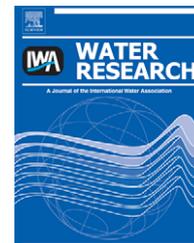


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Enhanced dewatering of waste sludge with microbial flocculant TJ-F1 as a novel conditioner

Zhiqiang Zhang^a, Siqing Xia^{a,*}, Jiao Zhang^b

^a State Key Laboratory of Pollution Control and Resource Reuse, Key Laboratory of Yangtze River Water Environment of Ministry of Education, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China

^b Department of Civil Engineering, Shanghai Technical College of Urban Management, Shanghai 200432, China

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ABSTRACT

Microbial flocculant (MBF) TJ-F1 with high flocculating activity was investigated to be used as a novel conditioner for the enhanced dewaterability of the waste sludge from wastewater treatment plant (WWTP). The experimental results showed that TJ-F1 was better than poly(acrylamide [2-(Methacryloyloxy)ethyl]trimethylammonium chloride) (P(AM-DMC)), the most commonly used conditioner in China, in improving the dewaterability of the waste sludge in terms of both the specific resistance in filtration (SRF) and the time to filter (TTF). The key parameters influencing the dewaterability of the waste sludge conditioned by TJ-F1, including the system pH, CaCl₂ concentration and TJ-F1 concentration, were systematically investigated. The favorite pH for the conditioning process was around the neutral. CaCl₂ was found to be a good conditioning aid to TJ-F1. A right dosage of TJ-F1 was decisive for the conditioning process. The optimized conditioning process is that about 0.17% (w/w) TJ-F1 and 1.3% (w/w) CaCl₂ are added into the sludge, and then the system pH was adjusted to 7.5. The compound use of TJ-F1 and P(AM-DMC) was also testified to be feasible in improving the dewaterability of the waste sludge.

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1. Introduction

The waste sludge has become a current problem and been focused for decades due to its huge production and potential environmental pollution (Vaxelaire and Cezac, 2004; Yu et al., 2008). The dewatering of the sludge is therefore necessary to obtain a product dry enough to allow a reduction in storage volume, facilitation of transportation, limitation of energy used in case of incineration, etc. (Colin and Gazbar, 1995; Lo et al., 2001). Chemical conditioning is often applied to improve the mechanical dewaterability of the waste sludge by flocculating the sludge particles with flocculants (Lo et al., 2001). In some sludge filtration applications, and in older literature, ferric chloride and lime were encountered as the conditioner in the wastewater treatment plants (WWTPs).

At present, the cationic derivatives of polyacrylamide (PAM) are the most commonly used conditioner in the WWTPs. Nevertheless, none of them are able to dewater the sludge as desired at acceptable conditioning dosages (Agarwal et al., 2005). As a consequence, for enhancing the dewaterability of the waste sludge, it is highly anticipated to develop efficient flocculants which can partly or even completely substitute the traditional conditioners (Zhang et al., 2007).

Microbial flocculants (MBFs) are microorganism-produced special natural organic macromolecule substances that can flocculate suspended solids, cells, colloidal solids, etc (Zhang, 2005). With the advantages of high efficiency, innocuity and biodegradability over traditional flocculants, MBFs have been paid more and more attention to recently (Zhang et al., 2007). Salehizadeh and Shojaosadati (2003) reported that the MBF

* Corresponding author. Tel.: +86 21 65980440; fax: +86 21 65986313.

E-mail address: siqingxia@tongji.edu.cn (S. Xia).

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produced by *Bacillus firmus* could effectively adsorb some heavy metal ions, such as Pb, Cu and Zn. The combination of $\text{Fe}_2(\text{SO}_4)_3$ and the MBF produced by *Bacillus* sp. was able to eliminate turbidity from raw water (Ma et al., 2008). The MBF produced by *Bacillus mucilaginosus* was successfully applied to remove chemical oxygen demand (COD), biological oxygen demand (BOD) and suspended solid (SS) from several wastewaters, including domestic, brewage and pharmaceutical wastewaters (Lian et al., 2008). The MBF from *Serratia ficaria* was used to treat pulp effluent, and the removal rate of color and COD were up to 99.9% and 72.1%, respectively, which were better than traditional chemical flocculants (Gong et al., 2008). The cells, like *Cryptosporidium* oocysts and *Salmonella*, could be effectively removed by the MBF produced by *Klebsiella terrigena* (Ghosh et al., 2009a,b). To our best knowledge, no previous work describing the enhanced dewaterability of the waste sludge by conditioning with MBF has been reported to date.

In the present study, the MBF (TJ-F1) produced by *Proteus mirabilis* TJ-1 screened out from the activated sludge was extracted and used as a novel conditioner for enhancing the dewaterability of the waste sludge. The dewaterability of the waste sludge treated by various conditioners, including poly(acrylamide [2-(Methacryloyloxy)ethyl]-trimethylammonium chloride) (P(AM-DMC)), CaCl_2 , TJ-F1, et al., was compared with each other. P(AM-DMC), the most commonly used cationic polyacrylamide derivatives in China, is used as the conditioner in the plant where we obtain the samples. The effects of the system pH, CaCl_2 concentration and TJ-F1 concentration on the dewaterability of the waste sludge were systematically investigated. The optimized conditioning process of the waste sludge by TJ-F1 was obtained, and the conditioning mechanism was proposed. Finally, the feasibility of the compound uses of TJ-F1 and P(AM-DMC) was also investigated.

2. Materials and methods

2.1. Microorganism culture and MBF preparation

P. mirabilis TJ-1 (GenBank accession No. EF091150) is a bio-flocculant-producing microorganism screened out from the mixed waste sludge of four WWTPs (Quyong, Anting, Dongqu and Tongjixinchun in Shanghai, China) by the State Key Laboratory of Pollution Control and Resource Reuse (SKL), Tongji University of China (Xia et al., 2008). A 150-mL flask containing 50 mL production medium was inoculated with 1.0 mL pre-culture of strain TJ-1 and incubated at 25 °C in a rotary shaker at 130 r/min for 48 h (Xia et al., 2008). The fermentation broth obtained was centrifuged (4000 × g, 30 min) to separate the cells. The cell-free culture supernatant was the liquid MBF and preserved at 4 °C in fridge for further use. About 1.33 g of the purified MBF, whose molecular weight (MW) was about 1.2×10^5 Da, could be recovered from 1.0 L of fermentation broth.

2.2. Reagents

P(AM-DMC) and CaCl_2 were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Other reagents are of analytical grade. P(AM-DMC) was dissolved in distilled water

to prepare the solutions (about 1.33 g/L) which is similar to the concentration of the liquid TJ-F1.

2.3. Waste sludge

Waste sludge samples were collected from the secondary settling tank of a municipal WWTP in Shanghai, China. The plant treats 75,000 m³/d of wastewater (93% domestic and 7% industrial sewage) using anaerobic-anoxic-oxic process. The collected samples had undergone gravity thickening and was ready to be dewatered by a belt press filter after adding P(AM-DMC). The samples were transported to the laboratory within 30 min following sampling. And the samples were subsequently stored at 4 °C and analyzed within 2 days. Then the new waste sludge would be sampled from the WWTP. The characteristics of the sludge is listed in Table 1.

2.4. Conditioning experiments

The dewaterability of the waste sludge was measured by the Buchner funnel test (figure not shown), one of the most common methods used in dewaterability measurement, and expressed in terms of specific resistance in filtration (SRF) and time to filter (TTF) (Lo et al., 2001). All experiments were performed in triplicate for the mean calculation. In each test, the conditioner was added into a 200-mL beaker with 50 mL of the waste sludge, and then the system pH was adjusted to the set value by NaOH (0.1 M) and HCl (0.1 M). After stirring for 1 min, the mixture was left still for 5 min. Then the mixed sludge was poured into the funnel fitted with a filter paper (Whatman No. 1). After 2 min of gravitational drainage, a vacuum of 50 kPa was applied. Then the volume of the filtrate collected at different times was recorded. TTF is defined as the time when the volume of the filtrate goes up to half of the volume of the sludge, and SRF is calculated by using the following equation (Lo et al., 2001):

$$\text{SRF} = \frac{2bPA^2}{\mu c} \quad (1)$$

where P is the pressure of filtration, N/m²; A is the filtration area, m²; μ is the filtrate viscosity, N s/m²; c is the weight of solids per unit volume of filtrate, kg/m³ = $1/C_f/(100 - C_i) - C_f/(100 - C_f)$; C_i is the initial moisture content, %; C_f is the final moisture content, %; b is the slope determined from the $t/V_f(y) - V_f(x)$ plot; V_f is the volume of filtrate, m³; and t is the filtration time, s.

3. Results and discussion

3.1. Comparison of the dewaterability of the waste sludge by various conditioners

Various conditioners, including 5 mL distilled water (blank), 5 mL CaCl_2 (1%, w/v), 5 mL TJ-F1, 2 mL TJ-F1 + 3 mL CaCl_2 (1%, w/v), and 5 mL P(AM-DMC), were separately added into the waste sludge. And then the system pH was adjusted to 7.5 for the Buchner funnel test. The volumes of the filtrates recorded at different time are shown in Fig. 1a, and the values of both SRF and TTF obtained for the various conditioners are shown in Fig. 1b.

Table 1 – Characteristics of waste sludge collected from municipal WWTP.

pH	Moisture content (%)	VSS/TSS (%)
6.23 ± 0.12	96.81 ± 0.64	55 ± 9

As shown in Fig. 1a, the biggest volume of the filtrate was obtained when 2 mL TJ-F1 together with 3 mL CaCl₂ were added into the waste sludge. A similar feature can also be noted in Fig. 1b. P(AM-DMC) were not able to improve the dewaterability of the sludge to such an extent. So it is feasible and meaningful to enhance the dewaterability of the sludge by the utilization of TJ-F1.

Following is the systematical investigation on the key parameters influencing the dewaterability of the waste sludge conditioned by TJ-F1. As can be seen from Fig. 1, the variation of the curve of the filtrate volume recorded every 1 min can directly reflect the dewaterability of the sludge. To simplify the calculation, the volume of the filtrate will be used to denote the dewaterability of the waste sludge conditioned by TJ-F1.

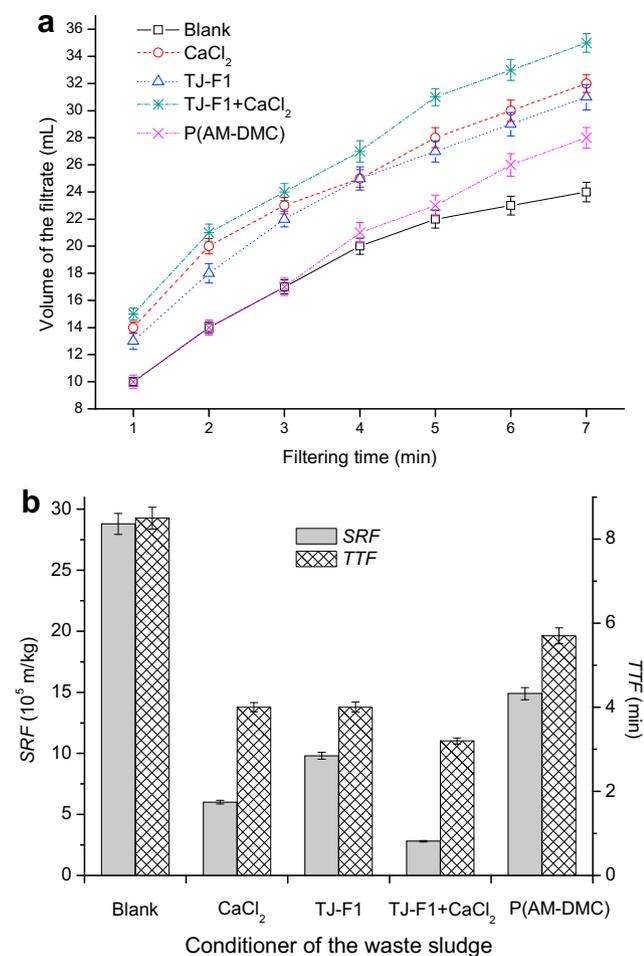


Fig. 1 – (a) Dewatering curves and (b) the specific resistance in filtration (SRF) and the time to filter (TTF) of the waste sludge conditioned by various conditioners.

3.2. Effect of the system pH on the dewaterability of the waste sludge

The effect of the system pH on the dewaterability of the waste sludge was investigated by adding 50 mL of the sludge into a 200-mL beaker, and then 2 mL of TJ-F1 and 3 mL of CaCl₂ were added into the beaker. Then the system pH was adjusted to 5.0, 6.0, 7.0, 7.5, 8.0, or 9.0 for the Buchner funnel test. The volumes of the filtrates recorded every 1 min are shown in Fig. 2. The system pH exerts an obvious effect on the dewaterability of the waste sludge, and pH 7.5 is the optimized value. Around the neutral pH, the suspended sludge particles were easy to be aggregated into big flocs by TJ-F1 and the proportion of free water in the sludge is then increased, facilitating the dewatering process (Chang et al., 1997).

3.3. Effect of CaCl₂ concentration on the dewaterability of the waste sludge

2 mL of TJ-F1 and various volumes of CaCl₂ (1%, w/v), including 0 mL (blank), 0.5 mL, 1.0 mL, 2.0 mL, 3.0 mL, 5.0 mL, and 7.0 mL, were separately added into 200-mL beakers with 50 mL of the waste sludge. Then the system pH was adjusted to 7.5 for the Buchner funnel test. The volumes of the filtrates recorded every 1 min are shown in Fig. 3. The biggest volume of the filtrate was obtained when 2.0 mL of CaCl₂ was used. The difference of the volumes of the filtrates under the same conditions between Figs. 2 and 3 was caused by the sludge sampled in different dates, which indicates the variation of the influent. Ca²⁺ can efficiently neutralize the negative charges of the suspended sludge particles and bridging the organic materials in the out layer of the waste sludge (Neyens et al., 2004; Xia et al., 2008). A deficient concentration of CaCl₂ cannot make all the suspended particles and the organic materials flocculated. On the other hand, an excessive concentration of CaCl₂ makes the suspended particles and the organic materials stable again in their original states because of superfluous positive charges (Xia et al., 2008).

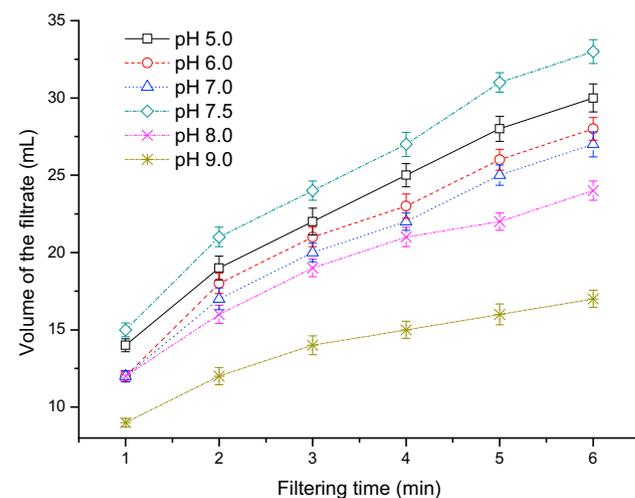


Fig. 2 – Effect of the system pH on the dewaterability of the waste sludge conditioned by 2 mL of TJ-F1 and 3 mL of CaCl₂ (1%, w/v).

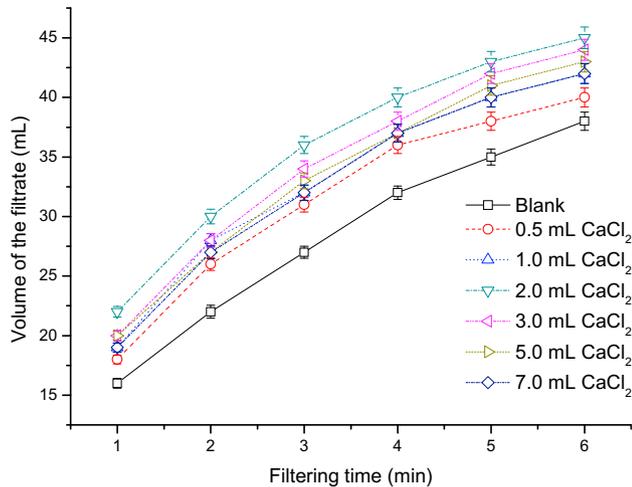


Fig. 3 – Effect of the CaCl_2 concentration on the dewaterability of the waste sludge conditioned by CaCl_2 (1%, w/v) and 2 mL TJ-F1 at pH 7.5.

3.4. Effect of TJ-F1 concentration on the dewaterability of the waste sludge

2 mL of CaCl_2 (1%, w/v) and various volumes of TJ-F1, including 0 mL (blank), 0.5 mL, 1.0 mL, 2.0 mL, 4.0 mL, and 6.0 mL, were separately added into 200-mL beakers with 50 mL of the waste sludge. Then the system pH was adjusted to 7.5 for the Buchner funnel test. The volumes of the filtrates recorded every 1 min are shown in Fig. 4. The biggest volume of the filtrate was obtained when the dose of TJ-F1 was 2.0 mL. The difference of the volumes of the filtrates under the same conditions between Figs. 3 and 4 was also caused by the sludge sampled in different dates. A deficient dosage of TJ-F1 cannot make all the sludge particles flocculated to become compact sludge flocs. On the other hand, an excessive concentration may prevent the small flocs to grow as big flocs because of the

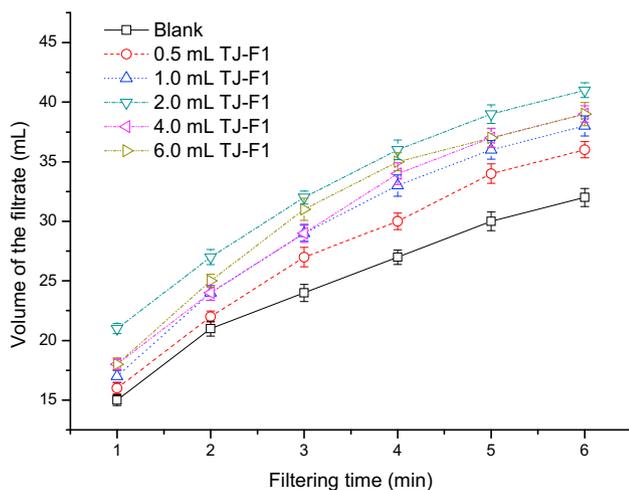


Fig. 4 – Effect of the TJ-F1 concentration on the dewaterability of the waste sludge conditioned by TJ-F1 and 2 mL CaCl_2 (1%, w/v) at pH 7.5.

same charges in them. Most of the restricted water still lays in the interior of the small flocs, improving the difficulty of the sludge dewatering (Yu et al., 2008).

On the basis of the above experimental results, the optimized conditioning process for improving the dewaterability of the waste sludge was identified as follows. 2 mL of TJ-F1 and 2 mL of CaCl_2 (1%, w/v) were added into a 200-mL beaker with 50 mL of the sludge. Then the system pH was adjusted to 7.5 for the Buchner funnel test. That is to say, the optimized conditioning process for improving the dewaterability of the sludge conditioned by TJ-F1 is that about 0.17% (w/w) TJ-F1 and 1.3% (w/w) CaCl_2 are added into the sludge, and then the system pH was adjusted to 7.5.

3.5. Conditioning mechanism of TJ-F1

Many elements, such as particle size, extracellular polymeric substances (EPS), cationic salts and conditioning, were reported to influence the sludge dewaterability (Chen et al., 2001; Vaxelaire and Cezac, 2004). Some cations in general, and bi-valent ones specifically, have been found to aid flocculation and dewatering by bridging negative sites on EPS, which can promote an increase in floc size, floc density and dewaterability (Neyens et al., 2004). The presence of EPS is believed to be one of the unfavorable elements in activated sludge dewatering (Chen et al., 2004, 2001). Li and Yang (2007) and Novak et al. (2003) reported that sludge dewaterability was correlated with loosely bound EPS (LB-EPS). Through centrifugation and ultrasound, Yu et al. (2008) stratified the sludge flocs from various WWTPs into five layers: (1) supernatant, (2) slime, (3) LB-EPS, (4) tightly bound EPS (TB-EPS) and (5) pellet. They found that the sludge should have good dewaterability if the organic material (mainly proteins) embedded in the sludge matrix does not enter the outer layers, i.e., the supernatant, slime and LB-EPS.

As early reported (Xia et al., 2008), TJ-F1 mainly contained proteins (30.9%, w/w) and acid polysaccharides (63.1%, w/w), including neutral sugar, glucuronic acid and amino sugar as the principal constituents in the relative weight proportions of 8.2:5.3:1. The similar components of TJ-F1 with the organic materials in the out layers of the waste sludge might make them have an excellent affinity potential. Its molecular weight (MW) was 1.2×10^5 Da, which means ample binding-sites and strong van der Waals forces with the sludge particles and the organic materials in the out layers. Scanning electron microscopy (SEM) image of the purified solid-state TJ-F1 showed that it had a crystal-linear structure, which assures the binding-sites to be functional and bridge more sludge particles and out layer organic materials to form compact sludge flocs (Salehizadeh and Shojaosadati, 2001; Zhang et al., 2007). Accordingly, the organic materials in the out layers of the waste sludge might be drove back into the sludge matrices by the strong adsorbability and bridging ability of TJ-F1 (Yu et al., 2008). Spectroscopic analysis of the MBF by Fourier-transform infrared (FTIR) spectrometry indicated the presence of carboxyl, hydroxyl and amino groups preferred groups for all flocculation processes. The strong adsorbability between the functional groups and the various heavy metal ions in the waste sludge could make the new produced sludge flocs more compact than the original ones (Salehizadeh and

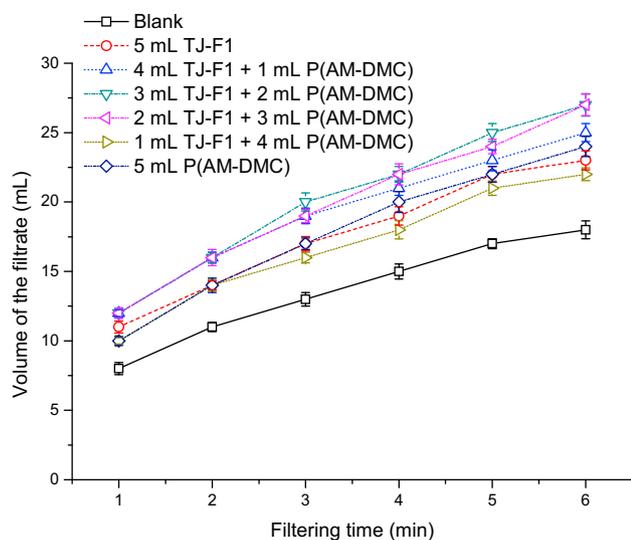


Fig. 5 – Effect of various ratios of compound conditioning of TJ-F1 and P(AM-DMC) on the dewaterability of the waste sludge.

Shojaosadati, 2003), which further promoted the dewaterability of the waste sludge by expelling the water in the exterior and the interior of the sludge flocs. As the conditioning aid of TJ-F1, CaCl_2 could further promote an increase in floc size, floc density and dewaterability of the waste sludge (Neyens et al., 2004).

3.6. Compound use of TJ-F1 and P(AM-DMC)

The compound use of TJ-F1 with P(AM-DMC) on the dewaterability of the waste sludge was investigated in the volume ratios of 5:0, 4:1, 3:2, 2:3, 1:4, and 0:5. 5 mL of the compound flocculants were added into 200-mL beakers with 50 mL of the waste sludge. Then the pH was adjusted to 7.5 for the Buchner funnel test. The volumes of the filtrates recorded every 1 min are shown in Fig. 5. The compound use of TJ-F1/P(AM-DMC) can markedly improve the dewaterability of the waste sludge. The optimized ratio for TJ-F1/P(AM-DMC) is 3:2. In the optimized process, the dewaterability of the sludge is better than that obtained when using only one of the conditioners. The compound use of TJ-F1 and P(AM-DMC) was also testified to be feasible in improving the dewaterability of the waste sludge.

The dewaterability tests used in this research, though commonly accepted, are also known to predict dewaterability only under low-shear conditions. Future research would assess the MBF under the actual shear of pilot or full-scale dewatering.

4. Conclusions

Microbial flocculant TJ-F1 was demonstrated to be an effective conditioner in enhancing the dewaterability of the waste sludge from WWTP. The experimental results showed that TJ-F1 was better than P(AM-DMC), in improving the

dewaterability of the waste sludge in terms of both SRF and TTF. The optimized conditioning process for improving the dewaterability of the sludge conditioned by TJ-F1 is that about 0.17% (w/w) TJ-F1 and 1.3% (w/w) CaCl_2 are added into the sludge, and then the system pH was adjusted to 7.5. The compound use of TJ-F1 and P(AM-DMC) was also testified to be feasible in improving the dewaterability of the waste sludge.

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