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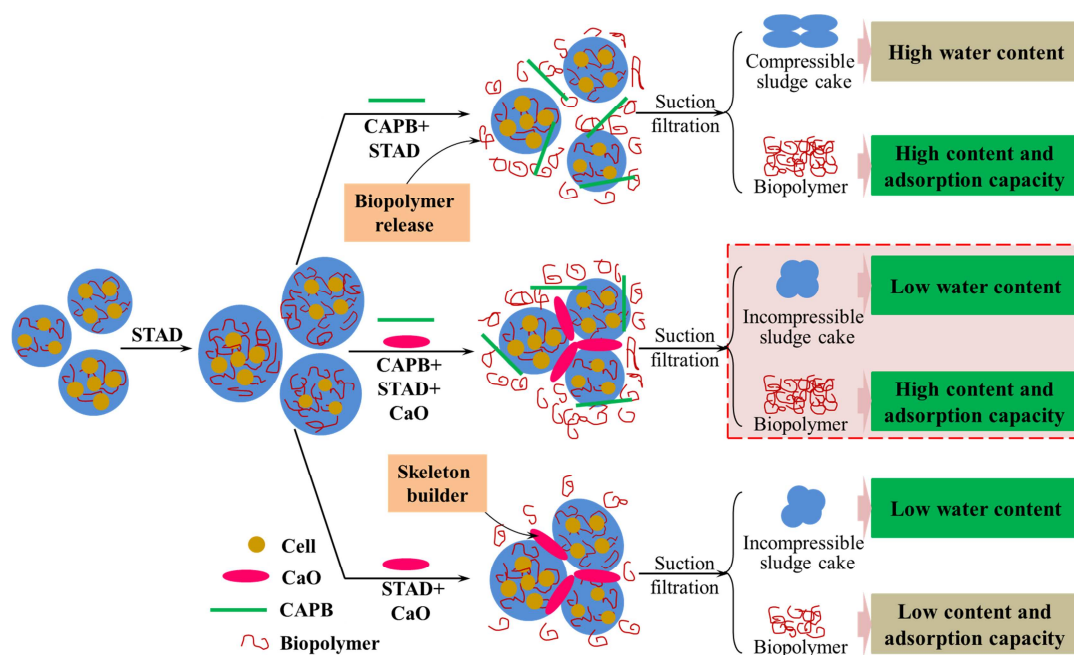
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Graphical Abstract



**Simultaneously enhanced biopolymers production and sludge dewaterability of
waste activated sludge by synergetic integration process of short-time aerobic
digestion with cocoamidopropyl betaine and calcium oxide**

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Abstract

Waste activated sludge (WAS) has seriously threatened the environment safety and the public health due to its rapid growth and complex components. Simultaneously enhanced the biopolymers production and the sludge dewaterability of WAS were investigated by synergetic integration process of the short-time aerobic digestion (STAD) with cocoamidopropyl betaine (CAPB) and calcium oxide (CaO). STAD could improve the biopolymers production by biosynthesis. CAPB could further significantly enhance the biopolymers production and optimized the constituents. CaO (0.1~0.2 g/g TSS) could dramatically enhance the sludge dewaterability by forming a multi-grid skeleton in WAS, while the biopolymers production could almost remain stable. Especially, the synergetic integration process of STAD with 0.1 g CAPB/g TSS for 8 h and 0.1 g CaO/g TSS could cost-effectively enhance both the biopolymers production and the sludge dewaterability. The produced biopolymers showed strong adsorbability for heavy metals (eg, 375 mg Cu^{2+} /g biopolymers). Accordingly, the developed novel process is of big significance for resource utilization and volume reduction of WAS.

Keywords: Waste activated sludge (WAS); Short-time aerobic digestion (STAD); Sludge dewaterability; Cocoamidopropyl betaine (CAPB); Calcium oxide (CaO)

1 Introduction

Waste activated sludge as a typical by-product is largely produced in wastewater treatment plants (WWTPs) (Kiff, 1978). According to the report of development prospect and investment forecast on China sewage treatment industry in 2017-2021 ((EIC), 2017), the yield of waste activated sludge (WAS) with 80% water content in urban WWTPs reached 40.88 million tons in 2015, which will further dramatically increase due to the advancement of the urbanization level. WAS has been seriously threatened the environment and public health, and it's imperative to develop effective processes for resource utilization and volume reduction of WAS (Campbell, 2000; Paul et al., 2006).

WAS contains about 60% of organic matters including proteins (PN), polysaccharides (PS), nucleic acids (NA), humic acids (HA) etc., and another 40% of inorganic matters contain calcium and magnesium salt (Fytili and Zabaniotou, 2008). Because of these organic and inorganic matters, WAS could be used as the source materials of fertilizer, building material, activated carbon, biopolymers for heavy metals removal and so on (Tyagi and Lo, 2013). Although aerobic digestion is widely utilized in middle and small WWTPs, the biomass is majorly mineralized by consuming lots of energy (Zhang et al., 2016). Short-time aerobic digestion (STAD) was found to improve the biopolymers production from WAS by biosynthesis. The biopolymers are excellent biosorbents for removing and recycling heavy metals from wastewater due to their large amounts of negatively charged functional groups such as carboxyl, hydroxyl, amino, phosphate and sulfate (More et al., 2012; Zhou et al., 2015; Zhou et al., 2016a). Surfactants like cocoamidopropyl betaine (CAPB), were further

found to promote the STAD of WAS to enhance the biopolymers production via forming micelles effective for improving the solubility of the macromolecular organic matters in EPS and IPS (Sengco et al., 2001; Xia et al., 2017; Zhou et al., 2017d). However, the moisture in the digested sludge after extracting the biopolymers was still high (Neyens et al., 2004).

The moisture in WAS contains free moisture, interstitial moisture, surface moisture and bound moisture (Tsang and Vesilind, 1990). Bound moisture is chemically bound to the solid phases in WAS, which contain extracellular polymeric substances (EPS) and intracellular polymeric substances (IPS) (Vaxelaire and Cézac, 2004). Unlike other three kinds of moistures, bound moisture proportion is normally lower than 3% in the total moisture of WAS, but which cannot be removed using the mechanical force separation methods containing gravitational settlement, centrifugation and negative pressure separation (Tsang and Vesilind, 1990; Lee, 1996). In order to convert the bound moisture stored in EPS and IPS to free moisture and achieve the fast solid and liquid separation, solubilization of EPS and even cell lysis that resulted to the release of IPS should be the significant step. Previous studies (Neyens et al., 2002; Neyens and Baeyens, 2003a, b; Brar et al., 2010) mentioned that thermal hydrolysis (acid, neutral and alkaline conditions) and chemical oxidation (advanced oxidation, ozonation, H_2O_2 oxidation, nanomaterials catalytic oxidation and so on) could be used to solubilize EPS and even cause cell lysis effectively. Additionally, as the commonly used multi-grid skeleton materials, calcium oxide (CaO), flyash and diatomite could be used to enhance the strength and reduce the compressibility of WAS, and then further enhance the dewaterability of WAS (Shi et

al., 2008; Thapa et al., 2009). In particular, CaO as a cheap dehydrant can react with water in WAS and raise the sludge temperature, cause cell lysis and kill pathogenic bacteria at the same time, which result in better dewaterability and stabilization of WAS (Zhai et al., 2012; Liu et al., 2015). Thus, CaO might be an optimal choice to further decrease the moisture in the digested sludge after extracting the biopolymers.

In this study, simultaneously enhanced biopolymers production and sludge dewaterability of WAS were investigated by comparing the synergetic integration process of STAD with CAPB and CaO with other two processes (CAPB+STAD, STAD+CaO). The effects of the three processes on the normalized CST of WAS and water content of sludge cake, and the production of PN, PS and NA in the biopolymers. The biopolymers with various proportions of fractions were used to test their absorbability for Cu^{2+} and the key fraction of the biopolymers responsible for binding Cu^{2+} were identified. Scanning electron microscopy (SEM) was used to characterize the variation of WAS surface structure after processed by the three methods. Mechanisms of simultaneously enhancing biopolymer productions and sludge dewaterability by the synergetic process of CAPB+STAD+CaO were elaborated.

98 2 Materials and Methods

99 2.1 Chemicals and waste activated sludge samples

100 Cocoamidopropyl betaine surfactant ($C_{19}H_{38}N_2O_3$, CAPB), with a molecular
101 weight of 342.52 g/mol, was purchased from Shanghai Chem. Co. Ltd., China.
102 $Cu(NO_3)_2 \cdot 3H_2O$ (>99% purity) was obtained from Runjie Chemistry Reagent
103 (Shanghai, China) and the stock solution of Cu^{2+} was prepared by dissolving
104 $Cu(NO_3)_2 \cdot 3H_2O$ in distilled water at an initial concentration of 1000 mg/L.

105 WAS samples were obtained from the secondary sludge settling tank in a
106 full-scale municipal wastewater treatment plant in Shanghai, China. Collected
107 samples were screened through a 1.2 mm sieve to remove grit and then gravity
108 concentration for 30 min. Supernatants were removed and the main parameters of
109 concentrated sludge were shown in Table 1. Concentrated sludge was stored at 4 °C
110 and used within 2 days.

111 2.2 Three processes of WAS

112 For the CAPB+STAD process experiments, CAPB with the dosage of 0.00, 0.02,
113 0.05, 0.10, 0.15 and 0.20 g/g TSS were added to the concentrated WAS and then
114 aerobic digested in six plastic cylindrical reactors simultaneously. The size
115 parameters and schematic configuration of the aerobic digestion reactor, and the
116 aerobic digestion of WAS were described in detail in our previous studies (Zhang et
117 al., 2016; Zhou et al., 2017b).

118 For the STAD+CaO process experiments, WAS without adding CAPB was
119 initially aerobic digested for 8 hours and CaO was added to the digested sludge with
120 the dosage of 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 g/g TSS, and then mixing the samples at

250 rpm for 2 min, followed by slow stirring at 150 rpm for 8 min with the temperature of 298.15 ± 1 K using a constant temperature – magnetic stirrer (RCT/RET, Guangzhou Boletai. Co., China).

For the synergetic integration process (CAPB+STAD+CaO) experiments, WAS with CAPB (0.10 g/g TSS) was initially aerobic digested for 8 hours, and then CaO was added to the digested sludge with the dosage of 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 g/g TSS. The samples were mixed immediately using the same method as presented above.

2.3 Biopolymer extraction and sludge dewatering

The vacuum filtration method was used for simultaneously biopolymer production and sludge dewatering. 100 mL of processed sludge was poured into a Buchner funnel (Figure S1), fitted with pre-wetted quantitative filter paper (Cat No. 92410552S), under a constant vacuum pressure of 0.045 MPa supplied by a vacuum pump (DAP-12, Ulvac Kiko Inc., Japan) for 30 min or until the vacuum could not be maintained (< 30 min). The sludge cake on the surface of the filter paper was dried at 105 °C until obtained a constant weight. The collected filtrates were centrifuged twice at 10800×g with a constant temperature of 277.15 K for 10 min. The supernatant was the raw biopolymer, which was further purified via cold acetone method (Zhou et al., 2015).

2.4 Adsorption of Cu^{2+} by the biopolymer

The biopolymers used in the adsorption experiments contain three parts: from the CAPB+STAD process with the dosage of CAPB 0.10 g/g TSS and aerobic digestion time 2, 4, 8, 12 and 24h (Part I); from the STAD+CaO process experiments with the

dosage of CaO 0.1, 0.2, 0.3, 0.4 and 0.5 g/g TSS (Part II); and from the synergetic integration process (CAPB+STAD+CaO) experiments with the dosage of CAPB and aerobic digestion time 0.10 g/g TSS and 8 h, respectively, and the dosage of CaO 0.3 g/g TSS (Part III). Adsorption experiments were carried out by adding the biopolymers into 250-mL Erlenmeyer flasks containing 50 mL of $\text{Cu}(\text{NO}_3)_2$ solutions with the initial concentration of 10 mg Cu^{2+} /L and weight ratio of biopolymer/ Cu^{2+} at 2.0. The flasks were sealed immediately after adding the biopolymers to decrease the evaporation of solution. Reaction conditions were controlled as follows: temperature 303.15 K, initial pH 5.5, isothermal shaking speed 150 rpm, and reaction time 30 min. Our previous studies (Zhang et al., 2014; Zhou et al., 2016c) demonstrated that the adsorption of Cu^{2+} by the biopolymers almost reached equilibrium after 30 min. Samples were taken from the solutions after agitation and separated from the precipitates prior to analysis through centrifugation at $10,800 \times g$ for 10 min with a temperature of 277.15 K, and then filtrated using 0.22- μm cellulose nitrate membrane filters. Filtrate was acidified with HNO_3 and then analyzed the residual Cu^{2+} using inductively coupled plasma atomic emission spectrometry (ICP-AES, Agilent 720ES, USA). The adsorbed Cu^{2+} by the biopolymers (q_e , mg/g) is calculated using Eq.(1) (Zhou et al., 2016b; Zhou et al., 2017c).

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentration of Cu^{2+} in the solution, respectively, mg/L; V is the volume of the solution, L; and W is the weight of the biopolymers, g.

2.5 Analytical methods

The pH of sludge samples were measured with a pH meter (HQ40d, Hach, USA). Water content of sludge cake, TSS and VSS of WAS were analyzed using the standard methods (American Public Health et al., 1915). The dewaterability of sludge was determined by measuring the capillary suction time (CST) with a CST instrument and a Whatman No. 17 chromatography grade paper, and then divided by the initial TSS for normalization (APHA, 2005). SEM image of the sludge samples were completed using Philips XL 30 ESEM. PN, PS and NA in the biopolymers were examined using the following colorimetric methods: Bradford method for PN content, bovine serum albumin as the standard (Frølund et al., 1996); phenol-sulfuric acid method for PS content, glucose as the standard (Frølund et al., 1996); diphenylamine colorimetric method for NA content, calf thymus deoxyribonucleic acid as the standard (Frølund et al., 1996).

2.6 Statistical analysis

Triplicate processes of activated sludge and the adsorption experiments of the biopolymers for Cu^{2+} were carried out at each condition, and each sample from each experiment was assayed one time for pH, TSS, VSS, CTS, water content of sludge cake, PN, PS, NA and residual Cu^{2+} . Results are expressed as the mean and standard deviation of the three measured samples (mean \pm SD). Pearson's correlation coefficient was used to evaluate the linear correlation between the dosage of CAPB and the fractions concentration in the biopolymers under various aerobic digestion times, and the adsorption capacity of Cu^{2+} and the proportions of PN, PS and NA in

187 the biopolymers. Correlations were considered statistically significance with a 95%
188 confidence interval ($P < 0.05$).

3 Results and discussion

3.1 Effects of CAPB on biopolymers production and sludge dewaterability of WAS by STAD

Fig.1 (a)-(d) shows the effects of CAPB dosage on the production of PN, PS, NA and total biopolymers, respectively, and Fig.S2 shows the corresponded proportions of PN, PS, NA and biopolymers at the noted STAD times in the CAPB+STAD process of WAS. Table 2 presents the parameters of the linear relationship between CAPB dosage and the biopolymers concentrations and its fractions. CAPB could enhance the solubilization of organic matters from WAS and resulted in the dramatic increase of the biopolymers, which also gradually increased with the increasing of CAPB dosage. CAPB dosage also had a strong and nearly linear relationship with the biopolymers and its fractions concentrations as all of the correlation coefficients (R^2) were above 0.95 (Table 2). PN were the key fraction and it also keep increasing as CAPB dosage increased, and PS was higher than NA as CAPB dosage lower than 10% (Fig.S2). While, NA was higher than PS as CAPB dosage higher than 10%, meaning cell lysis occur. During the STAD process, K , meaning the release of organic matters, gradually increased in the initial 8 h, but gradually decreased in the later stage (Table 2), which was consistent with the biopolymers and its fractions variations (Fig. 1). The long alkyl chain in CAPB can form micelles that could enhance the solubility of macromolecular organic matters (MOM) in WAS (Zhou et al., 2017a; Zhou et al., 2017d) and resulted in the biopolymers increase in the initial 8 h. Moreover, soluble biopolymers could be consumed by heterotrophic bacteria as

which could be the proper carbon sources and electron donor (Zevin et al., 2015), which was responsible for the biopolymers decrease in the later stage of STAD.

Fig.1(e)-(f) shows the effects of CAPB dosage on the normalized CST of WAS and water content of sludge cake at the noted STAD times. Fig.2 presents the Pearson correlations between the normalized CST and the PN, PS, NA and biopolymers concentrations. The normalized CST of WAS gradually increased with the increasing of CAPB dosage, meaning a deteriorated dewatering performance of WAS after adding CAPB. Especially, CAPB dosage higher than 10% caused a dramatically increase of the normalized CST, which also keep increasing during the STAD process. The normalized CST had a strong linear positive relationship with the concentrations of PN ($R^2 = 0.854$, $P < 0.01$), PS ($R^2 = 0.788$, $P < 0.01$), NA ($R^2 = 0.768$, $P < 0.01$) and biopolymers ($R^2 = 0.819$, $P < 0.01$). CAPB could enhance the solubilization of MOM containing EPS and even IPS in WAS, and high concentration of soluble organic matters in the mixed culture caused the deteriorated dewatering performance of WAS. Previous studies (Chen et al., 2001; Zhou et al., 2017d) also mentioned that hydrophilic organic matters could adsorb water and high concentration of soluble organic matters in the mixed culture led to the poor dewatering performance of WAS. CAPB could significantly increase the water content of sludge cake, lead to the deteriorated dewatering content of WAS. During the STAD process, the water content of sludge cake gradually decreased in the initial stage, but which increased again later. Results should that STAD could enhance the dewaterability of WAS, which is consistent with previous findings (Zhang et al., 2016).

3.2 Effects of CaO on biopolymers production and sludge dewaterability of WAS by STAD

Fig.3 (a)-(b) shows the effects of CaO dosage on the biopolymers and its fractions production and the variation of fractions proportion in the STAD+CaO process of WAS, respectively. PN, PS, NA and the biopolymers dramatically increased as CaO dosage increased from 0 to 0.3 g/g TSS, but which gradually decreased for a higher CaO dosage. The maximum biopolymers and proteins concentrations were 10.5 and 25.59 mg/gVSS, respectively. PN (41%~52%) were the key fraction in the biopolymers, followed by PS (35%~41%) and NA (13%~23%). Fig.3 (c)-(d) presents the normalized CST of WAS and water content of sludge cake. Normalized CST slightly increased as CaO dosage increased from 0 to 0.3 g/g TSS, but which dramatically decreased for a higher CaO dosage. Water content of sludge cake dramatically decreased from 78.1% to 73.5% after adding 0.1 g/g TSS of CaO, and which further gradually decreased after adding more CaO. Compared with CAPB+STAD process, adding CaO could significantly reduce the water content of sludge cake, but the biopolymers concentrations dramatically decreased.

3.3 Synergetic effects of CAPB and CaO on the biopolymers production and WAS dewaterability of WAS by STAD

Fig.4 (a)-(b) shows the synergetic effects of CAPB and CaO on the biopolymers production and its fractions, and the fractions proportion in the biopolymers of the synergetic integration process (CAPB+STAD+CaO) of WAS, respectively. Sludge was treated by aerobic digested for 8h with 0.10 g CAPB /g TSS, and then treated by various dosages of CaO. Concentrations of the biopolymers and its fractions almost

remained stable as CaO dosage increased from 0 to 0.2 g/g TSS, but which gradually decreased as CaO dosage higher than 0.2 g/g TSS. Proportions of the fractions almost remained stable and PN (61%~64%) were the key fraction in the biopolymers, followed by PS (24%~26%) and NA (11%~15%). Fig.4 (c)-(d) presents the normalized CST of WAS and water content of sludge cake after processed by CAPB and CaO. Normalized CST slightly increased as CaO dosage increased from 0 to 0.1 g/g TSS, but which dramatically decreased for a higher CaO dosage. Water content of sludge cake dramatically decreased from 78.3% to 74.9% after adding 0.1 g/g TSS of CaO, and which also further gradually decreased after adding more CaO.

Results should that low dosage of CaO in CAPB+STAD+CaO process has minimal effects on the biopolymers concentration, which was also similar with that after CAPB+STAD process but much higher than that by STAD+CaO process, and PN proportion is much higher than the separate process by CAPB+STAD or STAD+CaO. Water content of sludge cake after process by CAPB+STAD+CaO was much lower than that after CAPB+STAD process. Thus, CAPB+STAD+CaO process could simultaneously enhance biopolymers production and sludge dewaterability.

3.4 Adsorption capacity of the produced the biopolymers for Cu^{2+}

Fig.5 shows the adsorption capacity of Cu^{2+} by the biopolymers extracted from the three methods and the Pearson correlation between the adsorption capacity of Cu^{2+} and the proportion of PN, PS, and NA in these biopolymers. The biopolymers extracted after CAPB+STAD+CaO process showed the maximum adsorption capacity of 371-392 mg/g for Cu^{2+} , followed were treated by CAPB+STAD and STAD+CaO

with the adsorption capacity of 319-370 mg Cu²⁺/g biopolymers and 303-333 mg Cu²⁺/g biopolymers, respectively. Linear fitting results showed that the adsorption capacity of Cu²⁺ has a strong and nearly linear relationship ($R^2 = 0.956$, $P < 0.01$) with PN proportion in the biopolymers, but the linear regression between the adsorption capacity of Cu²⁺ and PS ($R^2 = 0.216$, $P = 0.19$) and NA ($R^2 = 0.348$, $P = 0.14$) in the biopolymers are not significant. Results showed that PN are the key fractions in the biopolymers that responsible for the adsorption of Cu²⁺, which is also consistent with previous study (Zhou et al., 2016c). CAPB+STAD+CaO process could produce high PN content of the biopolymers, which exhibit the excellent adsorbability for Cu²⁺.

3.5 Mechanisms for simultaneously enhanced biopolymers production and sludge dewaterability of WAS by the synergetic integration process

Fig.6 shows the SEM images of WAS after processed by the three methods, and Fig.7 presents the effect mechanisms of CAPB+STAD, STAD+CaO and CAPB+STAD+CaO on biopolymer productions and sludge dewaterability. Previous study (Zhang et al., 2016) demonstrated that STAD could enhance the production of the biopolymers from WAS. CAPB contains a long alkyl chain, which can form micelles that are effective for improving the solubility of these insoluble macromolecular organic matters in EPS and even IPS of WAS (Fig.6), which is consistent with previous study (Sengco et al., 2001). Thus, CAPB+STAD process could dramatically enhance the production of the biopolymers and its fractions (Fig.1 (a)-(d)). However, the normalized CST of WAS and water content of sludge cake increased during this process, led to a deteriorated dewatering performance and

content. For one thing, large amounts of solubilized hydrophilic organic matters in supernatant could adsorb free water and then cause poor dewaterability of WAS (Chen et al., 2001). Additionally, due to the high compressibility and low strength, the permeable filter layer of WAS dramatically decreased and even disappeared during the high pressure extrusion process (Thapa et al., 2009; Chen et al., 2010), which prevent the solid-liquid separation and lead to the deteriorated dewaterability of WAS.

CaO could increase the solution pH, which could enhance solubilization of organic matters and lead to the increase of the concentrations of the biopolymers and its fractions (Liu et al., 2012), but which were markedly lower than that after processed by CAPB+STAD process. Moreover, CaO could form a multi-grid skeleton by interact with the biopolymers in WAS, which enhances the strength and reduces the compressibility of WAS, and the permeable filter layer of WAS still exist during the high pressure extrusion process (Thapa et al., 2009). Thus, CaO could dramatically enhance the dewaterability of WAS (Fig.3 (c)-(d)).

In the CAPB+STAD+CaO process, CAPB could significantly increase the solubility of macromolecular organic matters in WAS and then dramatically enhances the biopolymers production. With subsequent addition of 0.1~0.2 g CaO/g TSS to the digested sludge, both of the biopolymers and PN concentrations almost remained stable at about 52 and 32 mg/g TSS, respectively, and the biopolymers showed the adsorption capacity of about 375 mg/g for Cu^{2+} . Additionally, CaO could form a multi-grid skeleton and dramatically enhance the dewaterability of WAS. For example, the water content of sludge cake dramatically decreased from 78.3% to 74.9% after adding 0.1 g/g TSS of CaO. Thus, CAPB+STAD+CaO process could

cost-effectively enhance both the biopolymers production and the sludge dewaterability.

For the sustainable development of both environment and society, the indiscriminate discharge of surfactant-containing wastewater after WAS reduction is not acceptable due to its toxicity to human beings and the environment. Thus, CAPB as a biodegradable amphoteric surfactant was selected. It has been demonstrated in the previous work that 91.2% of CAPB with the initial concentration of 0.08 g/g dry sludge could be biodegraded after 24 h by STAD system (Zhou et al., 2017d). Moreover, another previous study has also demonstrated continuous biodegradation of a set of surfactants using an oxygen-based membrane biofilm reactor (O₂-MBfR). Bubbleless O₂ transfer completely eliminated foaming, and biofilm accumulation helped the surfactant biodegraders resist toxicity (Lai et al., 2017). Thus, the surfactant biodegradation should prevent their discharge to the aquatic environment.

4 Conclusions

Investigating the effect of CAPB+STAD+CaO process on biopolymers production and sludge dewaterability, we found that CAPB could significantly increase the solubility of macromolecular organic matters in WAS and then dramatically enhance the biopolymers. CaO (0.1~0.2 g/g TSS) could dramatically enhance sludge dewaterability by forming a multi-grid skeleton in WAS, while the biopolymers production could almost remain stable at 52 mg/g TSS. The biopolymers showed strong adsorbability for Cu²⁺ (375 mg/g biopolymers, and PN

was the key fractions responsible for the biosorption. Especially, the synergetic integration process of STAD with 0.1 g CAPB/g TSS and for 8 h and 0.1 g CaO/g TSS could cost-effectively enhance both the biopolymers production and the sludge dewaterability.

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Abbreviations

WAS, waste activated sludge;

CAPB, cocoamidopropyl betaine;

STAD, short-time aerobic digestion;

CaO, calcium oxide;

WWTPs, wastewater treatment plants;

EPS, extracellular polymeric substances;

372 PN, proteins;
373 PS, polysaccharides;
374 NA, nucleic acids;
375 TSS, total suspended solids;
376 VSS, volatile suspended solid;
377 DO, dissolved oxygen;
378 EPS, extracellular polymeric substances;
379 IPS, intracellular polymeric substances;
380 SEM, scanning electron microscopy.

References

- (EIC), E.I.o.C., 2017. Analysis report of development prospect and investment forecast on China sewage treatment industry in 2017-2021.
- American Public Health, A., American Water Works, A., Water Pollution Control, F., Water Environment, F., 1915. Standard methods for the examination of water and wastewater. American Public Health Association.
- APHA, 2005. Standard methods for the examination of water and wastewater. American Public Health Association, New York.
- Brar, S.K., Verma, M., Tyagi, R.D., Surampalli, R.Y., 2010. Engineered nanoparticles in wastewater and wastewater sludge—Evidence and impacts. *Waste management* 30, 504-520.
- Campbell, H.W., 2000. Sludge management –future issues and trends. *Water science and technology : a journal of the International Association on Water Pollution Research* 41, 1-8.
- Chen, C., Zhang, P., Zeng, G., Deng, J., Zhou, Y., Lu, H., 2010. Sewage sludge conditioning with coal fly ash modified by sulfuric acid. *Chemical Engineering Journal* 158, 616-622.
- Chen, Y., Yang, H., Gu, G., 2001. Effect of acid and surfactant treatment on activated sludge dewatering and settling. *Water research* 35, 2615-2620.
- Frølund, B., Palmgren, R., Keiding, K., Nielsen, P.H., 1996. Extraction of extracellular polymers from activated sludge using a cation exchange resin. *Water research* 30, 1749-1758.
- Fytli, D., Zabaniotou, A., 2008. Utilization of sewage sludge in EU application of old and new methods-a review. *Renewable and sustainable energy reviews* 12, 116-140.
- Kiff, R.J., 1978. Study of the factors affecting bioflocculation in the activated sludge process. *Water pollution control* 77, 464-470.
- Lai, Y.S., Ontiveros-Valencia, A., Ilhan, Z.E., Zhou, Y., Miranda, E., Maldonado, J., Krajmalnik-Brown, R., Rittmann, B.E., 2017. Enhancing biodegradation of C16-alkyl quaternary ammonium compounds using an oxygen-based membrane biofilm reactor. *Water research* 123, 825-833.
- Lee, D.J., 1996. Moisture distribution and removal efficiency of waste activated sludges. *Water Sci. Technol.* 33, 269-272.
- Liu, H., Yang, J., Shi, Y., Li, Y., He, S., Yang, C., Yao, H., 2012. Conditioning of sewage sludge by Fenton's reagent combined with skeleton builders. *Chemosphere* 88, 235-239.
- Liu, H., Zhang, Q., Hu, H., Liu, P., Hu, X., Li, A., Yao, H., 2015. Catalytic role of conditioner CaO in nitrogen transformation during sewage sludge pyrolysis. *Proceedings of the Combustion Institute* 35, 2759-2766.
- More, T.T., Yan, S., Hoang, N.V., Tyagi, R.D., Surampalli, R.Y., 2012. Bacterial polymer production using pre-treated sludge as raw material and its flocculation and dewatering potential. *Bioresource technology* 121, 425-431.

- Neyens, E., Baeyens, J., 2003a. A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of hazardous materials* 98, 33-50.
- Neyens, E., Baeyens, J., 2003b. A review of thermal sludge pre-treatment processes to improve dewaterability. *Journal of hazardous materials* 98, 51-67.
- Neyens, E., Baeyens, J., Dewil, R., 2004. Advanced sludge treatment affects extracellular polymeric substances to improve activated sludge dewatering. *Journal of hazardous materials* 106, 83-92.
- Neyens, E., Baeyens, J., Weemaes, M., De Heyder, B., 2002. Advanced biosolids treatment using H₂O₂-oxidation. *Environmental engineering science* 19, 27-35.
- Paul, E., Camacho, P., Sperandio, M., Ginestet, P., 2006. Technical and Economical Evaluation of a Thermal, and Two Oxidative Techniques for the Reduction of Excess Sludge Production. *Process Saf Environ* 84, 247-252.
- Sengco, M.R., Li, A., Tugend, K., Kulis, D., Anderson, D.M., 2001. Removal of red-and brown-tide cells using clay flocculation. I. Laboratory culture experiments with *Gymnodinium breve* and *Aureococcus anophagefferens*. *Marine ecology progress series* 210, 41-53.
- Shi, R.M., Ning, P., Zhao, J.R., Yang, Y.H., 2008. Function of Fly Ash and Diatomite in Sludge Dewatering of Kunming Sewage Plant. *Journal of Kunming University of Science and Technology (Science and Technology)* 5, 015.
- Thapa, K.B., Qi, Y., Clayton, S.A., Hoadley, A.F.A., 2009. Lignite aided dewatering of digested sewage sludge. *Water research* 43, 623-634.
- Tsang, K.R., Vesilind, P.A., 1990. Moisture distribution in sludges. *Water Sci. Technol.* 22, 135-142.
- Tyagi, V.K., Lo, S.-L., 2013. Sludge: a waste or renewable source for energy and resources recovery? *Renewable and Sustainable Energy Reviews* 25, 708-728.
- Vaxelaire, J., Cézac, P., 2004. Moisture distribution in activated sludges: a review. *Water research* 38, 2215-2230.
- Xia, S., Zhou, Y., Eustance, E., Zhang, Z., 2017. Enhancement mechanisms of short-time aerobic digestion for waste activated sludge in the presence of cocoamidopropyl betaine. *Scientific reports* 7, 13491.
- Zevin, A.S., Nam, T., Rittmann, B., Krajmalnik-Brown, R., 2015. Effects of phosphate limitation on soluble microbial products and microbial community structure in semi-continuous *Synechocystis*-based photobioreactors. *Biotechnology and bioengineering* 112, 1761-1769.
- Zhai, L.F., Sun, M., Song, W., Wang, G., 2012. An integrated approach to optimize the conditioning chemicals for enhanced sludge conditioning in a pilot-scale sludge dewatering process. *Bioresource technology* 121, 161-168.
- Zhang, Z., Zhou, Y., Zhang, J., Xia, S., 2014. Copper (II) adsorption by the extracellular polymeric substance extracted from waste activated sludge after short-time aerobic digestion. *Environmental Science and Pollution Research* 21, 2132-2140.
- Zhang, Z., Zhou, Y., Zhang, J., Xia, S., Hermanowicz, S.W., 2016. Effects of short-time aerobic digestion on extracellular polymeric substances and sludge features of waste activated sludge. *Chemical Engineering Journal* 299, 177-183.

- Zhou, Y., Lai, Y.S., Eustance, E., Straka, L., Zhou, C., Xia, S., Rittmann, B.E., 2017a. How myristyltrimethylammonium bromide enhances biomass harvesting and pigments extraction from *Synechocystis* sp. PCC 6803. *Water research* 126, 189-196.
- Zhou, Y., Xia, S., Nguyen, B.T., Long, M., Zhang, J., Zhang, Z., 2017b. Interactions between metal ions and the biopolymer in activated sludge: quantification and effects of system pH value. *Frontiers of Environmental Science & Engineering* 11, 7.
- Zhou, Y., Xia, S., Zhang, J., Nguyen, B.T., Zhang, Z., 2017c. Insight into the influences of pH value on Pb (II) removal by the biopolymer extracted from activated sludge. *Chemical Engineering Journal* 308, 1098-1104.
- Zhou, Y., Xia, S., Zhang, J., Zhang, Z., Hermanowicz, S.W., 2016. Adsorption characterizations of biosorbent extracted from waste activated sludge for Pb (II) and Zn (II). *Desalination and Water Treatment* 57, 9343-9353.
- Zhou, Y., Xia, S., Zhang, Z., Zhang, J., Hermanowicz, S.W., 2016a. Associated Adsorption Characteristics of Pb (II) and Zn (II) by a Novel Biosorbent Extracted from Waste-Activated Sludge. *Journal of Environmental Engineering* 142, 04016032.
- Zhou, Y., Zhang, J., Zhang, Z., Zhou, C., Lai, Y.S., Xia, S., 2017d. Enhanced performance of short-time aerobic digestion for waste activated sludge under the presence of cocoamidopropyl betaine. *Chemical Engineering Journal* 320, 494-500.
- Zhou, Y., Zhang, Z., Zhang, J., Xia, S., 2016b. New insight into adsorption characteristics and mechanisms of the biosorbent from waste activated sludge for heavy metals. *Journal of Environmental Sciences* 45, 248-256.
- Zhou, Y., Zhang, Z., Zhang, J., Xia, S., 2016c. Understanding key constituents and feature of the biopolymer in activated sludge responsible for binding heavy metals. *Chemical Engineering Journal* 304, 527-532.

496 **TABLES**Table 1 The parameters of concentrated waste activated sludge used in this study ^a

Parameter	Unit	Value
pH	-	6.9 ± 0.2
TSS	g/L	8.04 ± 0.28
VSS	g/L	5.48 ± 0.31
CST	s·L/g	5.83 ± 0.36
TCOD	g/L	9.61 ± 0.12
SCOD	mg/L	74.1 ± 11.4

^a TSS, total suspended solids; VSS, volatile suspended solids; CST, capillary suction time normalized by sludge concentration; TCOD, total chemical oxidation demand; SCOD, soluble chemical oxidation demand.

Table 2 Parameters of the linear relationship between the CAPB dosage and the concentrations of the biopolymers and its fractions at the noted aerobic digestion times ^a

Time (h)	Proteins		Polysaccharides		Nucleic acids		Biopolymer	
	<i>K</i> (mg/g)	<i>R</i> ²	<i>K</i> (mg/g)	<i>R</i> ²	<i>K</i> (mg/g)	<i>R</i> ²	<i>K</i> (mg/g)	<i>R</i> ²
0	171	0.970	76.2	0.968	113	0.960	360	0.968
2	201	0.974	80.0	0.988	142	0.955	424	0.973
4	231	0.969	91.4	0.981	163	0.957	486	0.973
8	238	0.958	108	0.979	173	0.956	520	0.969
12	230	0.954	99.2	0.975	175	0.951	511	0.961
24	214	0.955	93.0	0.970	151	0.952	486	0.963

^a *K* is the slope of the linear relationship between the CAPB dosage and the concentrations of biopolymer and its fractions. $y = Kx + m$, where *y* is concentrations of the biopolymers and its fractions, *x* is the dosage of CAPB, and *m* is the intercept.

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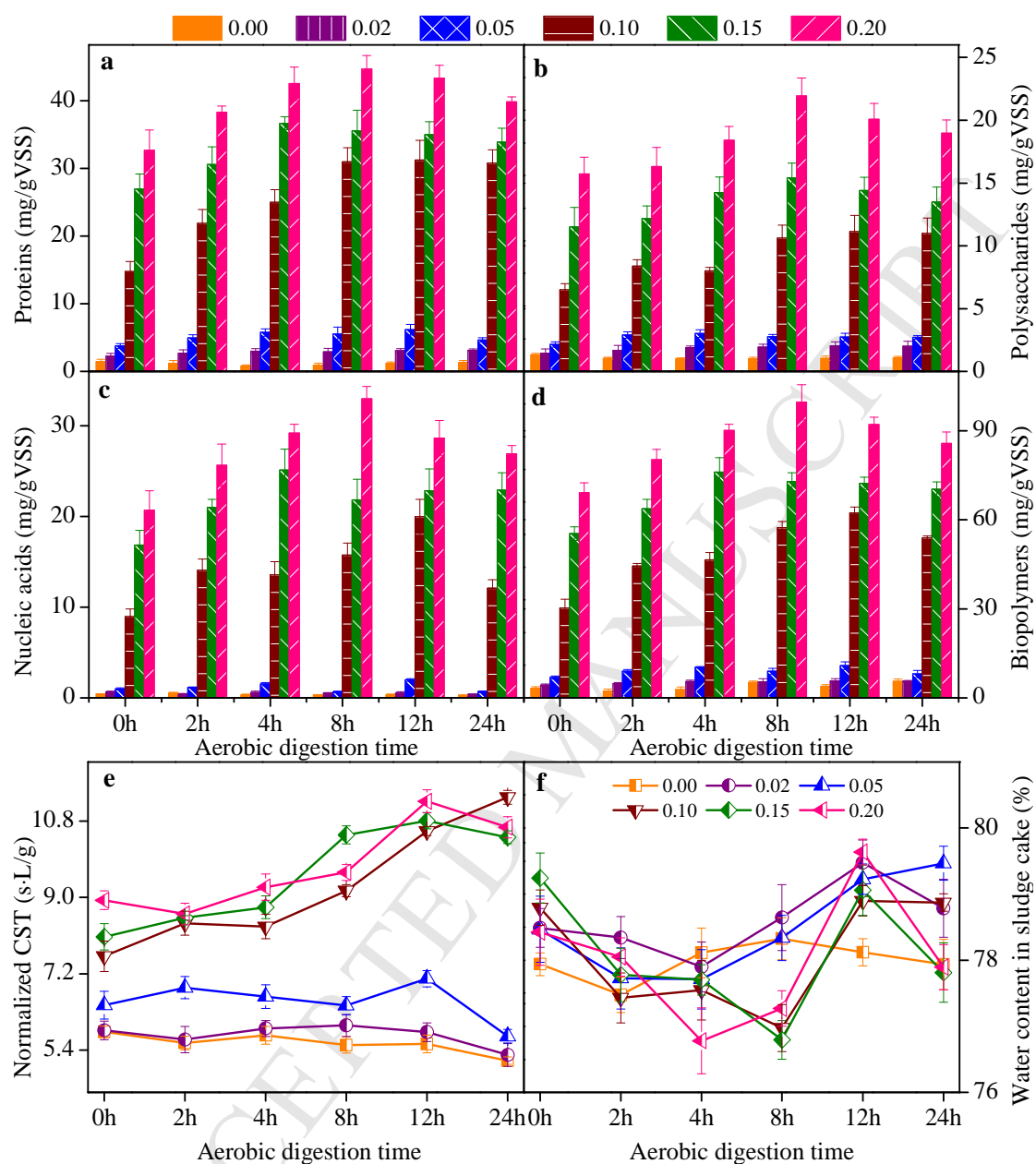


Figure 1 Effects of CAPB dosage on the production of (a) proteins, (b) polysaccharides, (c) nucleic acids, and (d) biopolymers and the (e) normalized CST of WAS and (f) water content of sludge cake at the noted aerobic digestion times.

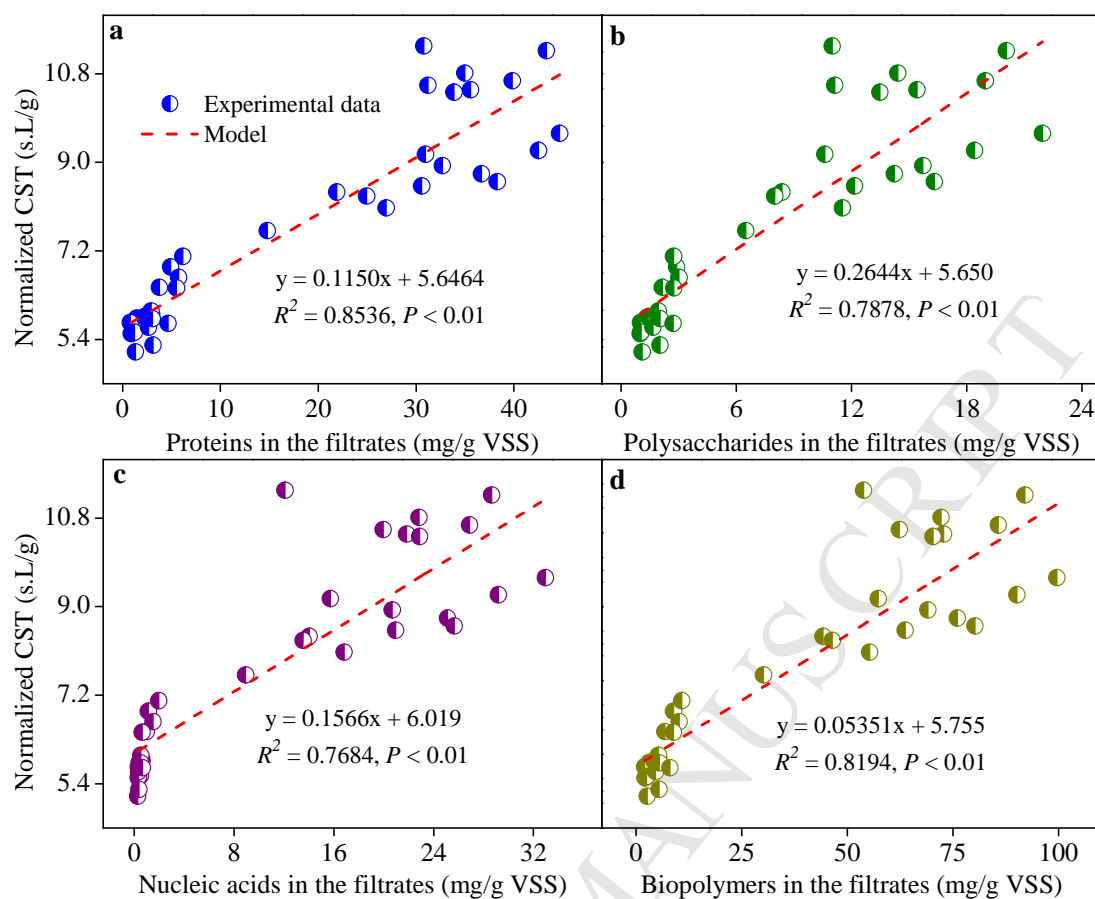


Figure 2 Pearson correlations between the normalized CST and the concentrations of proteins, polysaccharides, nucleic acids and the biopolymers in the filtrates.

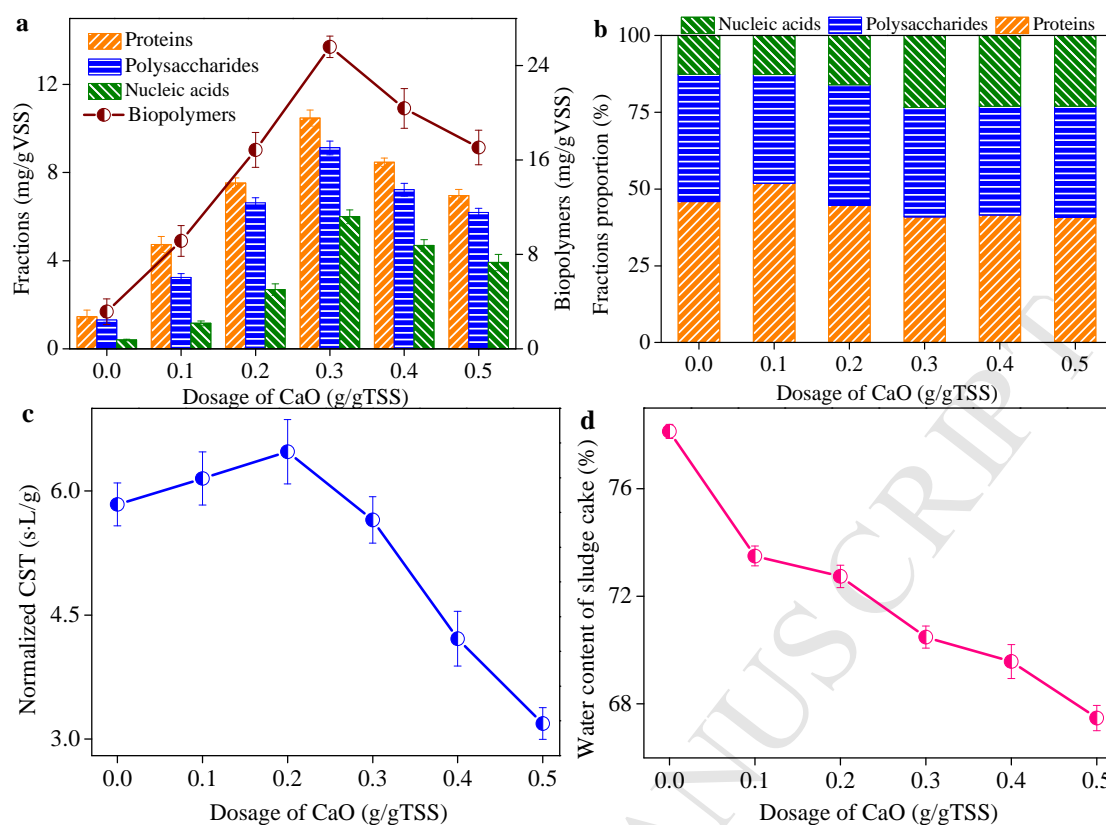


Figure 3 Effects of CaO dosage on the (a) production of biopolymers and its fractions, (b) fractions proportion in biopolymers, (c) normalized CST of WAS and (d) water content of sludge cake at aerobic digestion time of 8 h. PN, PS and NA represent proteins, polysaccharides and nucleic acids, respectively.

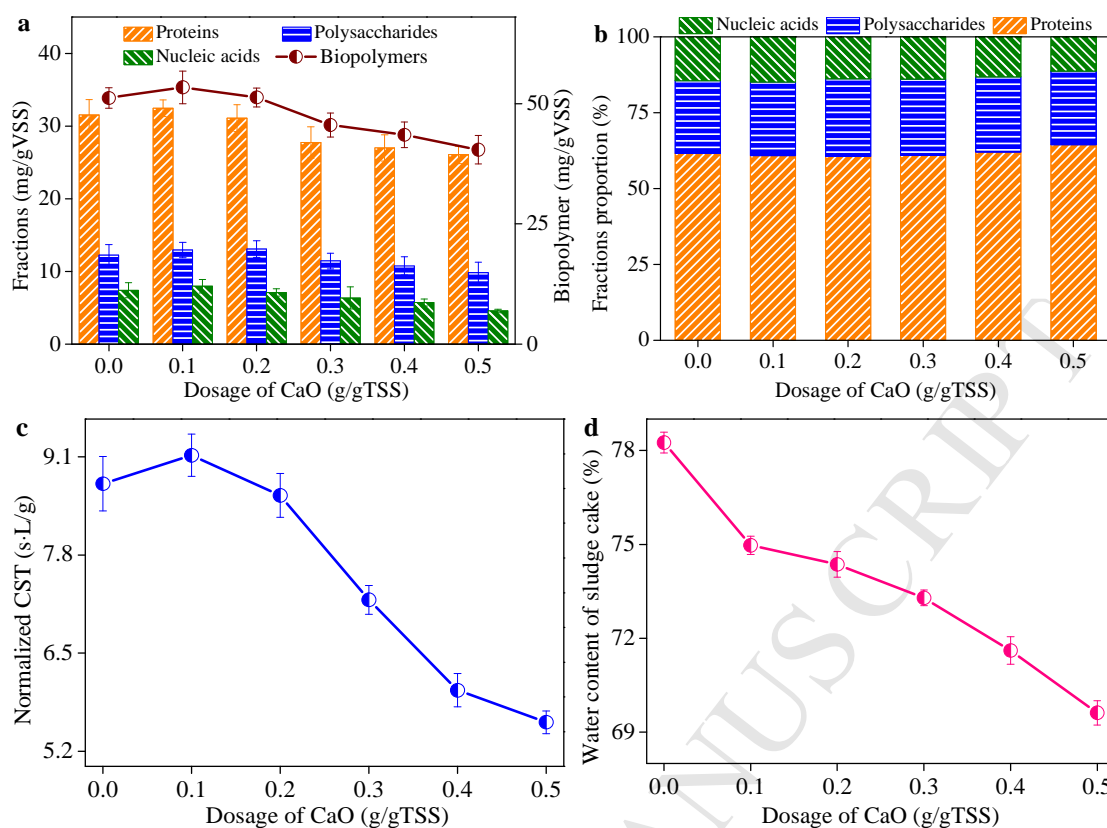


Figure 4 Synergetic effects of the STAD with CAPB and CaO on the (a) production of the biopolymers and its fractions, (b) fractions proportion in biopolymers, (c) normalized CST of WAS and (d) water content of sludge cake under the CAPB dosage of 0.10 g/g TSS and aerobic digestion time of 8 h. PN, PS and NA represent proteins, polysaccharides and nucleic acids, respectively.

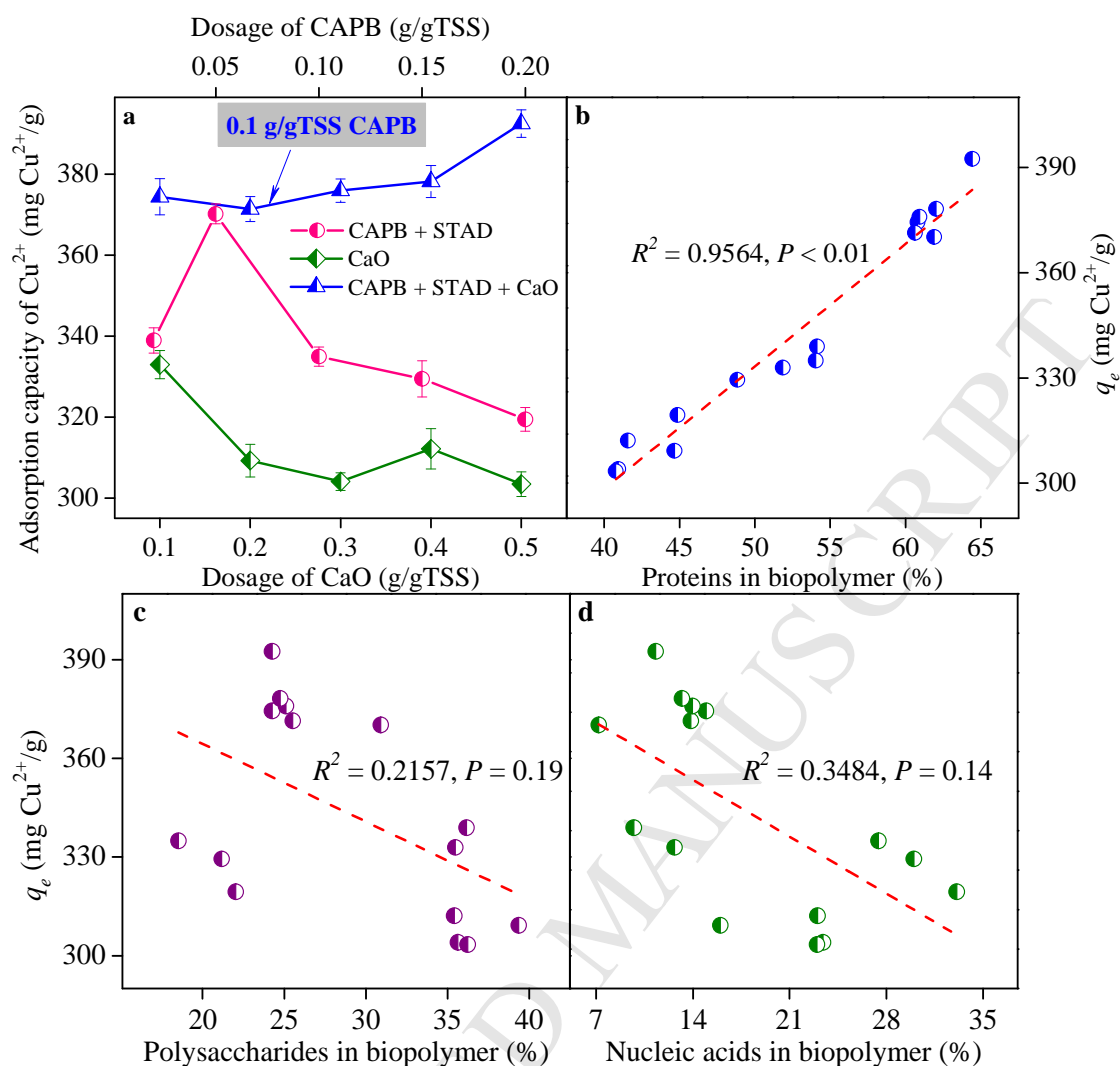


Figure 5 (a) Adsorption capacity of Cu^{2+} by the biopolymers extracted from the three processes and the Pearson correlation between the adsorption capacity of Cu^{2+} and the proportion of (b) proteins, (c) polysaccharides, and (d) nucleic acids in biopolymers.

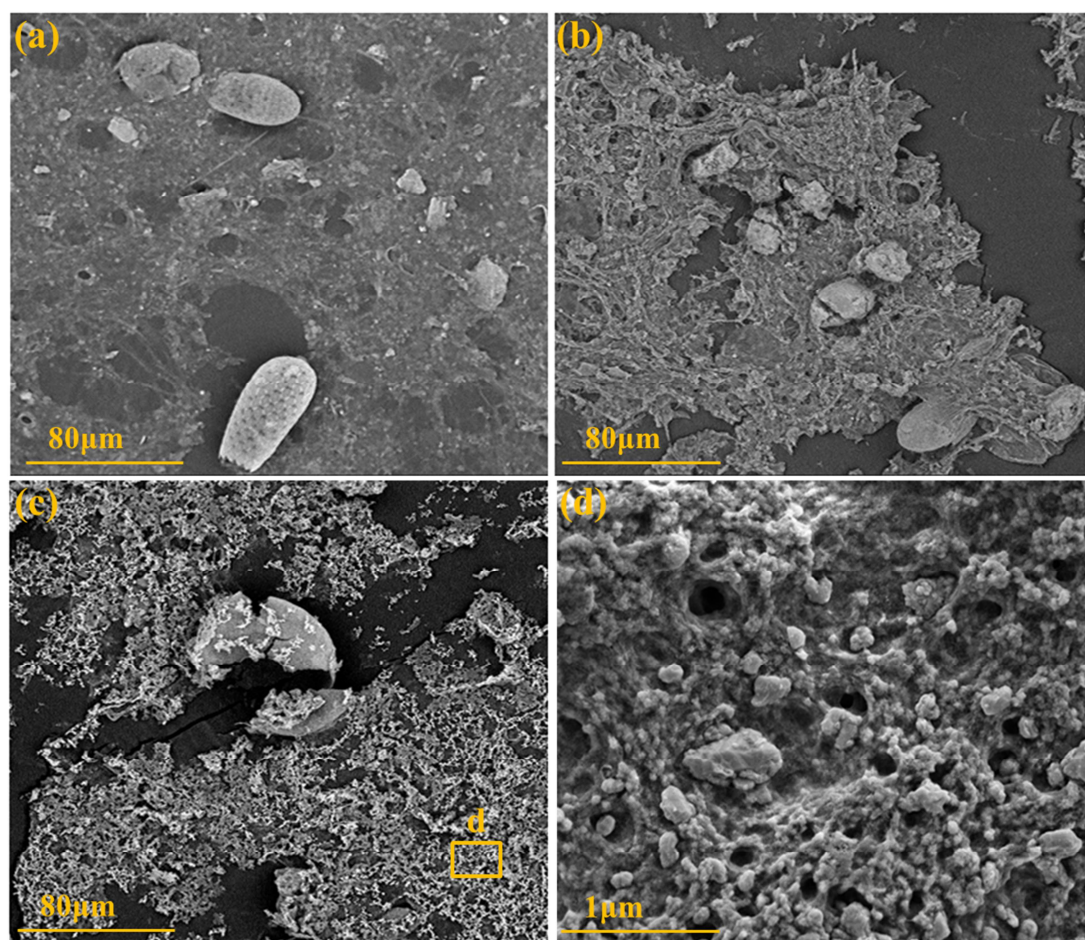


Figure 6 SEM images of waste activated sludge at the aerobic digestion of 8 h: (a) control, (b) adding 10% of CAPB, adding 10% of CAPB and 30% of CaO with the scale of (c) 80 μm and (d) 1 μm.

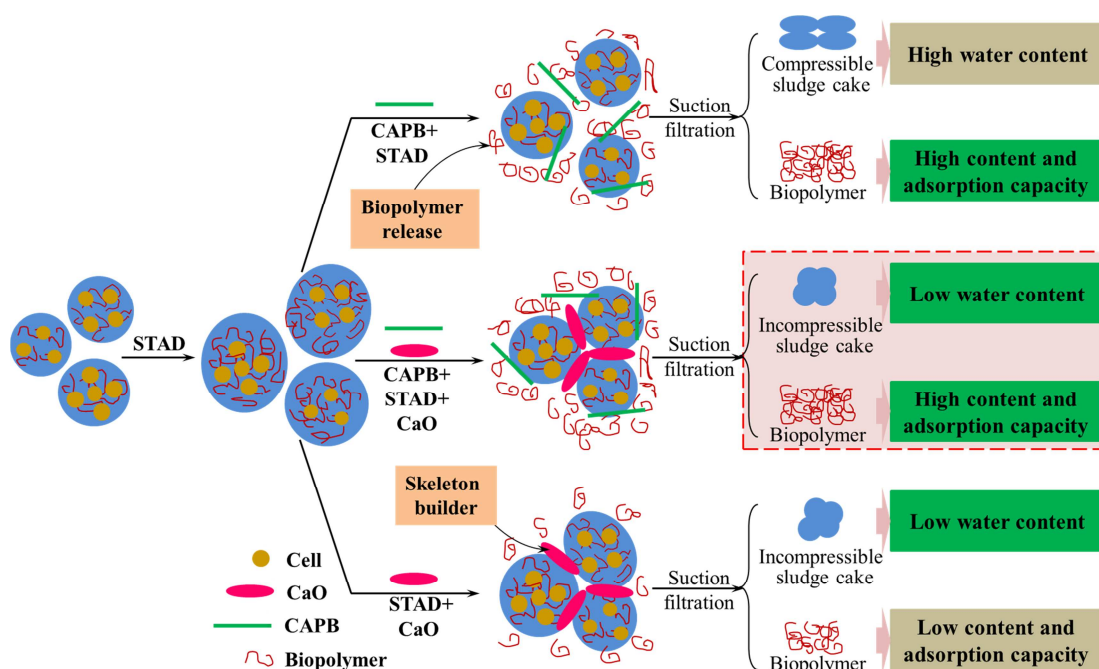


Figure 7 Mechanisms of simultaneously enhanced biopolymer productions and sludge dewaterability for WAS by the synergetic integration process of STAD with CAPB and CaO.

Highlights

- Simultaneous biopolymers production and sludge dewaterability of WAS was studied
- Short-time aerobic digestion (STAD) improved biopolymers production by biosynthesis
- CAPB further promoted STAD of WAS to enhance biopolymers production
- CaO enhanced sludge dewaterability but had minor effect on biopolymers production
- STAD with CAPB and CaO enhanced both biopolymers production and WAS dewaterability