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Understanding the impact of chemical conditioning with inorganic polymer flocculants on soluble extracellular polymeric substances in relation to the sludge dewaterability

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ABSTRACT

Generally, sludge conditioned with inorganic coagulants exhibits rigid structure and is suitable for high pressure dewatering process. Sludge flocs possess multilayered structure, and the sludge dewaterability is mainly dependent on the properties of soluble extracellular polymeric substances (SEPS). However, few studies have focused on influence of chemical conditioning on the characteristics of SEPS. In this study, the surplus sludge obtained from wastewater treatment plant (WWTP) was conditioned with two inorganic polymer flocculants (IPFs), PACl and HPAC, for improving the sludge dewaterability which was measured using specific resistance to filtration (SRF). Meanwhile, the variation in SEPS properties was investigated with combined high performance size-exclusion chromatography (HPESC) and fluorescence excitation–emission matrix (EEM). According to the experimental results, HPAC showed better performance in improving sludge dewaterability due to higher charge density and better bridging properties. EEM coupled to fluorescence region integration (FRI) demonstrated that protein-like substances were dominant fraction of soluble EPS. HPSEC analysis indicated that most of the SEPS with high molecular weight (>2000 Da) were effectively removed from aqueous phase after conditioning, they might play more important roles in sludge dewatering. SRF correlated well with zeta potential, dissolved organic carbon (DOC) and EPS content located in all four EEM regions under chemical conditioning. This result revealed that EEM in conjunction with FRI was an attractive way to evaluate the sludge conditioning efficiency of IPFs.

1. Introduction

The management of wastewater sludge accounts for a major portion of the cost of the wastewater treatment process and represents significant technical challenges. In many wastewater treatment facilities, the bottleneck of the sludge handling system is dewatering operation. Sludge is very complex colloidal system and consisted of highly dispersed and slimy particles at sizes around 10^{-9} m, thereby making solid–water separation very difficult [1]. Sludge particles are always negatively charged due to ionization of anionic functional groups such as carboxylic and phosphate, and form heterogeneous double layer structure. Generally, chemical conditioning is a required step prior to dewatering to achieve the desired efficiency. The application of chemical flocculants helps to increase the sludge particle size by agglomerating the small fines of the sludge colloids, which causes blinding, to form large flocs, which can be more easily separated from the water. The sludge flocs conditioned by organic polyelectrolytes are large and loose [2] and therefore fit for low-pressure dewatering process (centrifuge), while inorganic coagulants conditioning can produce a rigid floc, so they are often used in high-pressure process such as filter press and belt press [3,4].

Extracellular polymeric substances (EPS) are one of the most important constituents of activated sludge, and their molecular weight (MW), chemical nature and structure are of particular importance to contaminants removal and sludge properties [5].

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EPS is consisted of high MW polysaccharides, proteins, glycoproteins, nucleic acids, phospholipids and humic acids, affecting flocculation, settling and dewatering properties of activated sludge. Recently, multilayered structure model of sludge floc was proposed to understand the relationship between distribution and abundance of EPS and sludge dewaterability. Li et al. reported that EPS in activated sludge floc could be fractionated into loosely bounded EPS (LB-EPS) and tightly bounded EPS (TB-EPS), and the sludge dewatering behavior is mainly governed by characteristics of the former [6,7]. Furthermore, Yu et al. also suggested that sludge flocs were consisted of supernatant (bulk solution), slime, loosely bounded layer, tightly bounded layer and pellets, and sludge dewaterability is primarily influenced by the proteins (PN) and proteins/polysaccharides (PN/PS) in slime and bulk [8]. The organic compounds in the sludge bulk are composed primarily of SEPS [9,10] which is actually soluble microbial products (SMP) according to the report of Laspidou and Rittmann [11]. Fluorescence spectroscopy is proven to be an appropriate and effective method to characterize the EPS of activated sludge floc [12]. Yu et al. used three fluorescence excitation–emission matrix (3D-EEM) combined with parallel factor (PARAFAC) analysis to identify the key organic constituents affecting the sludge dewatering property, and the results indicated that the fluorescent intensity of protein-like substances in the bulk fraction correlated well with performance of sludge dewatering [13]. However, it is noted that the formation of EPS in activated sludge is a very complex bioprocess, so it is difficult to elucidate the nature of EPS. Combined EEM fluorescence spectroscopy and molecular weight analysis is able to provide unique and useful information on the better insight into the characteristics of EPS formed in biological process [14].

The influence of chemical conditioning on properties of sludge particles have been reported by many studies, but few of them focused on influence of chemical conditioning (especially inorganic coagulants) on soluble EPS properties. Both organic flocculants and inorganic conditioner can interact with sludge particles through charge neutralization and bridging, while inorganic coagulants should have greater effect on characteristics of SEPS due to their coagulation property. It is generally accepted that polyaluminum chloride (PACl) increases adsorption of organics in the bulk and improves sludge filterability [15]. The coagulation effectiveness of inorganic polymer flocculants (IPFs) is significantly affected by speciation distribution and physicochemical properties. Basically, the IPFs are intermediate compounds obtained from the hydrolysis-polymerization-settlement under artificially intensified conditions, and they are mainly composed by complexes of hydroxyl polynuclear species and various anions. Many studies demonstrated that the pre-formed polyhydroxy polymers exhibited better hydrolysis stability [16]. Therefore, IPFs are able to work more quickly than metal salts of low MW after entering into aqueous solution and show the better performance in coagulation process. In recent years, composite inorganic polymer flocculants are developed with both the advantages of IPFs and the additive coagulant aids, and the additives can improve the charge neutralization and bridging abilities of IPFs [17]. In this study, two IPFs, PACl and composite coagulant (HPAC), were used as sludge conditioners. Characteristics of SEPS were monitored in order to get an insight into relationship between SEPS and sludge dewatering behavior under IPFs conditioning. These results might provide useful information in controlling or optimizing chemical conditioning processes.

2. Materials and methods

2.1. Waste sludge

Surplus sludge 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 100 thousand ton, 40% of total flow is treated by anaerobic/anoxic/oxic (A/A/O) and other 60% is reused after treatment by MBR. Sample was stored at 4 °C and was analyzed within 5 days after sampling. The basic information of waste sludge and bulk can be found in Table 1.

2.2. Chemical agents

The sludge conditioners were two IPFs, polyaluminum chloride (PACl) and a composite coagulant (HPAC). Both coagulants were solutions with Al_2O_3 content of 10% and produced by a local factory (Beijing Wanshui Water Cleaning Agent Co., China). HPAC is made from specially controlled PACl with high yield of Al_{13} and different additives during the polymerization process. The basic information of two IPFs is given in Table 2, and the charge property of them is shown in Fig. S1 of Supporting materials (SM).

2.3. Jar test

Jar tests were conducted on a programmable jar test equipment (Daiyuan Jar Test Instruments, China). At first, Draw about 400 mL of sludge into a clean 600 mL beaker, and tester was started at rapid mixing of 200 rpm, coagulant solutions was quickly added followed by a reduction of the mixing speed to 30 rpm for 10 min and then let it stand for 30 min. Sludge sample was settled down at 2000 g for 15 min, and the supernatant (bulk solution) was collected as SEPS. Then, zeta potential and turbidity of sludge supernatant was measured. Cellulose acetate (CA) membranes with a pore size of 0.45 mm were used to remove the particulates present in the sludge supernatant. The filtered fractions were used for analyzing fluorescence EEM and dissolved organic carbon (DOC). In addition, the sample for HPSEC determination was filtered through a 0.22 μm membrane.

2.4. Analytical methods

2.4.1. SRF

SRF was measured with the standard Buchner funnel test using a using a quantitative filter paper. 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

Table 1
Characteristics of waste sludge and sludge bulk.

Physiochemical characteristics	Sludge					Sludge bulk	
	Solid (%)	pH	ZP (mV)	VSS/TSS	ZP (mV)	TOC (mg/L)	Turbidity (NTU)
Parameters	1.21 ± 0.02	7.12 ± 0.05	−20.6 ± 2.5	0.63 ± 0.02	−20.6 ± 2.5	4.99 ± 0.03	21.1 ± 3.2