Enhanced performance of short-time aerobic digestion for waste activated sludge under the presence of cocoamidopropyl betaine

Yun Zhou\textsuperscript{a,b}, Jiao Zhang\textsuperscript{c}, Zhiqiang Zhang\textsuperscript{a}, Chen Zhou\textsuperscript{b}, YenJung Sean Lai\textsuperscript{b}, Siqing Xia\textsuperscript{a,*}

\textsuperscript{a} State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China
\textsuperscript{b} Biodesign Swette Center for Environmental Biotechnology, Arizona State University, Tempe, AZ 85287, USA
\textsuperscript{c} School of Civil Engineering, Shanghai Urban Construction Vocational College, Shanghai 200432, China

\textbf{HIGHLIGHTS}

- Enhanced performance of the STAD for WAS under the presence of CAPB was found.
- CAPB markedly promote the removal of VSS and TCOD of WAS by the STAD system.
- CAPB aroused rapid release and gradual decreases of SCOD, PO\textsubscript{4}\textsuperscript{3-}, NH\textsubscript{4}^+ -N and TN.
- CAPB was also biodegraded by the system, and the removal rate at 24 h was 91.2%.
- Removal route contained extracellular adsorption/desorption, and biodegradation.

\textbf{ABSTRACT}

Short-time aerobic digestion (STAD) is a promising technique for waste activated sludge (WAS) stabilization. As a widely used surfactant, cocoamidopropyl betaine (CAPB) could enter wastewater treatment system and influence the WAS properties. It is of big significance to ascertain its influences on the STAD of WAS. CAPB was found to promote the fast removal of organics in WAS. Within 24 h, the removal rate of VSS was up to 28.3%, while no more than 20% was reported in previous studies. The biodegradation rate constants of both VSS and TCOD were increased over 65%. Due to special features of surfactant, CAPB aroused rapid releases of SCOD, PO\textsubscript{4}\textsuperscript{3-}, NH\textsubscript{4}^+ -N and TN within 2 h, and then their values gradually decreased under the aerobic digestion. CAPB was also biodegraded by the system, and the removal rate at 24 h was 91.2%. The biodegradation route contained extracellular adsorption/desorption and aerobic biodegradation. Biodegradable CAPB could lead to a promising performance of the STAD process for WAS and resulted in zero waste discharge from the treatment system.

© 2017 Elsevier B.V. All rights reserved.
during the 35 d aerobic digestion of activated sludge, aerobic digestion performance achieved the reduction of 42–53% mixed liquor suspended solid (MLSS), 53–64% mixed liquor volatile suspended solids (MLVSS), 53–81% settled sludge volume and full stabilization for domestic sludge. For pharmaceutical sludge, reductions of 4–18% MLSS and 6–25% MLVSS were achieved with full stabilization. Liu et al. [2] studied the autotrophic thermophilic aerobic digestion (ATAD) of the sewage sludge, and the digestion system achieved rapid degradation of the organic substrate at 55 °C. The MLVSS was removed by up to 45.3% and 50.4% at d 9 and 11d, respectively, while NH$_4^+$-N, chemical oxidation demand (COD) and total organic carbon (TOC) in the supernatant as well as total nitrogen (TN) didn’t exhibit obvious declines after 7 d.

With its low capital investment, few operational problems, short sludge retention time, efficient pathogen inactivation and fast degradation rate, aerobic digestion is typically applied in medium-sized and small sized wastewater treatment plants (WWTPs) [2,7]. According to the Ministry of Environment Protection, China, 4436 WWTPs were in operation in China by the end of 2015, and over 70% of them were medium- and small-size plants with the processing capacities of wastewater lower than 10 thousand tons per day [8]. Thus, aerobic digestion could be an attractive and better choice for the treatment of WAS in China due to its economy and practicability. However, most of the previous studies focused on the long-time aerobic digestion, which led to high treatment cost due to consuming higher oxygen demand. Our previous study showed that short-time aerobic digestion (STAD) could achieve better flocculability and dewaterability of sludge than the prolonged aerobic digestion [7], which provided some theoretical evidences for the STAD application to the sludge treatment.

Surfactants are widely used in household detergents, industrial and institutional cleaners, personal care products, flotation and petroleum production, and cosmetics all over the world [9,10]. As a commonly used amphoteric synthetic surfactant in personal care products and surface cleaners, cocoamidopropyl betaine (CAPB) could help to formulate products which are mild to the skin and eyes [11], and most of them were discarded into the municipal sewer systems after use and afterwards were converged at WWTPs. The biodegradable surfactant could be removed by a combination of biosorption and biodegradation by the activated sludge in the wastewater treatment process [12]. However, the residual surfactant would influence the properties of WAS, which might further influence the stabilization performance of WAS in the aerobic digestion process. CAPB has a non-polar linear hydrocarbon group which can form micelles and then increase aqueous solubility, thus accelerate the solubilization of macromolecular organic matters in WAS into aqueous solution [13]. Zhou et al. [14] suggested that both cetyl trimethyl ammonium bromide (CTAB) and linear alkylbenzene sulfonate (LAS) were effective to promote the extraction of biopolymers from activated sludge. CTAB was prominent in increasing the concentration of proteins, and LAS was prominent in increasing the concentrations of both polysaccharides and nucleic acids. Jiang et al. [15] also mentioned that upon sludge fermentation the nitrogen and phosphorus have been observed to release from activated sludge after adding anionic surfactant due to the biopolymer solubilization and even cell disruption. Thus, CAPB might influence the release of the biopolymers from the WAS and further influence the aerobic digestion of WAS.

Despite the extensive application of CAPB, little is known about how the CAPB influences the WAS digestion in the aerobic digestion system. This study systematically evaluated the influencing characteristics of CAPB on the STAD process of WAS, containing the removal of VSS and TCOD, and the variation of SCOD. The change of phosphorus (PO$_4^{3-}$–P), pH value, ammonia nitrogen (NH$_4^+$–N) and total nitrogen (TN) in sludge supernatant were also studied. The distribution of CAPB in aqueous and sludge phase during the STAD process and its biodegradation mechanisms were also evaluated.

2. Materials and methods

2.1. Chemicals and sludge samples

WAS used in this study was obtained from the secondary settling tank of a full-scale municipal WWTP in Shanghai, China. Sludge samples were subsequently screened through a 1.2 mm sieve to remove grit and then concentrated by settling at 4 °C for 2 h. Table 1 shows the main parameters of concentrated sludge. CAPB surfactant (C$_{19}$H$_{38}$N$_2$O$_3$), with a molecular weight of 342.52 g/mol, was obtained from Shanghai Chem. Co. Ltd., China.

2.2. Batch aerobic digestion tests

Experiments of CAPB effect on the STAD of WAS were carried out in two identical reactors, which were made of plastic cylindrical with the volume of 6.0 L (φ412 cm × 53 cm) and placed on an accurate strengthen electronic stirrer (JJ-1, Changzhou, China) with blades for mixing the samples at 350 rpm (Fig. S1). The liquid volume of each reactor was 4.0 L. The experiments were carried out under room temperature (25 ± 2 °C), and the dissolved oxygen (DO) was maintained at 2–3 mg/L using a microporous aeration disk at the bottom of the reactor. CAPB was added to one reactor with the dosage of 0.08 g/g dry sludge according to our former optimization experimental results, and the other reactor without adding CAPB was used as the control. We collected 200 mL samples each time – with the effluent tube at different aerobic digestion times.

2.3. Chemical analyses

After sampling, part of the digested sludge was directly used for the analyses of TCOD and pH value. Part of the sample was immediately centrifuged at 4000g for 20 min at 4 °C using a high-speed freezing centrifuge (Heraeus Multifuge X1R, Thermo Scientific, Germany). The supernatant was stored at 4 °C and further centrifuged at 12000g for 10 min to further remove particles prior to analyzing the SCOD, PO$_4^{3-}$–P, NH$_4^+$–N, TN and CAPB concentration in aqueous phase. The filter was assayed for VSS, total suspended solids (TSS) and solid phase CAPB.

CAPB concentration was determined using the Orange II colorimetric method [16]. CAPB in aqueous and solid phases were separated using centrifugation at 4000 rpm for 20 min. 50 mL of aqueous sample mixed with 10 mL buffer solution (consisting of 97 mL of 0.2 M HCl, 50 mL of 0.2 M KCl and 53 mL deionized water.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>VSS (g/L)</td>
<td>6.07 ± 0.12</td>
</tr>
<tr>
<td>TSS (g/L)</td>
<td>8.37 ± 0.41</td>
</tr>
<tr>
<td>TCOD (mg/L)</td>
<td>10371.5 ± 226.5</td>
</tr>
<tr>
<td>SCOD (mg/L)</td>
<td>96.9 ± 8.5</td>
</tr>
<tr>
<td>pH value</td>
<td>6.8 ± 0.3</td>
</tr>
<tr>
<td>PO$_4^{3-}$–P (Supernatant) (mg P/L)</td>
<td>7.53 ± 0.78</td>
</tr>
<tr>
<td>NH$_4^+$–N (Supernatant) (mg N/L)</td>
<td>2.54 ± 0.85</td>
</tr>
<tr>
<td>TN (Supernatant) (mg N/L)</td>
<td>4.19 ± 1.5</td>
</tr>
<tr>
<td>CAPB (Supernatant) (mg/L)</td>
<td>2.48 ± 0.17</td>
</tr>
<tr>
<td>CAPB (Solid phase) (mg/L)</td>
<td>6.83 ± 0.41</td>
</tr>
</tbody>
</table>
3. Results and discussion

3.1. Influence of CAPB on VSS removal of WAS by the STAD process

The removal of VSS is a crucial indicator for WAS digestion [19]. Fig. 1 shows the influence of CAPB on the concentration and removal rate of VSS, and Table 1 shows the biodegradation rate constant without and with adding CAPB during the STAD process. Without adding CAPB, the VSS concentration decreased from 6.07 to 4.95 g/L, and the VSS removal rate was 18.5% as the sludge digested for 24 h. With adding CAPB, the VSS concentration dramatically decreased to 4.28 g/L, and the VSS removal rate rose to 28.3% after 24 h. Previous studies showed that without adding CAPB, the VSS concentration decreased from 10371.2 to 8452.9 mg/L after 24 h. However, TCOD decreased from 10371.2 to 7319.9 mg/L after 24 h. The first order biochemical degradation kinetics also fitting well for the TCOD removal without and with adding CAPB as the correlation coefficients ($R^2$) with adding CAPB increased by 65.9% (from 0.0085 to 0.0141 h$^{-1}$). Benedek et al. [18] also reported that under the temperature of 28°C, the $K_{\text{TCOD}}$ of activated sludge was 0.20 d$^{-1}$ (0.0083 h$^{-1}$) in an aerobic stabilization reactor. Results showed that the STAD process with adding CAPB in this study considerably improved the removal rate and efficiency of sludge VSS.

3.2. Influence of CAPB on TCOD and SCOD of WAS by the STAD process

The influence of CAPB on TCOD and SCOD of WAS by the STAD process was also investigated. In Fig. 2, the TCOD of WAS gradually declined during the aerobic digestion process no matter whether CAPB was added or not. Without adding CAPB, TCOD decreased from 10371.2 to 8452.9 mg/L after 24 h. However, TCOD decreased to 7319.9 mg/L with adding CAPB. The first order biochemical degradation kinetics also fitting well for the TCOD removal without and with adding CAPB as the correlation coefficients ($R^2$) for both experiments were above 0.98. Compared with the control experiment, the biodegradation rate constant ($K_{\text{VSS}}$) with adding CAPB increased by 65.9% (from 0.0085 to 0.0141 h$^{-1}$). Benedek et al. [18] also reported that under the temperature of 28°C, the $K_{\text{VSS}}$ of activated sludge was 0.20 d$^{-1}$ (0.0083 h$^{-1}$) in an aerobic stabilization reactor. Results showed that the STAD process with adding CAPB in this study considerably improved the removal rate and efficiency of sludge VSS. This can be attributed to the presence of CAPB, which enhanced the biodegradation of organic matter.
proper carbon sources [20]. Once no more electron-donor substrates in supernatant support the growth of heterotrophic bacteria in the later stage of the STAD process, biopolymers might be released to the supernatant via hydrolysis [3]. This was responsible for the SCOD increase in the later stage of the STAD process. With adding CAPB, SCOD dramatically increased from 96.9 to 372.7 mg/L after mixing for 10 min, and further rose to 415.1 mg/L after 2 h. CAPB promoted the solubilization of macromolecule organic matters [13] which had been subsequently degraded by hydrolytic enzymes produced by the active biomass in the waste activated sludge [15]. Ponti et al. [21] also reported that the released enzymes in the organic matter solubilization or cell lysis process could enhance the degradation of activated sludge.

3.3. Influence of CAPB on $PO_4^{3-}/CO_4$-P in supernatant of WAS by the STAD process

The influence of CAPB on $PO_4^{3-}/CO_4$-P in supernatant of WAS by the STAD process was shown in Fig. 3a. Without adding CAPB, the $PO_4^{3-}/CO_4$-P concentration in the supernatant decreased from 7.53 to 0.11 mg/L from 0 to 8 h, but slightly increased in the latter stage. With adding CAPB, the $PO_4^{3-}/CO_4$-P concentration in the supernatant dramatically increased, and reached to 21.12 mg/L after 2 h, but then rapidly decreased to 0.35 mg/L after 24 h.

Phosphorus-accumulating organisms (PAOs) in WAS are considered to be the key microorganisms in the biological phosphorus removal process in wastewater treatment plant [22]. In the initial stage of STAD without CAPB, PAOs used the stored poly-$\beta$-hydroxyalkanoates (PHAs) as an energy source for the uptake of $PO_4^{3-}/CO_4$-P [22,23], resulted in the decrease of observed $PO_4^{3-}/CO_4$-P concentration. As a major component of sludge flocs, EPS are usually present on the surface of cells. These substance contain large number of functional groups, such as carboxyl, phosphoryl, and quaternary ammonium groups, which complex with negatively charged phosphate [24,25]. Binding of $PO_4^{3-}/CO_4$-P by the functional groups in EPS resulted in the accumulation of $PO_4^{3-}/CO_4$-P on the surface of activated sludge [22,25]. Previous study [26] also suggested that EPS is an important extracellular phosphate pool. In the latter stage of STAD without CAPB, the solubilization of EPS is accompanied by the release of $PO_4^{3-}/CO_4$-P, which resulted in the slightly increase of observed $PO_4^{3-}/CO_4$-P concentration.

### Table 2

<table>
<thead>
<tr>
<th>VSS</th>
<th>$K_{VSS}$ (h$^{-1}$)</th>
<th>$R^2$</th>
<th>TCOD</th>
<th>$K_{TCOD}$ (h$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.0085</td>
<td>0.9859</td>
<td>0.0082</td>
<td>0.9863</td>
<td></td>
</tr>
<tr>
<td>CAPB</td>
<td>0.0141</td>
<td>0.9887</td>
<td>0.0136</td>
<td>0.9910</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Variations of TCOD and SCOD of WAS without and with adding CAPB during the STAD process (dot: measured data; line: simulated).

Fig. 3. (a) Change of $PO_4^{3-}/CO_4$-P in supernatant without and with adding CAPB during the STAD process and (b) the relationship between the variation of SCOD and $PO_4^{3-}/CO_4$-P. A represents the increase of SCOD and $PO_4^{3-}/CO_4$-P from 12 to 24 h without adding CAPB; B represents the increase of SCOD and $PO_4^{3-}/CO_4$-P after adding CAPB; C represents the increase of SCOD and $PO_4^{3-}/CO_4$-P after the WAS digested for 2 h with adding CAPB.
With adding CAPB, the increase of \( \text{PO}_4^{3-} - \text{P} \) in the first 2 h should be resulted from the improved solubilization of EPS from the cells. Fig. 3b also shows the relationship between the change of SCOD and \( \text{PO}_4^{3-} - \text{P} \). A represents the increase of SCOD and \( \text{PO}_4^{3-} - \text{P} \) from 12 to 24 h without adding CAPB; B represents the increase of SCOD and \( \text{PO}_4^{3-} - \text{P} \) after the WAS digested for 2 h with adding CAPB. Results showed the good linear relationship \((R^2 = 0.998)\) between the increase of SCOD and \( \text{PO}_4^{3-} - \text{P} \), and the proportion of \( \text{PO}_4^{3-} - \text{P} \) in SCOD is 42.2 mg-P/g-SCOD. The dramatically decrease of \( \text{PO}_4^{3-} - \text{P} \) in the latter stage should be resulted from the accumulating of \( \text{PO}_4^{3-} - \text{P} \) by PAOs, and the remained concentration of \( \text{PO}_4^{3-} - \text{P} \) in the supernatant was almost the same compared with that of without adding CAPB after 12 h.

3.4. Influence of CAPB on pH value, \( \text{NH}_4^+ - \text{N} \) and TN in supernatant of WAS by the STAD process

The variations of sludge pH value, \( \text{NH}_4^+ - \text{N} \) and TN in supernatant without and with adding CAPB are shown in Fig. 4. The pH value of WAS increased dramatically within the first 2 h no matter whether CAPB was added or not (Fig. 5a), but decreased after 12 h. The pH value in STAD system tended to be alkalescence, which was consistent with the previous studies [3,27].

Without adding CAPB, the \( \text{NH}_4^+ - \text{N} \) concentration in the supernatant decreased from 2.54 to 0.04 mg/L after 24 h. The TN concentration in the supernatant also decreased in the first 8 h, but showed a slight increase in the latter stage. \( \text{NH}_4^+ - \text{N} \) could be oxidized to \( \text{NO}_2^- - \text{N} \) by the ammonia oxidizing bacteria in activated sludge [28], which resulted in the decrease of \( \text{NH}_4^+ - \text{N} \) concentration. As an essential nutrient for the growth of bacteria, nitrogen could be used for the anabolism [29], which resulted in the decrease of TN in the initial stage. The increase of TN in the supernatant in the later stage should be resulted from the solubilization of biopolymers as nitrogen exists in protein, lipid and nucleic acid [29].

With adding CAPB, both of the concentrations of \( \text{NH}_4^+ - \text{N} \) and TN in the supernatant increased in the first 2 h, but decreased gradually in the latter stage. Since the negative charges of biopolymers on the surface of sludge flocs, \( \text{NH}_4^+ - \text{N} \) could be adsorbed and stored on these polymers [30,31]. The solubilization of biopolymers resulted in the release of \( \text{NH}_4^+ - \text{N} \) and nitrogen containing organic compounds, and the concentrations of \( \text{NH}_4^+ - \text{N} \) and TN in supernatant increased in the initial stage. The decrease of \( \text{NH}_4^+ - \text{N} \) and TN in the later stage could be resulted from the autotrophic nitrification [32]. As endogenous decay is largely predominant over heterotrophic growth, the uptake of nitrogen for synthesis is largely overcome by the release of kjeldahl nitrogen due to the decay of dead biomass. The process of ammonification and subsequent nitrification of ammonium nitrogen explains the decrease of ammonium nitrogen over time. In addition, with the gradually increasing of pH value from 7.20 to 7.58 from 2 to 24 h, \( \text{NH}_4^+ - \text{N} \) could be continually stripped under the aeration of activated sludge [2,33], which also resulted in the decrease of the observed concentration of \( \text{NH}_4^+ - \text{N} \) and TN in supernatant.

![Graph](image-url)
3.5. Biodegradation of CAPB in the STAD system

Some surfactants including CAPB could be biodegraded under aerobic conditions [12,34]. The biodegradation of CAPB in the STAD process system was investigated. Fig. 5a shows the changes of CAPB in aqueous and sludge phase during the STAD process. The CAPB concentration in aquatic phase decreased steadily from 759.6 to 27.5 mg/L as the sludge digested for 24 h. The CAPB concentration in the sludge phase increased from 9.83 to 349.74 mg/L after 4 h, but which gradually decreased to 38.85 mg/L after 24 h. The total concentration of CAPB in the STAD system slightly decreased from 768.4 to 619.8 mg/L in the initial 4 h, but dramatically decreased in the latter stage. After digested for 24 h, the total concentration of CAPB was decreased to 66.4 mg/L, and the removal efficiency of CAPB was 91.4%.

The variation of CAPB in sludge phase could be resulted from the adsorption and desorption of EPS on the surface of sludge. EPS contain large amounts of carboxyl, hydroxyl, amine and phosphoric groups [35], and CAPB with the polar head of $\cdot N^\ominus(CH_2)_2CH_2COO^\ominus$ could be adsorbed by the activated sludge due to the interactions between the functional groups in sludge and the polar head of CAPB [12], resulted in the fast accumulation of CAPB in the sludge phase in the initial 4 h. However, as CAPB in aqueous phase dramatically decreased, CAPB in sludge phase also began to release into the aqueous phase due to the concentration gradient and EPS hydrolysis.

Biodegradation of CAPB could be the predominant in the latter stage of the STAD process as the total concentration of CAPB dramatically decreased. So far, two intracellular enzymes responsible for CAPB dealkylation have been identified. Tetradecyl trimethyl ammonium bromide monoxygenase (TTABMO) identified in *P. putida* ATCC 12633 is a typical flavoprotein that utilizes NADPH and FAD as cofactor [36]. On the other hand, the enzyme responsible for dealkylating CAPB by *Pseudomonas nitroreducens* was identified as a FAD-using amine oxidase [37]. Thus, CAPB could be biodegraded by the intracellular enzymes but not by EPS.

Thus, the degradation process and extracellular reaction processes were different and relatively independent, and the currently widely accepted CAPB metabolic model was improved with a consideration of EPS (Fig. 5b). Process I represents the adsorption of CAPB by EPS, process II represents desorption of CAPB from EPS and released into solution, and process III represents the biodegradation of CAPB by the aerobic microorganisms in WAS during the STAD process. Thus, when we fit the first order degradation kinetics of CAPB, the decrease of CAPB in aqueous phase should be consisting of adsorption, desorption and degradation processes, but not only the degradation kinetics.

4. Conclusions

The property effects of CAPB on the STAD of WAS were evaluated in the present study. CAPB was found to markedly promote the removal of VSS and TCoD of WAS by the STAD system. Due to special features of surfactant, CAPB led to rapid releases of SCOD, PO$_4^{3-}$, NH$_4^+$, and TN within 2 h, and then their values gradually decreased under the aerobic digestion. Most of CAPB could be biodegraded by the system. Biodegradable CAPB could lead to a promising performance of the STAD process for WAS and resulted in zero waste discharge from the treatment system.

Acknowledgements

This work was supported by the Foundation of State Key Laboratory of Pollution Control and Resource Reuse (Tongji University), China (No. PCRRRE16019), China Scholarship Council (No. 201506260022), National Natural Science Foundation of China (Nos. 51678422 and 51373868), Sheng Yun-Fei College Students Scientific and Technological Innovation Fund, and the higher school innovative engineering plan (111 Project).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2017.03.065.

References


499


