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Improvement of wastewater sludge dewatering performance using titanium salt coagulants (TSCs) in combination with magnetic nano-particles: Significance of titanium speciation

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A B S T R A C T

In this study, the effects of chemical conditioning using titanium salt coagulants (TSCs) of different hydrolysis speciation in combination with magnetic nano-particles on dewatering performance of waste activated sludge were evaluated by means of specific resistance to filtration (SRF) and capillary suction time (CST). The morphological and extracellular polymeric substances (EPS) properties under chemical conditioning were investigated in detail to understand the reaction mechanisms involved. The results showed that the TSC with basicity of 0.5 performed better in improving sludge dewatering performance than other TSCs. Sludge floc formed by $TSC_{0.5}$ treatment was characterized by larger floc size and higher floc strength than that conditioned by other TSCs. EPS compression and densification were the major mechanisms of sludge conditioning, and $TSC_{0.5}$ had better performance in compressing EPS structure. In addition, reduction of soluble EPS concentration, especially protein-like substances contributed to improvement of sludge filterability under conditioning. Furthermore, addition of Fe_2O_3 nanoparticles could further improve dewatering performance and decrease compressibility of sludge system by acting as skeleton builders and enhancing floc strength. The sludge particles aggregation efficiency was effectively improved with addition of nano-Fe_2O_3. They also were able to bind with protein-like substance in EPS component, which might contribute to promotion of sludge filterability.

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 (Neyens et al., 2004). Generally, the moisture in activated sludge can be classified into free water (about 70%), interfacial water (about 20%) and bound water (about 10%) (Vaxelaire and Cézac, 2004). Except for the sludge characteristics, the dewatering efficiency was mainly dependent on the selection of device and chemical conditioning process.

The extracellular polymeric substances (EPS) accounted for 60–80% of sludge biomass (Liu and Fang, 2003). Many studies have demonstrated that EPS properties had important influence on sludge settling, flocculation and dewatering properties. Again, EPS content also greatly affected the charge property and floc stability (Mikkelsen and Keiding, 2002). Houghton et al. (2001) found that there existed a certain EPS mass at which the sludge dewaterability reach the maximum (Houghton et al., 2001). Higgins and Novak

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(1997) demonstrated that the sludge dewaterability was mainly affected by the ratio of protein and polysaccharide. Proteins exhibited more significant influence on sludge dewaterability than polysaccharide, high protein/polysaccharide was always detrimental to dewatering process. This observation was in agreement with Murtgy and Novak's findings (1999). Recently, Li and Yang (2007) suggested that the spatial distribution and chemical compostion of EPS had more significant effects on sludge dewatering property, and sludge dewatering performance was mainly dependent on content of loosely-bound EPS (LB-EPS) rather than that of tightly bound EPS (TB-EPS). Furhter, Yu et al. (2008) demonstrated that soluble EPS also played an important role in sludge dewatering process. Zhang et al. (2015a) suggested that change in concentration and compostion of soluble EPS fraction caused fluctuation of sludge dewatering behavior with time.

Prior to dewatering, chemicals were always dosed to improve sludge dewatering performance (called chemical conditioning). Addition of traditional chemical conditioners (inorganic salt coagulants and organic polymers) can agglomerate fine sludge colloids to form large flocs through charge neutralization and bridging, which can be more easily separated from the water (Niu et al., 2013; Zhang et al., 2014a). $TiCl_4$ is novel environmentally friendly inorganic coagulants and has attracted much attention in water and wastewater treatment (Shon et al., 2007; Zhao et al., 2011). It was found that $TiCl_4$ performed well in removing particles and natural organic matters (NOMs) in drinking water treatment. And it has many advantages of larger floc, low dosage and more settleable than traditional iron and aluminum salts coagulation etc. (Shon et al., 2009a, 2009b). Due to its strongly hydrolytic and acidic properties, addition of $TiCl_4$ would cause serious acidification of water. Poly-titanium salt coagulants (TSC) were prepared with pre-hydrolyzed process which can abate this problem. TSC exhibited better hydrolytic stability and coagulation performance for NOM and turbidity removal (Tomaszewska et al., 2004). In addition, the residuals produced from titanium salt coagulation can be converted into TiO_2 materials through high-temperature calcination (Shon et al., 2009a, 2009b; Kim et al., 2011), which is known to be an environmentally friendly photocatalyst. Nano materials, especially nano oxides have exhibited excellent physical and chemical properties and have many advantages over traditional adsorption materials, so they attracted much attention in recent years (Liang et al., 2004). Compared with traditional flocculation and adsorption materials, nano-Fe_2O_3 had better adsorption and flocculation performance for humic acid and protein-like substances (Wang et al., 2009a,b). In addition, nano-Fe_2O_3 particles were able to act as skeleton builders and enhance sludge floc strength, so they were selected as a co-conditioner of TSCs to decrease compressibility and improve dewaterability of wastewater sludge in this work."

So far, few investigations have focused on effects of sludge conditioning using titanium salt coagulants (TSC) in combination with nano-Fe_2O_3. Therefore, the aims of this study are to: (1) test the conditioning efficiency of TSC with different speciations; (2) understand the variations in morphological and EPS properties (distribution and composition) of sludge flocs to unravel the underlying mechanism involved; (3) investigate the conditioning efficiency and changes in floc properties under conditioning using TSC in combination with nano-Fe_2O_3; (4) provide a novel sludge pre-conditioning technique prior to dewatering process.

2. Material and methods

2.1. Source and properties of wastewater 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 200 thousands ton. The wastewater is reclaimed with combined process of MBR and ozonation. The sludge properties were given in Table 1. The volatile suspended solid (VSS), total suspended solid (TSS) and moisture content were measured according to standard methods (Apha, 1998).

2.2. Chemical reagents

All of reagents used in this study are of chemical grade. Spherical α-nanoFe_2O_3 was purchased from Sinopharm group in China (99.5% metals basis).

2.3. Experimental procedures

2.3.1. Preparation of different titanium salt coagulants

Slow alkali spotting was used to prepare the polytitanium chloride (TSC) as follow. Firstly, $TiCl_4$ solution (20%, wt/wt) was put into the ice-bath. 5 mol/L NaOH solution was dropped in the $TiCl_4$ solution with slow rate under vigorous agitation supplied by magnetic stirrer. Three TSCs were synthesized by controlling the molar ratio of OH^-/Ti^{4+} (B value) under 0.5 ($TSC_{0.5}$), 1.5 ($TSC_{1.5}$) and 2.5 ($TSC_{2.5}$) respectively.

2.3.2. Sludge conditioning procedures

Sludge samples were reacted with coagulants by using magnetic stirrer, the reacted procedure can be described as follows: a rapid mix period for 2 min at 400 rpm followed by a slow mix period for 8 min at 40 rpm. The titanium salt coagulants with different speciation were added under agitation using graduated pipette. For combined conditioning, the Fe_2O_3 was dosed prior to titanium salt coagulants addition.

2.4. Analytical methods

2.4.1. Sudge dewaterability assessment

2.4.1.1. SRF and compressibility. Specific resistance to filtration (SRF) is widely used to evaluate sludge dewatering performance in filtration process. It can be obtained by equation (1):

$$r = \frac{2PA^2b}{\mu\omega} \tag{1}$$

Where P ($Kg \cdot m^{-2}$) denotes pressure, A (m^2) is filtration area, μ ($Kg \cdot s \cdot m^{-2}$) is kinetic viscosity, ω ($kg \cdot m^{-3}$) 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 10s before surface cracking was observed.

The sludge cake compressibility measures the ability to compact the sludge when a normal pressure is applied (Qi et al., 2011). In practice sludge compressibility is often quantified as the slope of a log-log plot of the SRF versus the applied differential pressure. The coefficient of compressibility (s) is obtained by fitting data to Eq. (1)(Zhao and Bache, 2001).

$$\frac{SRF_1}{SRF_2} = \left(\frac{P_1}{P_2}\right)^s \tag{2}$$

In which P_1 and P_2 are two different filtration pressures (Pa), SRF_1 and SRF_2 are measured at P_1 and P_2, respectively.