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Using sulfite pretreatment to improve the biodegradability of waste activated sludge

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This study presents a novel strategy to improve the biodegradability of the waste activated sludge (WAS) based on sulfite pretreatment. Experiments were conducted to demonstrate the effects of sulfite on the WAS and its biodegradability by sulfite pretreatment. The results show that the concentration of the released substrate in the sulfite (0.2–0.48 g S/L) pretreated WAS increased 2–5 times after 12–36 h, at the pH of 5–7, compared with the WAS without pretreatment. The concentration of soluble chemical oxygen demand (SCOD) produced had a strong correlation with the concentration of sulphurous acid (H_2SO_3), suggesting that H_2SO_3 may directly cause the lysis of microorganisms in WAS. Biogenic sulfide production (BSP) was applied for the assessment of anaerobic biodegradability. The results indicated that the biodegradability of the WAS after sulfite pretreatment improved by approximately 51% compared with the control system. Moreover, the rate of sulfate/sulfite reduction in the Experimental reactor was 1.62 times higher than the value in the Control reactor, thereby further confirming the improvement observed in the biodegradability of the sulfite pretreated WAS. The released substrates and produced sulfide can be further applied as renewable sources of energy.

Introduction

The activated sludge process (ASP) has been successfully applied in biological wastewater treatment, to protect human health and the environment, for over 100 years.[1-3] However, the ASP produces large amounts of sludge, which need to be treated and disposed of safely.[4,5] For instance, in 2010, 8.9 million dry metric tons of waste activated sludge (WAS) were produced in the EU, while in 2013, 6.25 million tons of dry solids WAS were produced in China.[6,7] The costs of treating the excess sludge range from 30% to 60% of the total annual operation cost of wastewater treatment plants globally.[8,9] Stringent environmental legislation and environmental friendly sludge management measures are needed, to remediate this problem. These management measures should regard the excess sludge (biosolids) as a resource rather than as a waste owing its high chemical energy content.[10,11] Hence, the viability of reducing sludge production and extracting energy from the excess sludge thereof should receive more attention in biological wastewater treatment.

Currently, the reduction and/or energy recovery of the excess sludge following sewage treatment is normally performed in two ways, through online and offline sludge reduction processes.[5] Various treatment approaches rely on thermal[8], ultrasonication[12], chemical (ozone[13], alkali[14], poly(hydroxyalkanoate)[15], surfactant[16], free nitrite acid (FNA)[17] treatment), and combined pretreatment.[18-22] The main purpose of these methods is to accelerate the lysis-cryptic growth of the excess sludge used as secondary substrates, resulting from the cell lysis.[23-25]

Apart from the aforementioned physical and/or chemical based technologies, more recently, a biological-based process named the Sulfate reduction Autotrophic denitrification and Nitrification Integrated (SANI®) process was developed for the treatment of saline/sulfate containing sewage. The SANI process can achieve reductions of up to 90% of sludge and 35% of energy consumption compared to conventional biological wastewater treatment systems.[26,27] The development of the SANI process benefits from the seawater toilet flushing system (for freshwater saving), which is widely applied in Hong Kong and results in sulfate-laden sewage. Sulfate in the sewage is used as the electron carrier to convert more than 80% of the chemical oxygen demand (COD) into alkalinity by the mediation of the sulfate-reducing bacteria (SRB), resulting in limited sludge production (0.04 g VSS/g COD).[28,29]

For wastewaters that contain low/insufficient sulfur, the SANI system can also be implemented by adding low-cost sulfur wastes including all forms of oxidized sulfur (S_0, $S_2O_3^{2-}$, SO_3^{2-}, and SO_4^{2-}). Also, in fossil power plants a sulfite-rich waste can be widely produced from the wet flue gas desulfurization (FGD) process.[30,31] Qian et al.[32,33] reported that the FGD-SANI

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could provide an approach for the application of the SANI process to achieve sludge minimization in inland areas. A similar co-treatment system has been demonstrated by Poinapen et al.[34] using primary settled sludge as the carbon source for the biological sulfate reduction of acid mine drainage. Additionally, the biocidal effect of sulfite has demonstrated that the sulfite-sensitive cell walls could be irreversibly destroyed by 0.1 M of sodium sulfite.[35] Based on the above information, a new approach to chemical and biological sludge reduction is proposed, namely the pretreatment of the excess sludge with sulfite-rich waste and the subsequent handling of the sludge through the sulfate reduction or SANI process.

Two issues must be investigated prior to the implementation of the sulfite-rich chemical and biological sludge reductions, viz. 1) the possibility of applying the biocidal effect of sulfite to the lysis of the waste activated sludge, and 2) the possibility to further degrade the sulfite pretreated sludge biologically via the sulfate reduction or SANI® process.

To verify this, a feasibility study was carried out in two stages. Firstly, the waste activated sludge (WAS) was treated at the different sulfite concentrations of 0–0.48 g S/L, pH values of 5–7, and exposure times of 12–36 h. Secondly, the evaluation of the biodegradability of the sludge pretreated with sulfite was determined in the sulfate reduction batch tests.

Experimental

Sludge sources

The WAS used in this study was collected from a local activated sludge biological wastewater treatment plant at Sha Tin, in Hong Kong. The sludge retention time (SRT) was 11 days. The total suspended solids (TSS) and volatile suspended solids (VSS) of the WAS were 44.5 ± 0.2 g/L and 37.4 ± 0.3 g/L, respectively, and the pH was 7.34 ± 0.01.

Biological Sulfate Reducing (BSR) sludge was collected from a sulfate reduction upflow sludge blanket (SRUSB) reactor (at the same sewage treatment plant) having a SRT of 16 days. Its main characteristics were TSS of 43.5 ± 0.2 g/L, VSS of 32.8 ± 0.2 g/L, and pH of 7.72 ± 0.01.

Effect of sulfite on waste activated sludge

Batch tests were conducted to assess the effects of sulfite on the characteristics of the WAS. The sludge was initially washed three times with a buffered saline solution of 0.01 M phosphate (1×PBS) to eliminate the residual substrate and ensure a stable pH condition for the subsequent batch tests. Following this, 0.3 L of washed WAS was added to each batch reactor. The sulfite level was achieved by adding a solution of sodium sulfite based on the typical FGD wastewater,[32,36,37] which had been prepared prior to the tests. Pure nitrogen was bubble diffused in the batch reactors for 15 mins. Subsequent to that, the sealed batch reactors were put onto the rotator with a speed of 60 rpm. The three operating parameters monitored were sulfite concentration, exposure time, and pH, as summarized in Table 1. A control solution of 0 mg S/L was also prepared.

In all the tests, the TSS, VSS, soluble chemical oxygen demand (SCOD) (SCOD donated by soluble organic carbon, i.e. organic SCOD), sulfite (SO_3^{2-}), sulfate (SO_4^{2-}), soluble total nitrogen (TN) (TN = soluble TKN + NO^{2-} + NO^{3-}), ammonia nitrogen (NH_4^+-N), soluble protein, and soluble polysaccharides were measured in triplicates both at test start and at the end of each test.

Table 1 Experimental conditions used in the batch tests

Test NO.	Exposure (hour)	pH	Sulfite (mg S/L)
1	12	7	0, 200, 340, 480
2	12	6	0, 200, 340, 480
3	12	5	0, 200, 340, 480
4	24	7	0, 200, 340, 480
5	24	6	0, 200, 340, 480
6	24	5	0, 200, 340, 480
7	36	7	0, 200, 340, 480
8	36	6	0, 200, 340, 480
9	36	5	0, 200, 340, 480

The lysis of the sulfite pretreated WAS was also studied to explore the potential relation of the different species of sulfite (H_2SO_3, HSO_3^-, and SO_3^{2-}). The concentration of H_2SO_3, HSO_3^-, and SO_3^{2-} were calculated based on the sulfite concentration and pH (Table 2).

Table 2 Concentration of H_2SO_3, HSO_3^-, and SO_3^{2-} under different sulfite and pH conditions

Sulfite = 0.20 g S/L			
pH	5	6	7
H_2SO_3 (mg/L)	0.4136	0.0391	0.0025
HSO_3^- (mg/L)	502.52	474.87	304.97
SO_3^{2-} (mg/L)	3.28	30.95	198.79
Sulfite = 0.34 g S/L			
pH	5	6	7
H_2SO_3 (mg/L)	0.7031	0.0664	0.0043
HSO_3^- (mg/L)	854.29	807.28	518.45
SO_3^{2-} (mg/L)	5.57	52.62	337.95
Sulfite = 0.20 g S/L			
pH	5	6	7
H_2SO_3 (mg/L)	0.9926	0.0938	0.0060
HSO_3^- (mg/L)	1206.06	1139.69	731.92
SO_3^{2-} (mg/L)	7.86	74.29	477.11

The dissociation of sulfurous acid:

$$H_2SO_3 \leftrightarrow HSO_3^- + H^+ \quad pK_1 = 1.91 \quad (at\ 25℃) \qquad (1)$$

$$HSO_3^- \leftrightarrow SO_3^{2-} + H^+ \quad pK_2 = 7.18 \quad (at\ 25℃) \qquad (2)$$

Evaluation of biodegradability

The experiments on sulfite/sulfate reduction were conducted to assess the biodegradability of the WAS with/without sulfite pretreatment. The biochemical methane potential (BMP) was determined for the assessment of the anaerobic biodegradability as per convention.[38] However, in the presence

of sulfur, the BMP is not suitable for the assessment of biodegradability. Therefore, the biogenic sulfide production (BSP) was used for the assessment of anaerobic biodegradability. In a BSP test, the electron donor capacity is given by the production of sulfide instead of methane in a BMP test.

A sulfite concentration of 340 mg S/L with pH of 7.00 ± 0.01 was dosed for 24 h to one WAS sample, while another WAS sample, i.e. the control sample, was pretreated under the same conditions but without sulfite dosing. Then, two batch reactors were filled with 0.1 L of BSR sludge and 1.4 L of WAS, respectively, at pH of 7.34 ± 0.01 with and without sulfite pretreatment. Subsequently, a stock solution of sulfate was added to the batch reactors to achieve a total sulfur concentration of 900 mg S/L, thereby also providing sufficient electron acceptor for the biodegradability assessment. The above tests lasted 10 days.

Free and Saline Sulfide (FSS) ($FSS=H_2S+HS^-+S^{2-}$) was measured daily until the sulfide concentration reached the constant value. The increased sulfide concentration illustrates the transfer of electron from the biodegradable substrates of the WAS to the sulfide, which is mediated by the sulfate-reducing bacteria (SRB). The slope of the sulfide versus the time line was applied to describe the sulfite/sulfate reduction rate or sulfide production rate as follow:

$$r = \frac{dC}{dt} \qquad (3)$$

r = reaction rate, mg/(L • d)
t = the reaction time, d
C = concentration of sulfide at time t, mg/L

Analytical methods

Samples for the soluble chemical oxygen demand (SCOD), soluble total nitrogen (TN), sulfite (SO_3^{2-}), sulfate (SO_4^{2-}), ammonium nitrogen (NH_4^+-N), soluble protein, and soluble polysaccharides were filtered through disposable Millipore filter units (0.45 µm pore size). The TSS, VSS, SCOD, and SO_3^{2-} were determined according to the Standard Methods.[39] The SO_4^{2-} was measured by using an ion chromatograph (Shimadzu Corporation, HIC-20A super) equipped with a conductivity detector and an IC-SA2 analytical column. The Free and Saline Sulfide (FSS) was measured with methylene blue method.[39] The TN was assessed using a TOC/TN analyzer (Shimadzu TOC-5000A). The ammonium nitrogen was determined by using a Flow Injection Analyzer (FIA) (QuikChem FIA+8000 Series). The soluble proteins were measured by the bicinchoninic acid assay (BCA assay) with Bovine serum albumin (BSA) as standard,[40] while soluble polysaccharides were determined by using the colorimetric method.[41]

Results and discussion

Characterization of the sulfite pretreated WAS

Changes in the characteristics of the WAS after different exposure times (12, 24, and 36 h), at different sulfite concentrations (0, 0.20, 0.34, and 0.48 g S/L), and with different pH (5, 6, and 7) are illustrated in Fig. 1 and 2. Fig. 1A indicates that for the WAS treated at the highest sulfite concentration of 0.48 g S/L, the production of SCOD increased three times as a result of the prolonged exposure time, i.e. from 0.045 g SCOD/g VSS after 12 h to 0.14 g SCOD/g VSS after 36 h at the pH of 5. An increase of 0.09 g SCOD/g VSS was obtained compared with the much smaller increase of 0.016 g SCOD/g VSS (0.027 g SCOD/g VSS for 36 h versus 0.011 g SCOD/g VSS for 12 h) for the untreated WAS (exposed to 0 g S/L) under similar conditions.

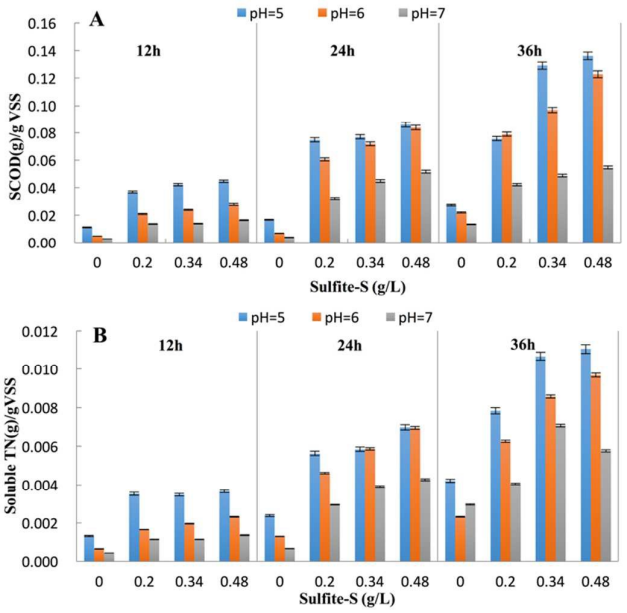

Fig. 1 SCOD (A) and soluble TN (B) produced from the biomass at different sulfite concentrations (0, 200 mg S/L, 340 mg S/L, 480 mg S/L), pH conditions (5, 6, 7), and exposure times (12h, 24h, 36h). The error bars indicate the standard errors resulting from the triplicate tests.

Apart from the exposure time, the increases in sulfite concentrations resulted in more release of SCOD. In the control WAS sample, the SCOD only increased by approximately 0.003 g SCOD/g VSS after 12 h at the pH of 7. In contrast, for the WAS pretreated at 0.48 g S/L of sulfite concentration, the SCOD increased by approximately 0.016 g SCOD/g VSS under the same conditions, which suggests that this WAS was solubilized nearly five times (0.016 g SCOD/g VSS versus 0.003 g SCOD/g VSS) compared with the control. Moreover, the decrease of pH induced further production of SCOD. After 24 h of pretreatment, the concentrations of SCOD released at the pH of 5 were 0.017, 0.075, 0.077, and 0.086 g SCOD/g VSS, which were higher than the concentrations released at the pH of 7, at different sulfite concentrations (i.e. approximately 1.7–2.3 times higher). In the case of the WAS pretreated with sulfite, these results imply that more cells

and/or extracellular polymeric substances (EPS), originating from the particulate organics, became soluble substrates.

Similar trends were observed for TN, soluble proteins, and soluble polysaccharides (see Fig. 1B, 2A and 2B). The TN increased from 0.0042 g N/g VSS in the control WAS sample, at the pH of 5 at 36 h, to approximately 0.0111 g N/g VSS in the WAS pretreated with the sulfite concentration of 0.48 g S/L under the same conditions. This is equivalent to a three-fold release of TN. The concentrations of soluble proteins and soluble polysaccharides both increased more than three times when compared with the control WAS sample. Soluble proteins and soluble polysaccharides increased from 0.07 g/g VSS and 0.007 g/g VSS, respectively, in the untreated WAS sample at the pH of 5 at 36 h, to approximately 0.27 g/g VSS and 0.022 g/g VSS, respectively, in the WAS sample pretreated with the sulfite concentration of 0.48 g S/L under the same conditions. This implies that more intracellular and/or extracellular constituents are released from the cells and/or EPS, which correlate with the results of SCOD. However, in all the tests the results of NH4+-N did not reflect any trend (data not shown).

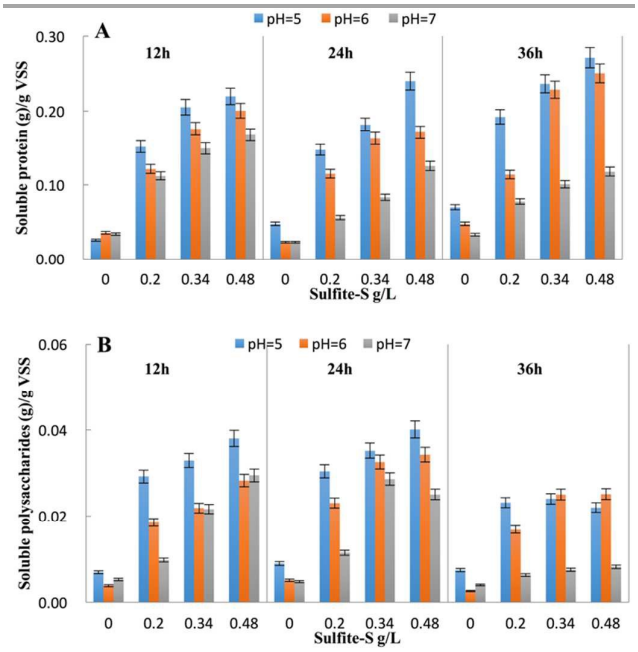

Fig. 2 Production of soluble protein and soluble polysaccharides at different sulfite concentrations (0, 200 mg S/L, 340 mg S/L, 480 mg S/L), pH conditions (5, 6, 7), and exposure times (12h, 24h, 36h). The error bars indicate the standard errors resulting from the triplicate tests.

Lysis of WAS with sulfite pretreatment

In the batch tests, sulfide or thiosulfate was not detected though residual sulfite and sulfate were found (sulfite/sulfate ≈1). Hence, no biological sulfate/sulfite reduction took place in the batch tests pretreated with sulfite. Blank batch tests were conducted with water and sulfite only. It was found that approximately 2-4% of sulfite was oxidized to sulfate in the test system with 15 mins of nitrogen gas sparging prior to the tests. Thus, the production of sulfate in the batch tests (containing sludge and sulfite) may be attributed to the biological and/or chemical reactions or reductive organic matter, and more intensive studies are needed.

Fig. 3A&B show a plot of the production of SCOD against the total sulfite (SO_3^{2-} + HSO_3^- + H_2SO_3) and sulfurous acid (H_2SO_3) concentrations at different sulfite levels (0, 0.20, 0.34, and 0.48 g S/L) at different pH values (5, 6, and 7). A positive impact of total sulfite on the SCOD released was observed. Higher total sulfite concentration induced higher SCOD production (Fig 3A). However, the concentrations of SCOD varied with different exposure times and pH values. Longer exposure time (12, 24 and 36 h) resulted in insignificant differences in the concentrations of SCOD at low pH values (pH=5 and pH=6), and lower pH values stimulated higher productions of SCOD, suggesting that the total sulfite concentration is not the sole factor contributing to the production of SCOD; pH is also likely to impact on the production of SCOD.

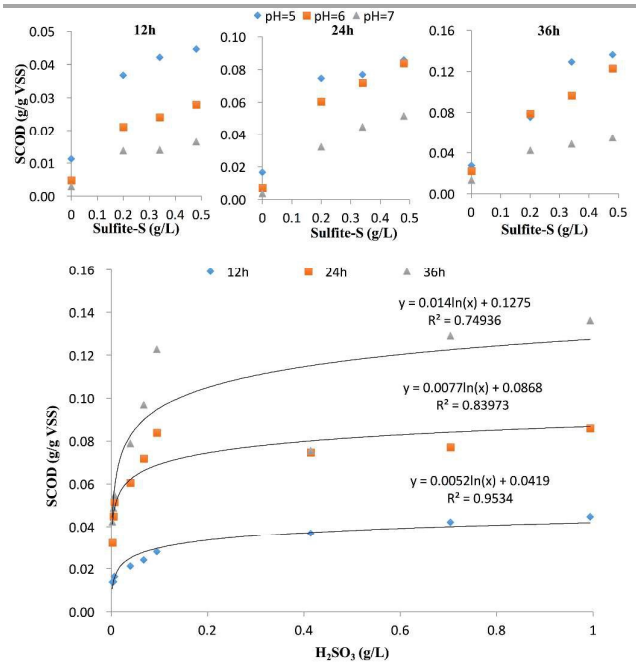

Fig. 3 The dependency of SCOD on total sulfite concentration (A), sulphurous acid (B) after 12h, 24h and 36h of pretreatment at different concentrations of sulfite (0 to 0.48 g S/L), at different pH values (5 to 7).

Although the concentration of SO_3^{2-} and HSO_3^- were much higher than the concentration of H_2SO_3 (e.g. at pH of 5 and sulfite of 0.20 g S/L, the SO_3^{2-} and HSO_3^- were 3.28 mg/L and 502.52 mg/L, respectively, and the H_2SO_3 was 0.4136 mg/L), little was found on the relationship between SO_3^{2-} and/or HSO_3^- and substrates production.

Fig. 3B shows that the release of SCOD had a stronger dependence upon the concentration of sulfurous acid (H_2SO_3),

indicating that sulfurous acid may directly cause the lysis of the microorganisms in the WAS. The production/experimental data of SCOD could be fitted by an exponential model (y=aln(x)+b) as shown in Fig. 3B. However, the correlation coefficient (R^2) decreased with longer exposure time. Longer exposure times resulted in lower total concentration of sulfite due to the production of sulfate leading to a relatively impaired production of substrates.

The lysis of biomass caused by sulfite or sulfurous acid may be attributed to the cleavage of the bonds of disulfide and irreversible destruction of the structure of the sulfite-sensitive sodium of the cell wall.[35] Bonds of protein disulfide formed in the endoplasmic reticulum of eukaryotic cells and the periplasmic space of prokaryotic cells.[42] The reaction between the bonds of sulfite/sulfurous acid and disulfide in proteins was studied by many researchers.[43-46] However, more studies need to be conducted to elucidate the mechanisms and improve the understanding.

Biodegradability of sulfite pretreated WAS

To provide sufficient source of sulfur as the electron acceptor in the evaluation of biodegradability, an additional concentration of 560 mg S/L sodium sulfate was dosed to the Experimental reactor and 900 mg S/L sulfate to the Control reactor. After mixing the BSR sludge and sulfite pretreated WAS, the sulfite and sulfate concentrations in the experimental system were approximately 100 mg S/L and 800 mg S/L, respectively.

Fig. 4 shows the dissolved sulfide generation in two batches (Control-BSR sludge seeded with untreated WAS and Experimental-BSR sludge seeded with pretreated WAS) for 10 days after the addition of the BSR sludge.

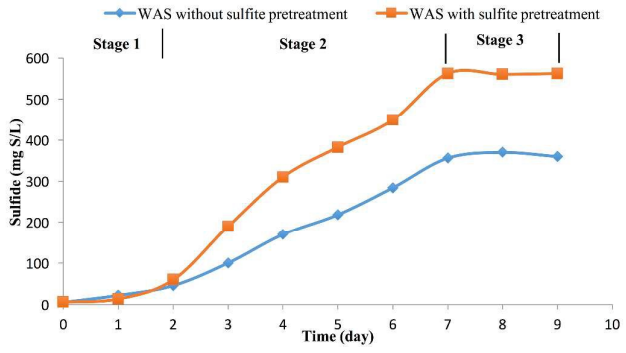

Fig. 4 Sulfate/sulfite reduction in batch reactors, which were performed with BSR sludge and WAS with or without sulfite pretreatment.

Based on the rate of sulfide production, the process was divided into three stages:

Stage 1 (day 0–day 2), the sulfide concentration increased slowly to 45.75 mg S/L in the Control reactor and 59.50 mg S/L in the Experimental reactor, and the sulfite/sulfate reduction rates were nearly the same in both reactors (20.12 mg S/L/day in the Control reactor and 26.92 mg S/L/day in the Experimental reactor). Stage 2 (day 2–day 7), the sulfide concentration increased faster in the Experimental reactor than in the Control reactor after two days acclimation. The rate of sulfite/sulfate reduction was 62.05 mg S/(L•d) in the Control reactor and 100.50 mg S/(L•d) in the Experimental reactor, and the rates of sulfide production were in agreement with previous studies.[47-50] The rate of reaction in the Experimental reactor was 1.62 times faster than the Control reactor. The higher concentration of biodegradable substrate (for the reduction of sulfate) caused the faster rate of reaction observed in the Experimental reactor.

In the final phase, stage 3 (day 7–day 9), the reduction of sulfate was complete after approximately 7 days, and the final sulfide concentrations were 562 mg S/L and 356 mg S/L in the Experimental and Control reactors, respectively. The concentration of sulfide of 210 mg S/L was produced in the Experimental reactor more than in the Control reactor. The pH reached 8.3 ± 0.01 in the Experimental reactor and 7.9 ± 0.01 in the Control reactor after sulfate reduction. In the Experimental reactor, 100 mg S/L of sulfide could be attributed to the reduction of sulfite and the rest to the reduction of sulfate. Therefore, the biodegradability of the WAS with the sulfite pretreatment improved by approximately 51% compared with the WAS without sulfite pretreatment.

Table 3 Reaction rate *r* under different conditions at different stage (with 95% Confidence Intervals)

	$r_{control}$ (mg S/(L•d))	$r_{experiment}$ (mg S/(L•d))	r_e/r_c
Stage 1 (day 0-2)	20.12± 0.02	26.92± 0.02	1.34
Stage 2 (day 2-7)	62.05± 0.03	100.50± 0.04	1.62
Stage 3 (day 7-9)	stable	stable	---

In the final step of sulfate reduction, sulfite is reduced to sulfide by the dissimilatory sulfite reductase (DSR), requiring the input of 6 electrons from the electron flow chain. Accordingly, the remaining sulfite in the batch reactor is utilized first. However, in the current study this result did not reflect in the sulfide that was produced, which could be attributed to the initial low sulfur content (11% of total sulfur).

Potential applications of excess sludge with sulfite pretreatment

The above results demonstrated that sulfite pretreated sludge releases a high concentration of substrate, which becomes a potential source of biodegradable COD for other microorganisms, e.g. sulfate/sulfite reduction bacteria. This can achieve sludge reduction in wastewater treatment, which is beneficial in sludge management.

As previously mentioned, many sludge pretreatment techniques have been applied in the past. However, either intensive energy input (ultrasonication or high temperature) or large consumption of chemical (alkali or ozone) is needed to achieve high hydrolysis rate and/or extent hydrolysis of sludge.[51] The sulfite pretreatment of WAS is potentially more environmental friendly and economically viable given that the FGD waste can be reused as a sulfite source. This co-treatment

of WAS and FGD waste also provides an alternative way for reusing and/or recycling FGD waste. Furthermore, the sulfite pretreated sludge can be recycled to the sulfate reduction bioreactor as substrate for the SRB. On one hand, the sulfate reduction bioreactor works as a biological incinerator for the reduction of the excess sludge; on the other hand, the high concentration of dissolved sulfide could be used for the removal of heavy metal ions (Cu^{2+}, Zn^{2+}, Pb^{2+}) from sewage, where sulfide is considered as an effective precipitant with many advantages.[52]

From the perspective of energy recovery, excess sludge is normally disposed of anaerobically for methane production. Instead of methane production, the produced sulfide (from the sludge reduction process) can act as fuel for the energy harvesting through sulfide-based microbial fuel cell (MFC).[53,54] In terms of the efficiency of energy harvesting, methane-based electricity production systems can currently only achieve about 14% of the original potential energy contained in the biodegradable wastewater organics.[11,55] Sulfide-based MFC offers good energy efficiency, environmental compatibility, possibility for automation, versatility, and cost effectiveness.[53,54,56]

However, more research must be done in this field to realize its actual potential.

Conclusions

The effects of the pretreatment by sulfite on the solubilization and biodegradability of waste activated sludge (WAS) were investigated in this study. The main conclusions can be summarized as follow:

1) Sulfite concentrations in the range of 0.20–0.48 g S/L can achieve lysis of secondary sludge with an exposure time of 12–36 hours or longer at the pH values of 5 to 7. The production of soluble COD increased up to five times, while TN, soluble protein, and soluble polysaccharides increased 2–3 times compared with the control system.

2) The biodegradability of the WAS pretreated with sulfite increased by 51% and the resulting biodegradable COD produced could subsequently be used as substrates for the sulfate/sulfite reduction bacteria.

3) The pretreatment of the WAS with sulfite provides an alternative way for the desulphurization of waste (e.g. FGD waste) treatment, and it represents a potential technology for sludge reduction in biological wastewater treatment. The resulting sulfide produced can be further utilized as a renewable source of energy.

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Graphical abstract

Significant improvement (~51%) in biodegradability of waste activated sludge with sulfite pretreatment