content after dewatering step [1]. These techniques include (photo) Fenton oxidation [11–13], acid/alkaline [14] and thermal treatment [1] and enzymatic treatment or the integrated processes.

Potassium ferrate (K_2FeO_4) is known as a new generation green chemical which can oxidize and degrade a wide variety of organic contaminants in water [15]. Additionally, ferrate(VI) ions will be reduced to Fe(III) ions or ferric hydroxide, which can serve as a coagulant in the mixing unit process. K_2FeO_4 has been used as sludge conditioner in some previous studies [16,17], but the underlying mechanism was not fully understood, and some results are contradictory. Zhang et al. stated that sludge dewaterability was improved with ferrate treatment at pH of 3, while it was deteriorated at pH values above 4 [16]. Ye et al. found that K_2FeO_4 treatment resulted in deterioration of sludge filterability while improvement of settleability and dewatering performance. Meanwhile, the loosely bound (LB)-EPS concentration was increased with increasing K_2FeO_4 dosage, while tightly bound (TB)-EPS content showed an opposite pattern under conditioning [17].

Most of previous studies focused on effect of K_2FeO_4 conditioning on sludge dewatering performance, but few of them investigated the variation in EPS characteristics (distribution and composition) with advanced analytical techniques in chemical conditioning. Thus, the objectives of this study are to: (1) understand the impact of pH on sludge conditioning efficiency with ferrate; (2) unravel the underlying mechanism of different sludge conditioning processes by analyzing the variation in distribution and composition of EPS.

2. Materials and method

2.1. Waste activated sludge

Surplus sludge (Table 1) was sampled from sludge return line of membrane bioreactor (MBR) in Northern brook wastewater treatment plant of Beijing. Now the daily wastewater treatment capacity is 200 thousand ton. The wastewater is reclaimed with combined process of MBR and ozonation.

2.2. Sludge conditioning with K_2FeO_4

A 200 mL of sludge sample was added in a 500 Erlenmeyer flask. Then, under vigorous stirring using a magnetic stirrer, appropriate amounts of ferrate potassium were added in the beaker at varying pH values. After 2 h reaction, the solution was adjusted to pH 7. The suspension was used to extract the SEPS and bound EPS. Each experiment was performed in triplicate.

2.3. Analytical methods

2.3.1. Determination of sludge dewaterability

Specific resistance to filtration (SRF) is widely used to evaluate sludge dewatering performance in filtration process [9,10,16,17]. It can be obtained by eq. (1):

$$r = \frac{2PA^2b}{\mu\omega} \quad (1)$$

where P (kg m^{-2}) denotes pressure, A (m^2) is filtration area, μ (kg s m^{-2}) is kinetic viscosity, ω (kg m^{-3}) denotes dry solid weight per unit volume sludge on the filtrate media, b is slope of filtration equation-dt/dV = bV + a, and t (s) is time, V (m^3) denotes volume of filtrate. The raw and conditioned waste sludge was poured into a Buchner funnel with a 0.45 μm cellulose acetate membrane to filter under a pressure of 0.6 MPa of vacuum filtration. Volume of filtrate was recorded every 10 s before surface cracking was observed.

2.3.2. EPS extraction procedure

Firstly, raw sludge sample was settled down at 5000 g for 10 min, and the supernatant was collected as SEPS. The sediment was resuspended to its initial volume with 0.05% NaCl solution. And then the suspension was transferred and heated for 30 min in water-bath at the temperature of 60 °C. The extracted solution was centrifuged at 5000 × g for 10 min and separated as bound EPS [18]. 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.

2.3.3. EPS analysis

2.3.3.1. Protein and polysaccharide measurement. All chemical analyses were carried out in duplicate using chemicals of analytical grade. The protein and carbohydrate in extracted EPS were

Table 2
Fluorescent intensity of EPS under different pH levels.

pH	SEPS				pH	BEPS			
	Tryptophan protein	Aromatic protein	Humic acid	Fulvic acid		Tryptophan protein	Aromatic protein	Humic acid	Fulvic acid
$\lambda_{ex/em}$	280/335	225/340	330/410	275/425	$\lambda_{ex/em}$	280/335	225/340	330/410	275/425
2	74.922	50.044	69.376	79.665	2	23.422	54.795	2.796	7.304
3	74.322	61.084	39.286	43.785	3	62.802	90.175	3.35	6.317
4	71.712	56.974	28.726	30.965	4	48.872	76.805	2.214	5.167
5	73.062	70.684	26.566	29.815	5	156.162	228.705	5.105	3.987
7	69.062	74.784	27.176	32.615	7	192.462	263.405	5.426	6.657
9	134.802	141.134	47.366	71.675	9	203.262	284.405	14.355	9.697
11	344.102	116.034	50.556	73.115	11	289.062	371.105	13.775	4.317

Sample of SEPS and BEPS were diluted by 20 and 100 times respectively.