



pH dependent of the waste activated sludge reduction by short-time aerobic digestion (STAD) process

Yun Zhou^{a,b}, Jiao Zhang^{a,c}, Zhiqiang Zhang^{a,b}, Pan Wang^d, Siqing Xia^{a,b,*}

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

^b Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China

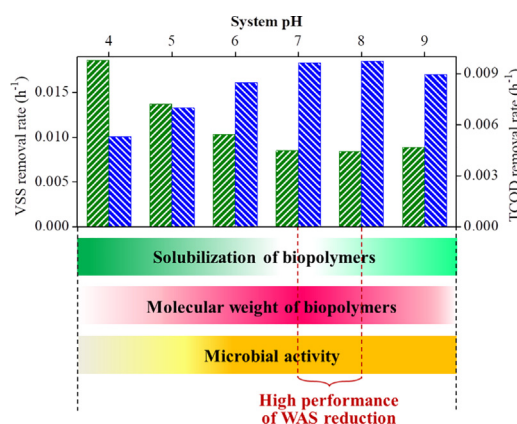
^c School of Civil and Transportation Engineering, Shanghai Urban Construction Vocational College, Shanghai 200432, China

^d Shanghai Jianke Environmental Consulting Co., Ltd., Shanghai 200032, China

HIGHLIGHTS

- Effects of pH on short-time aerobic digestion of waste activated sludge were studied.
- Unlike acidic/alkaline, neutral/weak alkaline led to low VSS removal but high for TCOD.
- Appropriate pH improved microbial activity and organic matters biodegradation.
- Extreme pH promoted biopolymers solubilization but inhibited microbial activities.
- pH between 7.0 and 8.0 is suitable for short-time aerobic digestion of waste sludge.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 28 July 2018

Received in revised form 24 August 2018

Accepted 28 August 2018

Available online 29 August 2018

Editor: Zhen (Jason) He

Keywords:

Waste activated sludge

Short-time aerobic digestion

System pH

Soluble biopolymers

Molecular weight distribution

ABSTRACT

The short-time aerobic digestion (STAD) process has been found to be a unique and significant technique for the stabilization of waste activated sludge (WAS), but the influences of the system pH on the STAD process was unclear. This study systematically disclosed the influences of the system pH on the STAD process of WAS. Under neutral or weak alkaline conditions, although the biodegradation rates of VSS ($\sim 0.0085 \text{ h}^{-1}$) were low, high biodegradation rates of TCOD (k_{TCOD}) ($\sim 0.0096 \text{ h}^{-1}$) were achieved. Less releases of the biopolymers from the WAS led to low concentrations of STOC, UV₂₅₄, the low MW organic matters, $\text{NH}_4^+ - \text{N}$ and $\text{PO}_4^{3-} - \text{P}$ in the supernatant. However, the appropriate pH for the microorganisms improved SOUR, indicating that the released substances were further reused or biodegraded by the microorganisms. Under acidic or alkaline conditions, the biodegradation rates of VSS ($0.009\text{--}0.019 \text{ h}^{-1}$) and TCOD (k_{TCOD}) ($0.005\text{--}0.009 \text{ h}^{-1}$) were opposite with those under neutral or weak alkaline conditions. The releases of the biopolymers were increased, leading to high concentrations of STOC, UV₂₅₄, the low MW organic matters, $\text{PO}_4^{3-} - \text{P}$ and $\text{NH}_4^+ - \text{N}$ in the supernatant. However, the extreme pH inhibited the microbial activity. The SOURs were only 0.0097 h^{-1} and 0.0053 h^{-1}

Abbreviations: WAS, waste activated sludge; STAD, short-time aerobic digestion; WWTPs, wastewater treatment plants; TSS, total suspended solids; VSS, volatile suspended solids; TCOD, total chemical oxygen demand; DO, dissolved oxygen; STOC, soluble total organic carbon; MWD, molecular weight distribution; SOUR, specific oxygen uptake rate; PN, proteins; PS, polysaccharides; NA, nucleic acids; EPS, extracellular polymeric substances; k_{TCOD} , biodegradation rate of TCOD.

* Corresponding author at: State Key Laboratory of Pollution Control and Resource Reuse, Key Laboratory of Yangtze River Water Environment, Ministry of Education, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China.

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

for system pH of 8.0 and 4.0, respectively. Accordingly, neutral and weak alkaline conditions should be more suitable for the STAD process of WAS. This work lays the foundation for optimizing system pH for the reduction of WAS in STAD system.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

As a common used biological process in wastewater treatment plants (WWTPs), activated sludge process has been used over a hundred years (Bitton, 2005). However, the process also produces a large amount of waste activated sludge (WAS), which have impacted both of the environment and human health due to the pathogenic organisms, toxic organic substances and heavy metals in waste activated sludge (WAS) (Campbell, 2000; Paul et al., 2006). Especially in China, the yield of wet WAS with water content of 80% in WWTPs reached 40.88 million tons in 2015, which will further dramatically increase due to the advancement of the urbanization level ((EIC), 2017). Thus, it should be imperative to develop effective methods to achieve reduction, harmlessness and recycling to meet the stringent environmental regulations of WAS (Paul et al., 2006).

Various technologies have been reported for the treatment and disposal of WAS, e.g., ambient temperature anaerobic digestion (Jiang et al., 2007; Ma et al., 2018), mesophilic-mesophilic anaerobic digestion and thermophilic-mesophilic anaerobic digestion (Roberts et al., 1999; Sung and Santha, 2003), thermophilic hydrolysis (Kepp et al., 2000), aerobic digestion (AD) (d'Antonio, 1983) and short-time aerobic digestion (STAD) processes (Xia et al., 2017; Zhang et al., 2016; Zhou et al., 2017b). For the normal aerobic digestion process, a large amount of oxygen required by the long-time digestion will increase the cost of sludge treatment and disposal. However, as a novel and significant technique for the reduction of WAS, STAD has aroused wide attention recently due to the low capital investment, few operational problems, short sludge retention time and fast degradation rate of organic matters (Xia et al., 2017; Zhang et al., 2015; Zhou et al., 2017b). During the STAD process, aerobic microorganisms consume the biodegradable organic matters, resulting in the reduction and solubilization of WAS (Bernard and Gray, 2000). Zhou et al. (Zhou et al., 2017b) mentioned that the volatile suspended solid (VSS) removal rate reached about 18.5% and TCOD decreased from 10,371.2 to 8452.9 mg/L as the WAS digested for 24 h in the STAD system.

A number of factors can influence the properties and microbial communities of WAS, containing system pH, temperature, dissolved oxygen, toxins and nutrients level (Chen et al., 2007; Datar and Bhargava, 1988), which may further influence the sludge solubilization and reduction efficiency in the STAD system. Especially, system pH showed a significant potential to influence the characteristics of WAS (Zhao et al., 2015a; Zhao et al., 2018; Zhao et al., 2015b). Firstly, system pH influences the physicochemical properties of WAS. Increasing of both solution acidity and alkalinity resulted to a breakage of the electrostatic interactions, thereby improve the solubilization of extracellular polymeric substances (EPS) and even the releasing of intracellular polymeric substances (IPS) from WAS (Wingender et al., 1999). Chen et al. (2007) found that either acidic pH (pH = 4.0, 5.0) or alkaline pH (pH = 9.0–11.0) improved the SCOD concentration during the WAS hydrolysis process. All of the released organic matters in supernatant could serve as a good source of carbon and electrons for the bacteria (Zevin et al., 2015), and which could be biodegraded by the microorganisms in WAS during the STAD process. Secondly, system pH can influence the activity and community of the microorganisms in WAS. For the activated sludge process, the suitable pH should be 6.5–8.5, which showed a high activity of functional microorganisms and fast biodegradation rate of pollutants (Painter and Loveless, 1983). However, extreme conditions (acidity and alkalinity) cause cell lysis and the release of IPS,

leading to the decrease of both activity and amount of the living microorganisms functional for the biodegradation of organic matters (Painter and Loveless, 1983; Yavuz and Celebi, 2000). Yavuz and Celebi (2000) mentioned that solution pH of 7.5 showed the maximum substrate removal rate and the microorganism growth rates, but both of which gradually decreased when further increase or reduce the solution pH. Although system pH has been widely indicated to affect the sludge characteristics, but no published papers revealed how system pH affects WAS reduction by STAD process. Deep understanding could help to lay the foundation for optimizing system pH for the reduction of WAS in STAD system and also accelerate the practical application of this novel system in WAS treatment.

In this study, the influencing characteristics of system pH on the STAD process of WAS were investigated by examining the variations of some key parameters in the system, including volatile suspended solids (VSS), total chemical oxygen demand (TCOD), soluble total organic carbon (STOC), UV_{254} , $NH_4^+ - N$, and $PO_4^{3-} - P$. The influencing mechanisms of system pH on the SATD process of WAS were revealed via analyzing the releases of biopolymers and their molecular weight distribution (MWD), the activity changes of aerobic microorganisms denoted as the specific oxygen uptake rate (SOUR) of WAS, and the biodegradation rate for TCOD (k_{TCOD}).

2. Materials and methods

2.1. Sludge samples and chemical reagents

Sludge samples were obtained from the secondary settling tank of a full-scale municipal WWTP in Shanghai, China. Sludge samples were screened through a 1.2 mm sieve to remove grit and then concentrated by setting at 4 °C for 2 h. The main parameters of concentrated sludge were shown in Table 1. Concentrated sludge was stored at 4 °C and used within 48 h. All the used chemical agents, which were of analytical grades (AR), were obtained from Runjie Chemistry Reagents Co. Ltd. (Shanghai, China). NaOH with the concentration of 0.1 M was prepared by dissolving AR grade of NaOH into distilled water, and HCl with the concentration of 0.1 M was prepared by diluting 12 M of HCl into distilled water. Their combined use to make the system pH adjusted to the objectives.

2.2. Aerobic digestion of WAS and sample collection

Experiments of the system pH on the STAD of WAS were carried out in six identical reactors, and the parameters were detailedly described in our previous studies (Xia et al., 2017; Zhang et al., 2015; Zhou et al., 2017b). The conditions of STAD system were controlled as following: work volume 5.0 L, temperature 24 ± 2 °C, and dissolved oxygen (DO) 2–3 mg/L. The system pH was adjusted to 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 using 0.1 M NaOH and 0.1 M HCl, respectively. During adjusting process, solution pH always varied, so adding acid or alkali was not

Table 1
Parameters of concentrated waste activated sludge used in this study.^a

Parameter	TSS (g/L)	VSS (g/L)	TCOD (mg/L)	SCOD (mg/L)	pH
Value	8.37 ± 0.41	6.05 ± 0.18	10,709 ± 136	81.6 ± 3.1	6.9 ± 0.3

^a TSS, total suspended solids; VSS, volatile suspended solids; TCOD, total chemical oxidation demand; SCOD, soluble chemical oxidation demand.

stopped until the pH basically kept stable as the deviation of pH is <0.1 within 5 min. Sludge samples were collected at the noted digestion times and then characterized directly. Part of the sample from each reactor was centrifuged at 4000 ×g and 4 °C for 20 min using a high-speed freezing centrifuge (Heraeus Multifuge X1R, Thermo Scientific, Germany) and the supernatant was collected and stored at 4 °C for the analyses of biopolymers, STOC, UV₂₅₄, soluble PO₄³⁻ - P and NH₄⁺ - N, and MWD. Supernatant was centrifuged again at 12,000 ×g and 4 °C for 10 min to further remove particles prior to the liquid phase analyses. Part of the samples was directly used to determine the pH, SOUR, TCOD and VSS.

2.3. Chemical analyses

Supernatant proteins (PN) was determined by the Bradford method using bovine serum albumin as the standard (Frølund et al., 1996); supernatant polysaccharides (PS) was measured by the phenol-sulfuric acid method using glucose as the standard (Frølund et al., 1996); supernatant nucleic acids (NA) was determined by the diphenylamine colorimetric method using calf thymus deoxyribonucleic acid as the standard (Frølund et al., 1996). The molecular weight distribution (MW) of the biopolymer in supernatant was analyzed using a high performance size exclusion chromatography (LC-10AD, Shimadzu, Japan). The system pH and DO of WAS were measured using a pH & DO meter (HQ40d, Hatch, USA). TSS, VSS and TCOD of sludge sample, and soluble PO₄³⁻ - P, NH₄⁺ - N and UV₂₅₄ in the supernatant were analyzed following the standard methods (American Public Health et al., 1915). TOC analyzer (TOC-V CSH, Shimadzu, Japan) has been used to characterize the STOC of supernatant. For the determination of the oxygen uptake rate (OUR) of WAS, we measured the DO concentration using the DO meter and continuously monitored by a computer. The OUR of sludge sample was calculated by a linear regression analysis of DO variations and then quantified to SOUR based on VSS (Lasaridi and Stentiford, 1998).

The removal rate of organic components containing VSS and TCOD are approximated as a first order biochemical degradation kinetics (Benedek et al., 1972):

$$dS/dt = -kS \tag{1}$$

where *S* is the concentration of biodegradable organic components (mg/L), *t* is the aerobic digestion time (h) and *k* is the removal rate constant (h⁻¹).

2.4. Statistical analyses

We withdrew samples from each reactor and then assayed three times for VSS, TCOD and SOUR of WAS, and soluble PN, PS, NA, NH₄⁺ - N, PO₄³⁻ - P, STOC and UV₂₅₄ of the supernatant. Results are expressed as the mean and standard deviation of the three measured samples (mean ± SD). When presenting the results of MWD of biopolymers, we show one representative result for each sample. Statistical analysis with Origin 8.1.5 software (Origin Lab Inc., USA) was used to identify the strength of the relationship between two parameters. The Quadratic regressions coefficient, *R*², was used to estimate the linear correlation between the system pH and the concentration of biopolymers and its fractions. Correlations were considered statistically significance at a 95% confidence interval (*P* < 0.05).

3. Results and discussion

3.1. Influences of system pH on the removal of VSS and TCOD in the STAD system

The removal of VSS and TCOD is the crucial indicator for the aerobic digestion of WAS (Layden et al., 2007; Zhang et al., 2016). Fig. 1 shows

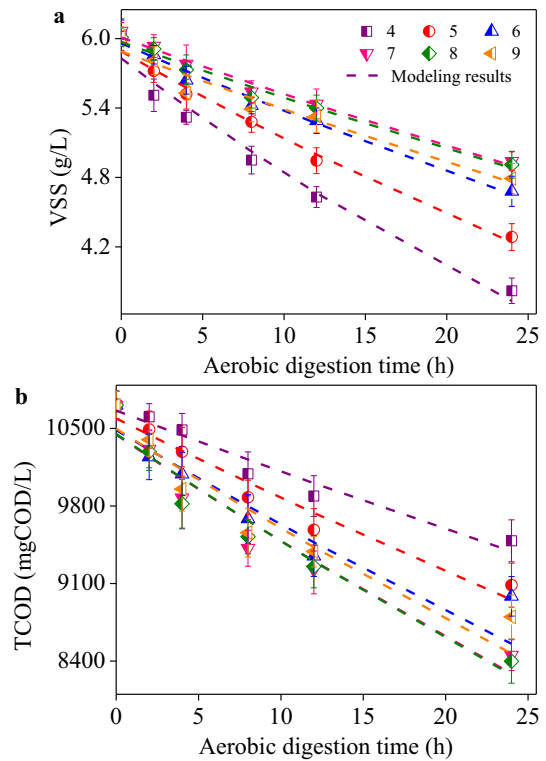


Fig. 1. Effects of system pH on the (a) VSS and (b) TCOD of aerobic digested waste activated sludge at the noted digestion times (dot: experiment results; dashed line: modeling results).

the influences of system pH on VSS and TCOD of WAS at the noted aerobic digestion times and Table 2 presents the corresponded removal rate constants of VSS and TCOD using the first order biochemical degradation kinetics. VSS of WAS gradually decreased throughout the STAD process at all of the system pH conditions and the first order biochemical degradation kinetics also fitting well with the VSS removal as the correlation coefficients (*R*²) were above 0.96 the modeled initial VSS were almost the same with the experimental results. Additionally, the removal rate of VSS (*k*_{VSS}) gradually decreased from 0.0186 h⁻¹ to 0.0084 h⁻¹ as system pH increased from 4.0 to 8.0, but it just slightly increased to 0.0089 h⁻¹ as system pH further increased to 9.0. Results showed that acidic and alkaline conditions could improve the solubilization of EPS and even IPS (Sheng et al., 2005), resulted to the increase of soluble organic matters in the supernatant and the decrease of VSS.

TCOD of WAS gradually decreased throughout the STAD process at all of the system pH conditions and the first order biochemical degradation kinetics also fitting well with the TCOD removal as the correlation coefficients (*R*²) were above 0.93. Additionally, the biodegradation rate (*k*) of TCOD gradually increased from 0.0053 h⁻¹ to 0.097 h⁻¹ as system pH increased from 4.0 to 8.0, but which slightly reduced to

Table 2 Removal rate constants of VSS and TCOD using the first order biochemical degradation kinetics under various system pH conditions.

pH	VSS		TCOD	
	<i>k</i> _{VSS} (h ⁻¹)	<i>R</i> ²	<i>k</i> _{TCOD} (h ⁻¹)	<i>R</i> ²
4.0	0.0186	0.965	0.0053	0.948
5.0	0.0137	0.989	0.0070	0.949
6.0	0.0103	0.981	0.0085	0.951
7.0	0.0085	0.982	0.0096	0.933
8.0	0.0084	0.978	0.0097	0.939
9.0	0.0089	0.968	0.0090	0.936

0.0090 h^{-1} at pH of 9.0. Results showed that acidic and alkaline conditions could cause cell lysis and inhibit the activity of functional bacterial responsible for biological removal of organic matters (Yavuz and Celebi, 2000), resulted to the decrease of TCOD biodegradation rate (k_{TCOD}). Neutral or weak alkaline conditions should be more suitable for the TCOD biodegradation during the STAD of WAS.

3.2. Influences of system pH on biopolymers release from WAS in the STAD system

Biopolymers release indicates the organic matters solubilization and hydrolysis from WAS, which is the first and important step for the aerobic digestion of WAS (Liu et al., 2011; Zhang et al., 2016). Fig. 2 shows the influences of system pH on the production of PN, PS, NA and biopolymers from WAS at the noted aerobic digestion times, and Table 3 shows the parameters of the linear relationship between the concentration of biopolymers fractions and system pH at the noted STAD time. Neutral condition shows the lowest concentration of biopolymers and its fractions, but which gradually increased with the increasing of both system acidity and alkalinity. System pH had a strong and nearly quadratic regressions relationship with the concentrations of biopolymers and its fractions as all of the correlation coefficients (R^2) were above 0.95 (Table 3). During the STAD process, biopolymers and its fractions decreased in the initial 2 h but gradually increased in the later stage under acidic conditions, but which gradually decreased in the initial 12 h and then showed slight increased after 24 h under neutral and weak alkaline conditions. Results showed that acidic and alkaline conditions could improve the solubilization of EPS and even IPS (Sheng et al., 2005), resulted to the increase of biopolymers and its fractions in the supernatant. Microorganism's activity will be inhibited under acidic conditions (Yavuz and Celebi, 2000) and the predominant reaction should be biopolymers solubilization but not biodegradation in the later stage of STAD. However, the biodegradation of biopolymers should be predominant as the activity of functional bacteria should be unimpaired under neutral and weak alkaline conditions.

Table 3

Parameters of the quadratic regressions between the system pH and soluble proteins, polysaccharides, nucleic acids and biopolymers from waste activated sludge at the noted aerobic digestion times.^a

Fractions	Parameters	0 h	2 h	4 h	8 h	12 h	24 h
Proteins	<i>a</i>	0.184	0.110	0.111	0.104	0.101	0.107
	<i>b</i>	-2.34	-1.39	-1.58	-1.56	-1.54	-1.60
	R^2	0.956	0.979	0.933	0.960	0.970	0.962
Polysaccharides	<i>a</i>	0.121	0.116	0.108	0.188	0.169	0.137
	<i>b</i>	-1.74	-1.71	-1.59	-2.69	-2.52	-2.07
	R^2	0.963	0.967	0.982	0.976	0.949	0.968
Nucleic acids	<i>a</i>	0.066	0.077	0.010	0.012	0.011	0.031
	<i>b</i>	-1.00	-1.11	-0.17	-0.24	-0.16	-0.45
	R^2	0.988	0.977	0.976	0.984	0.965	0.955
Biopolymers	<i>a</i>	0.371	0.303	0.228	0.304	0.282	0.274
	<i>b</i>	-5.09	-4.21	-3.34	-4.48	-4.23	-4.12
	R^2	0.964	0.989	0.998	0.987	0.967	0.974

^a The equation of quadratic regression is $Y = aX^2 + bX + c$, where Y is the concentrations of biopolymers and its fractions and X is the system pH.

3.3. Influences of system pH on the soluble TOC and UV₂₅₄ of WAS in STAD system

Soluble TOC and UV₂₅₄ represent the organic matters, which could be act as the organic carbon and electron acceptor for the heterotrophic bacteria (Zhou et al., 2016; Zhou et al., 2017a), and both of them are important parameters during the STAD of WAS. Fig. 3 shows the STOC and UV₂₅₄ in the supernatant of WAS under various system pH conditions at the noted digestion times. Neutral condition shows the lowest STOC concentration and UV₂₅₄ value, but both of which gradually increased with the increasing of both system acidity and alkalinity. During the STAD process, both of supernatant STOC and UV₂₅₄ gradually decreased in the initial 4 h and then increased in the later stage under acidic conditions, but which gradually decreased in the initial 12 h and then showed slight increased after 24 h under neutral and weak alkaline conditions. As the activity of functional bacteria will not be influenced under neutral and weak alkaline conditions, the soluble organic matters

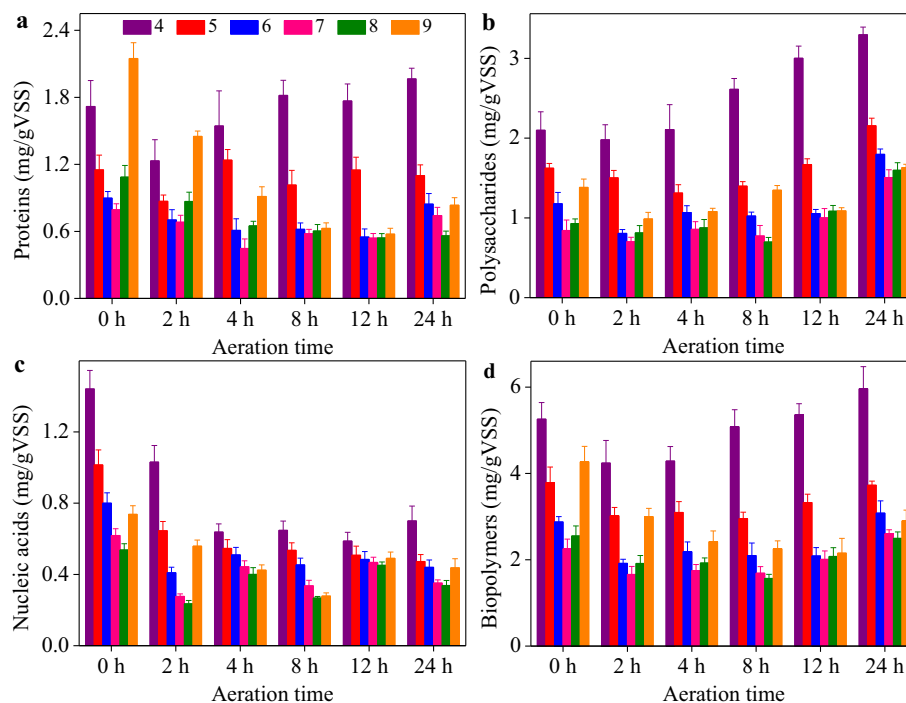


Fig. 2. Effects of system pH on the concentration of soluble (a) proteins, (b) polysaccharides, (c) nucleic acids and (d) biopolymers during the short-time aerobic digestion of waste activated sludge at the noted digestion times.

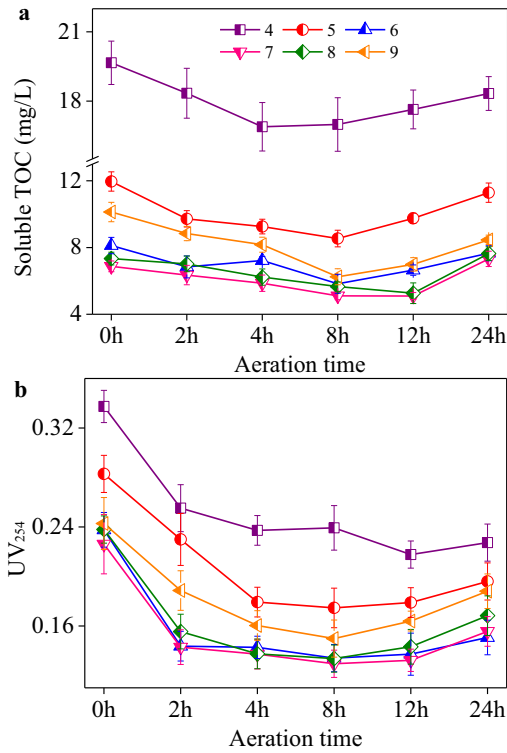


Fig. 3. Effects of system pH on the (a) soluble TOC and (b) UV₂₅₄ in supernatant at the noted digestion times.

in supernatant could be the excellent carbon sources and electron-donor substrates for heterotrophic bacteria, resulted to the continuous decrease of both STOC and UV₂₅₄ initially (Ni et al., 2011). The shortage of biodegradable carbon sources caused the hydrolysis of EPS or even the cellular lysis (Liu et al., 2010; Liu et al., 2011), resulted to the increase of STOC and UV₂₅₄ in the latter stage of STAD.

3.4. Influences of pH on the MWD of soluble biopolymer in STAD system

The molecular weight distribution of soluble organic matters could significantly affect its degradation by heterotrophic bacteria (Eskicioglu et al., 2006). Fig. 4 shows the MW distributions of biopolymers in the supernatant under various system pH conditions and aerobic digested for 4 h. Neutral and weak alkaline conditions show the lowest specific intensity and area of the peaks, but which gradually increased with the increasing of both system acidity and alkalinity, indicating the improved solubilization of biopolymers from WAS under acidic and alkaline conditions, which is consistent with previous study (Sheng et al., 2005). Additionally, the MW of biopolymers lower than 100 kDa was 59.8% under neutral condition, but which increased to 87.5% and 76.5% at pH of 4 and 9, respectively. Results showed that acidic and alkaline conditions could improve the releasing of biopolymers and increase the proportion of low MW fractions, which could be easily biodegraded during the STAD process (Xia et al., 2017; Zhang et al., 2016). However, as acidic condition will inhibit the activity of the microorganism functional for the biodegradation of organic matters (Yavuz and Celebi, 2000), neutral and weak alkaline conditions should be more suitable for the STAD of WAS.

3.5. Influences of system pH on supernatant NH₄⁺ - N and PO₄³⁻ - P and the SOUR of WAS in STAD system

Fig. 5a shows the soluble NH₄⁺ - N concentration under various initial system pH conditions at the noted digestion times. Neutral and weak alkaline conditions show the lowest concentration of soluble

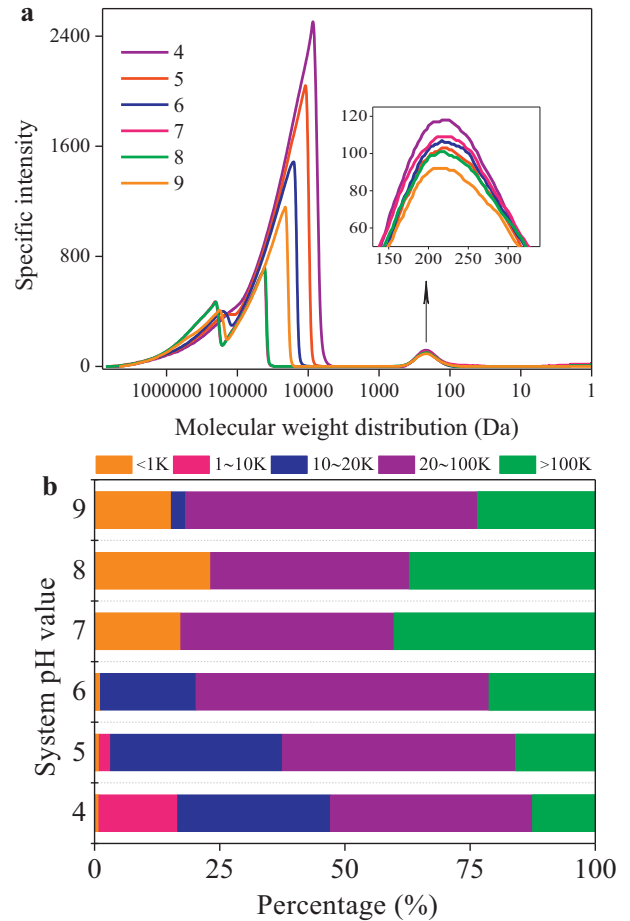


Fig. 4. Effects of system pH on the MW distributions of the soluble biopolymers in supernatant of waste activated sludge after aerobic digested for 4 h.

NH₄⁺ - N, but which gradually increased with the increasing of both system acidity and alkalinity, resulting from the solubilization of biopolymers and releasing of stored NH₄⁺ - N in biopolymers (Schwitalla et al., 2008; Temmink et al., 2001). Under acidic conditions, soluble NH₄⁺ - N gradually increased in the initial 4 h and lower pH leads to a higher soluble NH₄⁺ - N, but which gradually decreased and almost remained stable after digested for 4 h under neutral and weak alkaline conditions, which should be resulted from the reuse of nitrogen by the heterotrophic bacteria (Zevin et al., 2015).

Fig. 5b shows the soluble PO₄³⁻ - P concentration under various initial system pH conditions at the noted digestion times. Neutral and weak alkaline conditions show the lowest concentration of soluble PO₄³⁻ - P, but which gradually increased with the increasing of both system acidity and alkalinity, resulting from the solubilization of biopolymers (Fig. 1) and releasing of adsorbed PO₄³⁻ - P in EPS (Zhou et al., 2017b). Under acidic conditions, PO₄³⁻ - P slightly increased and remained stable. Soluble PO₄³⁻ - P concentration gradually decreased and then remained stable under neutral and weak alkaline conditions, which should be resulted from the adsorption and accumulating of PO₄³⁻ - P by EPS and PAOs, respectively (Zhang et al., 2013; Zhou et al., 2017b).

SOUR is an important indicator of the microbial activity, which is an important indicator for the biodegradation of organic matters by these heterotrophic bacteria (Miyatake and Iwabuchi, 2006). Fig. 5c shows the SOUR of WAS under various initial system pH conditions at the noted digestion times. Neutral and weak alkaline conditions show the highest SOUR, but which gradually decreased with the increasing of both system acidity and alkalinity, which should be resulted from that

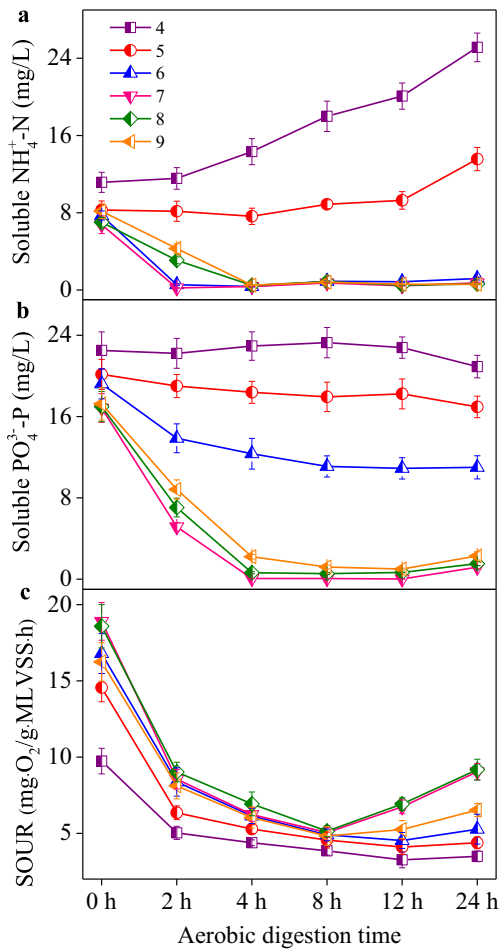


Fig. 5. Effects of system pH on the soluble (a) NH_4^+ - N, (b) PO_4^{3-} - P and (c) SOUR of aerobic digested sludge at the noted digestion times.

acidic and alkaline conditions caused cell lysis and inhibited the microbial activity (Yavuz and Celebi, 2000). During the STAD process, SOUR for all pH conditions gradually decreased in the initial 8 h and it keeps decreasing under acidic conditions, but which gradually increased thereafter under neutral and weak alkaline conditions. Results also showed that acidic condition will inhibit the microorganism activity, neutral and weak alkaline conditions should be more suitable for the stabilization of WAS in STAD system.

3.6. Influencing mechanisms of system pH on the STAD process of WAS

Fig. 6 synthesizes the results in terms of the mechanisms acting to how system pH influences the WAS reduction by STAD process.

Under acidic conditions, decreasing system pH could improve the solubilization of organic matters and increase the proportion of low MW fractions from WAS (Figs. 2 and 4), leading to the decrease of VSS and the increase of STOC, UV_{254} and biopolymers and its fractions (Figs. 2 and 3), which could be easily biodegraded by the aerobic microorganisms in the later stage of STAD. Simultaneously, NH_4^+ - N and PO_4^{3-} - P also increased during the solubilization of biopolymers in the initial 4 h (Fig. 5a and b), but which gradually decreased due to the storage and reuse by the functional microorganisms. Additionally, the activity of aerobic microorganisms (denoted as SOUR) decreased (Fig. 5c), leading to the decreased k_{TCOD} (Table 2).

Under neutral and weak alkaline conditions, less solubilization of organic matters leads to the low concentrations of PO_4^{3-} - P, NH_4^+ - N, STOC, UV_{254} and biopolymers and the low MW fractions, all of which

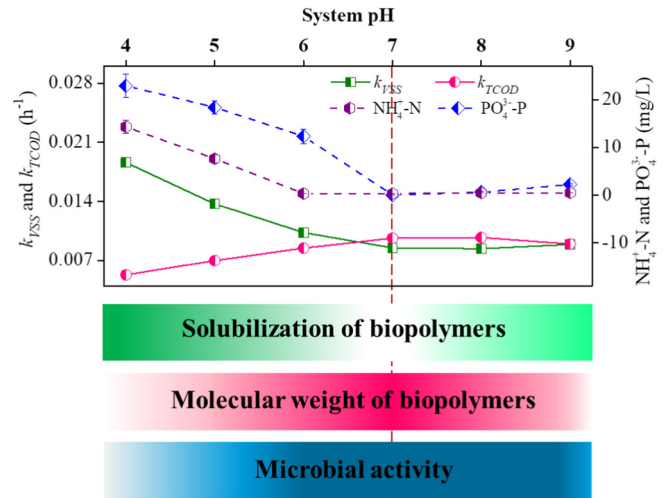


Fig. 6. Influencing mechanisms of system pH on the STAD process of WAS. The dark-colored and the light-colored in the bars signify high and low values of the parameters, respectively. (For interpretation of the references to color in this figure legend, the readers are referred to the web version of this article).

could be further reused or biodegraded by the functional microorganisms in the later stage of STAD process. High microbial activity (denoted as SOUR) functional for the biodegradation of organic matters led to high k_{TCOD} (Table 2).

For the practical application of STAD process on the reduction of WAS, easy operation and low treatment cost should be crucial. Our results indicated that neutral and weak alkaline conditions could achieve the high microbial activity and organic matters biodegradation rate, leading to the high WAS reduction efficiency. Because of the neutral and weak alkaline for concentrated WAS, we needn't to adjust the system pH and add the WAS into STAD system directly, which achieve the easy operation and dramatically decrease the treatment cost.

4. Conclusions

STAD is a unique and significant technique for WAS stabilization. The influences of system pH on the STAD process of WAS were systematically disclosed. Under neutral or weak alkaline conditions, although the biodegradation rates of VSS were low, high k_{TCOD} was achieved. Less releases of the biopolymers from the WAS led to low concentrations of STOC, UV_{254} , the low MW organic matters, NH_4^+ - N and PO_4^{3-} - P in the supernatant. However, the appropriate pH for the microorganisms improved SOUR, indicating that the released substances were further reused or biodegraded by the microorganisms. Under acidic or alkaline conditions, the biodegradation rates of k_{VSS} and k_{TCOD} were opposite with those under neutral or weak alkaline conditions. The releases of the biopolymers were increased, leading to high concentrations of STOC, UV_{254} , the low MW organic matters, NH_4^+ - N and PO_4^{3-} - P in the supernatant. However, the extreme pH inhibited the microbial activity. The SOURs were only 0.0097 h^{-1} and 0.0053 h^{-1} for system pH of 8.0 and 4.0, respectively. Accordingly, neutral and weak alkaline conditions should be more suitable for the STAD process of WAS.

Acknowledgements

This work was supported by the Foundation of Key Laboratory of Yangtze River Water Environment, Ministry of Education of China (Tongji University) (No. YRWEF201805); the Foundation of State Key Laboratory of Pollution Control and Resource Reuse (Tongji University), China (No. PCRRE16019); National Key R&D Program of China (No. 2017YFC0403400); the Fundamental Research Funds for the Central Universities; National Natural Science Foundation of China (No. 51678422).

and No. 51378368); Shanghai Tongji Gao Tingyao Environmental Science & Technology Development Foundation; and the higher school innovative engineering plan (111 Project).

References

- (EIC) EIoC, 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. vol. 2. American Public Health Association.
- Benedek, P., Farkas, P., Literathy, P., 1972. Kinetics of aerobic sludge stabilization. *Water Res.* 6, 91–97.
- Bernard, S., Gray, N.F., 2000. Aerobic digestion of pharmaceutical and domestic wastewater sludges at ambient temperature. *Water Res.* 34, 725–734.
- Bitton, G., 2005. Activated sludge process. *Wastewater Microbiology*, third ed., pp. 225–257.
- Campbell, H.W., 2000. Sludge management—future issues and trends. *Water Sci. Technol.* 41, 1–8.
- Chen, Y., Jiang, S., Yuan, H., Zhou, Q., Gu, G., 2007. Hydrolysis and acidification of waste activated sludge at different pHs. *Water Res.* 41, 683–689.
- d'Antonio, G., 1983. Aerobic digestion of thickened activated sludge: reaction rate constant determination and process performance. *Water Res.* 17, 1525–1531.
- Datar, M.T., Bhargava, D.S., 1988. Effects of environmental factors on nitrification during aerobic digestion of activated sludge. *J. Inst. Eng. (India) EN Environ. Eng. Div.* 68, 29–35.
- Eskicioglu, C., Kennedy, K.J., Droste, R.L., 2006. Characterization of soluble organic matter of waste activated sludge before and after thermal pretreatment. *Water Res.* 40, 3725–3736.
- Frølund, B., Palmgren, R., Keiding, K., Nielsen, P.H., 1996. Extraction of extracellular polymers from activated sludge using a cation exchange resin. *Water Res.* 30, 1749–1758.
- Jiang, S., Chen, Y., Zhou, Q., 2007. Influence of alkyl sulfates on waste activated sludge fermentation at ambient temperature. *J. Hazard. Mater.* 148, 110–115.
- Kepp, U., Machenbach, I., Weisz, N., Solheim, O.E., 2000. Enhanced stabilisation of sewage sludge through thermal hydrolysis—three years of experience with full scale plant. *Water Sci. Technol.* 42, 89–96.
- Lasaridi, K.E., Stentiford, E.I., 1998. A simple respirometric technique for assessing compost stability. *Water Res.* 32, 3717–3723.
- Layden, N.M., Mavinic, D.S., Kelly, H.G., Moles, R., Bartlett, J., 2007. Autothermal thermophilic aerobic digestion (ATAD)—part I: review of origins, design, and process operation. *J. Environ. Eng. Sci.* 6, 665–678.
- Liu, S., Song, F., Zhu, N., Yuan, H., Cheng, J., 2010. Chemical and microbial changes during autothermal thermophilic aerobic digestion (ATAD) of sewage sludge. *Bioresour. Technol.* 101, 9438–9444.
- Liu, S., Zhu, N., Li, L.Y., 2011. The one-stage autothermal thermophilic aerobic digestion for sewage sludge treatment. *Chem. Eng. J.* 174, 564–570.
- Ma, Y., Gu, J., Liu, Y., 2018. Evaluation of anaerobic digestion of food waste and waste activated sludge: soluble COD versus its chemical composition. *Sci. Total Environ.* 643, 21–27.
- Miyatake, F., Iwabuchi, K., 2006. Effect of compost temperature on oxygen uptake rate, specific growth rate and enzymatic activity of microorganisms in dairy cattle manure. *Bioresour. Technol.* 97, 961–965.
- Ni, B.-J., Rittmann, B.E., Yu, H.-Q., 2011. Soluble microbial products and their implications in mixed culture biotechnology. *Trends Biotechnol.* 29, 454–463.
- Painter, H.A., Loveless, J.E., 1983. Effect of temperature and pH value on the growth-rate constants of nitrifying bacteria in the activated-sludge process. *Water Res.* 17, 237–248.
- 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.
- Roberts, R., Davies, W.J., Forster, C.F., 1999. Two-stage, thermophilic-mesophilic anaerobic digestion of sewage sludge. *Process. Saf. Environ. Prot.* 77, 93–97.
- Schwitalla, P., Mennerich, A., Austermann-Haun, U., Müller, A., Dorninger, C., Daims, H., et al., 2008. NH₄⁺ ad-/desorption in sequencing batch reactors: simulation, laboratory and full-scale studies. *Water Sci. Technol.* 58.
- Sheng, G.-P., Yu, H.-Q., Yu, Z., 2005. Extraction of extracellular polymeric substances from the photosynthetic bacterium *Rhodospseudomonas acidophila*. *Appl. Microbiol. Biotechnol.* 67, 125–130.
- Sung, S., Santha, H., 2003. Performance of temperature-phased anaerobic digestion (TPAD) system treating dairy cattle wastes. *Water Res.* 37, 1628–1636.
- Temmink, H., Klapwijk, A., De Korte, K.F., 2001. Feasibility of the BIOFIX-process for treatment of municipal wastewater. *Water Sci. Technol.* 43, 241–249.
- Wingender, J., Neu, T.R., Flemming, H.-C., 1999. What are bacterial extracellular polymeric substances? *Microbial Extracellular Polymeric Substances*. Springer, pp. 1–19.
- 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. *Sci. Rep.* 7, 13491.
- Yavuz, H., Celebi, S.S., 2000. Effects of magnetic field on activity of activated sludge in wastewater treatment. *Enzym. Microb. Technol.* 26, 22–27.
- 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. *Biotechnol. Bioeng.* 112, 1761–1769.
- Zhang, H.-L., Fang, W., Wang, Y.-P., Sheng, G.-P., Zeng, R.J., Li, W.-W., et al., 2013. Phosphorus removal in an enhanced biological phosphorus removal process: roles of extracellular polymeric substances. *Environ. Sci. Technol.* 47, 11482–11489.
- Zhang, Z., Zhang, J., Zhao, J., Xia, S., 2015. Effect of short-time aerobic digestion on bioflocculation of extracellular polymeric substances from waste activated sludge. *Environ. Sci. Pollut. Res. Int.* 22, 1812–1818.
- 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. *Chem. Eng. J.* 299, 177–183.
- Zhao, J., Wang, D., Li, X., Yang, Q., Chen, H., Zhong, Y., et al., 2015a. Free nitrous acid serving as a pretreatment method for alkaline fermentation to enhance short-chain fatty acid production from waste activated sludge. *Water Res.* 78, 111–120.
- Zhao, J., Yang, Q., Li, X., Wang, D., An, H., Xie, T., et al., 2015b. Effect of initial pH on short chain fatty acid production during the anaerobic fermentation of membrane bioreactor sludge enhanced by alkyl polyglycoside. *Int. Biodeterior. Biodegrad.* 104, 283–289.
- Zhao, J., Wang, D., Liu, Y., Ngo, H.H., Guo, W., Yang, Q., et al., 2018. Novel stepwise pH control strategy to improve short chain fatty acid production from sludge anaerobic fermentation. *Bioresour. Technol.* 249, 431–438.
- Zhou, Y., Nguyen, B.T., Lai, Y.S., Zhou, C., Xia, S., Rittmann, B.E., 2016. Using flow cytometry to evaluate thermal extraction of EPS from *Synechocystis* sp. PCC 6803. *Algal Res.* 20, 276–281.
- Zhou, Y., Nguyen, B.T., Zhou, C., Straka, L., Lai, Y.S., Xia, S., et al., 2017a. The distribution of phosphorus and its transformations during batch growth of *Synechocystis*. *Water Res.* 122, 355–362.
- Zhou, Y., Zhang, J., Zhang, Z., Zhou, C., Lai, Y.S., Xia, S., 2017b. Enhanced performance of short-time aerobic digestion for waste activated sludge under the presence of cocoamidopropyl betaine. *Chem. Eng. J.* 320, 494–500.