water

MDPI

Article

Effects of the Combined Utilization of Ultrasonic/Hydrogen Peroxide on Excess Sludge Destruction

Dehao Yuan [1,2], Xu Zhou [1,2], Wenbiao Jin [1,2,*], Wei Han [1,2,*], Huizhong Chi [1,2], Wanqing Ding [1,2], Yan Huang [1,2], Zhongqi He [1,2], Shuhong Gao [1,2] and Qilin Wang [3]

1 Shenzhen Engineering Laboratory of Microalgal Bioenergy, Harbin Institute of Technology (Shenzhen), Shenzhen 518055, China; Yuandehao@hit.edu.cn (D.Y.); zhouxu@hit.edu.cn (X.Z.); chihuizhong@hit.edu.cn (H.C.); dingwanqing@hit.edu.cn (W.D.); huangyan@hit.edu.cn (Y.H.); hezhongqi@hit.edu.cn (Z.H.); gaoshuhong@hit.edu.cn (S.G.)
2 State Key Laboratory of Urban Water Resource and Environment, School of Environment, Harbin Institute of Technology, Harbin 150090, China
3 Centre for Technology in Water and Wastewater Treatment, School of Civil and Environmental Engineering, University of Technology Sydney, Ultimo, NSW 2220, Australia; Qilin.Wang@uts.edu.au
* Correspondence: jinwb@hit.edu.cn (W.J.); hanwei2020@hit.edu.cn (W.H.); Tel.:/Fax: +86-755-2603-3512 (W.J.); Tel.:/Fax: +86-755-2603-3506 (W.H.)

Abstract: Excess sludge reduction has been a research hotspot for a long time. Ultrasonic treatment of excess sludge was an efficient and green pretreatment method, and also can be combined with the addition of oxidants. To improve the effect of ultrasound treatment on sludge destruction, hydrogen peroxide (H_2O_2) was added to examine the combined results in the current study. The effects of the ultrasound/hydrogen peroxide system on the release of sludge organic matter during the destruction process were studied. Single-factor experiments were carried out to determine the optimal operating conditions. With the initial pH of 11.0, H_2O_2 concentration of 0.5 mmol/L, initial sludge concentration of 17 g/L, and 15 min ultrasonic treatment, the maximum soluble chemical oxygen demand (ΔSCOD) in the sludge supernatant after destruction was achieved at 3662.78 ± 239.21 mg/L, with a disintegration degree of 28.61 ± 2.14%, sludge reduction rate of 19.47 ± 0.82%, and the change of mixture sludge concentration (ΔMLSS) of 3.31 ± 0.06 g/L. Meanwhile, the release of nitrogen and phosphorus were greatly improved. Under the optimal conditions, the release of total nitrogen (TN), ammonia nitrogen (NH_3-N) and total phosphorus (TP) were 282.30 ± 24.06 mg/L, 25.68 ± 2.09 mg/L, and 105.69 ± 7.84 mg/L, respectively. The current work had provided solid evidence showing the addition of hydrogen peroxide can effectively strengthen the treatment effects of ultrasound on sludge destruction.

Keywords: sludge destruction; sludge reduction; ultrasound; hydrogen peroxide; lysis

Citation: Yuan, D.; Zhou, X.; Jin, W.; Han, W.; Chi, H.; Ding, W.; Huang, Y.; He, Z.; Gao, S.; Wang, Q. Effects of the Combined Utilization of Ultrasonic/Hydrogen Peroxide on Excess Sludge Destruction. *Water* **2021**, *13*, 266. https://doi.org/10.3390/w13030266

Received: 12 December 2020
Accepted: 18 January 2021
Published: 22 January 2021

1. Introduction

Biological methods are often used to deal with water pollution problems [1,2]. As the mainstream biological method, the activated sludge method is often used in the treatment of urban wastewater because of its low price, good treatment effect, and short residence time [3]. However, as a by-product produced in the activated sludge process, excess sludge has become a difficulty in the downstream treatment process in most wastewater treatment plants (WWTP), owing to its large quantity, high water content, richness of organic components, pathogens, and heavy metals [4]. A number of studies have shown that the investment and operating costs for the treatment and disposal of excess sludge are as high as 25% to 65% of the investment and operating costs for the entire WWTP [5]. Thereby, the recycling utilization [6] and reduction of excess sludge [7,8] has been a research hotspot over a long time, yet it is difficult for the conventional sludge treatment method to achieve sludge utilization and reduction simultaneously [9,10].

In most WWTPs, the denitrification efficiency is often reduced due to insufficient organic matter. Commonly used carbon sources such as glucose and sodium acetate can increase the carbon–nitrogen ratio of the influent, thereby achieving more efficient nitrogen removal, but long-term dosing causes increased operating costs. Using excess sludge as a low-cost carbon source to improve denitrification efficiency for WWTP is an attractive option for researchers recently, as releasing its own organic matter could also facilitate the reduction of excess sludge. A number of studies have focused on sludge lysis technology, such as ozone [11], Fenton [12], acid-base [13,14], ultrasound [15], microwave [16,17], and mechanical [18]. Among those sludge lysis methods, ultrasonic pretreatment has been widely studied, as it is usually regarded as a simple method for operation, with wide application range, high efficiency, none secondary pollution [19] and can be combined with other processes [20,21].

A reduction rate of 60–70% residual sludge solids was found by Wu et al. [22] when ultrasonic specific energy was 1.0–1.5 kJ/mL. He et al. [23] reported a sludge reduction rate of 67.6%, energy efficiency at 0.012 kgTS/kWh, and sludge destruction rate of 15% after a 15 min ultrasonic treatment process. Ultrasonic treatment of excess sludge was more efficient and green than many other pretreatment methodologies, and the combined addition of oxidants could be employed to further enhance sludge destruction.

H_2O_2 is a low-cost strong oxidant, which produces clean oxidation product-water [24]. The combination of H_2O_2 and ultrasound can strengthen the destruction of sludge and improve the biodegradability of the product. This work compares the effects of ultrasonic and ultrasonic/H_2O_2 on the release of sludge organic matter and sludge reduction efficiency, optimizes the associated parameters, and determines working conditions to provide a theoretical basis for the application of the system in sludge treatment.

2. Materials and Methods

2.1. Excess Sludge Source

The sludge used in the experiments was obtained from the thickening tank of a municipal wastewater treatment plant (WWTP) in Shenzhen, China. After it was retrieved, the sludge was stored in a refrigerator at 4 °C for less than 72 h. In the experiment, the sludge and its supernatant were proportioned to the required concentration. The basic properties of thickened sludge are showed in Table 1.

Table 1. Properties of the excess sludge.

Properties	Range
pH	6.5–6.9
Water content (%)	97.5–98
MLSS (g/L)	16.5–20.2
MLVSS (g/L)	8.64–9.74
MLVSS/MLSS	0.45–0.50

2.2. Ultrasonic/H_2O_2 Destruction Experiment

The experiment was conducted in 1 L open glass beakers (400 mL sludge) which were half-immersed in an ultrasonic generator (JP-100PLUS), as shown in Figure A1. The experiment was carried out under room temperature (23~25 °C) and the energy density for ultrasonic treatment was 0.2 w/mL with a treatment frequency of 40 kHz. The effects of different initial pH (3.0, 5.0, 7.0, 9.0, 11.0), H_2O_2 dosage (0, 0.1, 0.5, 1.0, 2.0, 5.0 mmol/L), initial sludge concentration (8, 11, 14, 17, 20 g/L), and ultrasonic treatment time (5, 10, 15, 20, 30 min) on sludge destruction were examined by single-factor experiments using sequential batch tests. ΔSCOD, lysis rate, ΔMLSS, and sludge reduction were used to evaluate the degree of sludge destruction. The release effects of NH_3-N, TN, TP were investigated. To adjust pH, NaOH solution (4 mol/L) and HCl solution (4 mol/L) were applied. The experiment was repeated twice. To prevent an excessive temperature during

the treatment, cooling water from the ultrasonic generator was exchanged after each trial of the ultrasonic treatment.

2.3. Analysis

2.3.1. Evaluation of the Destruction Effect of Sludge

The destruction effect of sludge is measured by disintegration degree, which is calculated by Formula (1):

$$\mathrm{DD}_{SCOD} = \frac{SCOD_t - SCOD_0}{TCOD - SCOD_0} \times 100\% \quad (1)$$

where DD_{SCOD} is the disintegration degree of the excess sludge (%); $TCOD$ is total chemical oxidation demand of the original sludge (mg/L); $SCOD_0$ is the dissolved chemical oxygen demand in the sludge supernatant before treatment (mg/L); $SCOD_{\mathrm{t}}$ is the dissolved chemical oxygen demand in the sludge supernatant after treatment (mg/L).

2.3.2. Evaluation of Sludge Reduction

The sludge reduction is evaluated by the sludge reduction rate, as shown in Formula (2).

$$\mathrm{SS}_{Reduce} = \frac{MLSS_0 - MLSS_t}{MLSS_0} \times 100\% \quad (2)$$

where SS_{Reduce} represents the sludge reduction rate (%); $MLSS_0$ is the suspended solids concentration of raw sludge mixture (g/L); $MLSS_t$ is the suspended solids concentration of the sludge after treatment (g/L).

2.3.3. The Analysis of Other Indexes

The analysis of conventional indicators such as NH_3-N, TN, COD, TP, mixed liquid suspended solids (MLSS), mixed liquid volatile suspended solids (MLVSS), were all carried out by national standard methods [25].

2.3.4. Statistical Analysis

Student's *t*-tests were conducted to analyze the significant differences ($p < 0.05$) between parallel samples.

3. Results and Discussion

3.1. The Effect of Initial pH on Sludge Destruction

3.1.1. The Effect of Initial pH on the Release of N and P

The effect of initial pH on the release of nitrogen and phosphorus in the system is shown in Figure A2a. The effect of improving the release of NH_3-N under acidic conditions was not significant. The release of NH_3-N and TN increased with the increase of pH. Under alkaline conditions, the lysis efficiency of sludge was significantly improved. The results showed that the increase of pH could significantly improve the dissolved cells of sludge ($p < 0.05$). Compared with the release of TN at pH 9.0, the TN release at pH 11 under the ultrasonic/H_2O_2 treatment increased from 52.27 ± 9.00 mg/L to 137.53 ± 8.06 mg/L, where the solubilization effect had been elevated by 1.63 times, meaning that OH^- could be involved in the sludge destruction process. It was found that destruction effect of sludge was improved after adding H_2O_2. Especially under neutral and acidic conditions, the improvement was more significant. This was probably due to the fact that redox potential of H_2O_2 under alkaline conditions cannot effectively exert its strong oxidizing properties [26]. In addition, H_2O_2 under alkaline conditions mainly exists in the form of ions, and the dissolved organic matter can be directly oxidized [27,28]. From Figure A2b, it was found that adding H_2O_2 under neutral and acidic conditions cannot effectively enhance the release of phosphorus; but on the contrary, it might inhibit the effect. The reason was probably that, under acidic and neutral conditions, the H_2O_2 molecule attached to the surface of the sludge would decompose into oxygen and water [29], which could

thereby enhance the aerobic state of the sludge, and subsequently strengthen the adsorption of phosphorus.

3.1.2. Effect of Initial pH on the Release of Organic Matter

The release of organic matter can directly characterize the degree of destruction to the sludge, and it can also be used to determine whether the supernatant of the sludge can be used as a carbon source. The effect of initial pH on the release of organic matter in the system is shown in Figure A2c. Under acidic conditions, the lysis rate of sludge and the eluted SCOD of the sludge were similar between the groups (with and without adding H_2O_2). While at pH 9.0, adding H_2O_2 could increase ΔSCOD from 482.0 ± 6.0 mg/L to 662.0 ± 22.0 mg/L, which was about 37% elevation ($p < 0.05$). At pH 11.0, adding H_2O_2 could enhance the disintegration degree by 1.85% and SCOD by 168 mg/L, respectively. Although there was a certain increase in the release of organic matter, the increase at this concentration is not significant ($p > 0.05$). This might be owing to the reason that the sludge was easier to dissolve under alkaline conditions, and the originally loose sludge flocs could further decompose by the oxidation of H_2O_2. While initial pH was larger than 11.0, most of the H_2O_2 exists as HO_2^-, which would weaken the mineralization of COD [30]. However, under acidic conditions, the redox potential of H_2O_2 was higher, which could oxidize and mineralize the SCOD, thereby reducing the concentration of organic matter and resulting in a more significant lysis rate.

3.1.3. Effects of Initial pH on the Reduction of Sludge

During cell lysis, the organic matter originally presenting in the sludge flocs will gradually be released into the liquid phase, resulting in the reduction of MLSS and the quantity sludge. ΔMLSS and sludge reduction rate can be indicators that reflect the effect of the system on sludge reduction. The influence of initial pH on the system's sludge reduction is shown in Figure A2d. Sludge is composed by organic matter and inorganic matter, and the reduction of MLSS is mainly caused by the removal of organic matter.

In acidic conditions, ΔMLSS and sludge reduction rate showed a decreasing trend along with the increase of pH, while in alkaline conditions, ΔMLSS and sludge reduction rate increased along with the increase of pH. It can be seen from Figure A2d that the sludge reduction rate was the lowest at pH 7.0, which was only 2.81% after adding H_2O_2. At pH 11.0, adding H_2O_2 enhanced the sludge reduction rate from 12.64 ± 1.28% to 14.16 ± 0.56% and ΔMLSS from 1.73 ± 0.18 g/L to 1.93 ± 0.08 g/L ($p < 0.05$). The reason for the phenomenon is that the sludge is soaked in the alkaline environment, the organic matter in it will be looser and more likely to be attacked by ultrasonic cavitation through mechanical and chemical effects [31]. Studies have shown that ultrasound and alkali can quickly improve the solubilization of sludge, which was around 2.8 times that of alkali treatment alone [32]. However, it is worth noting that, at pH 3.0, the sludge reduction rate before and after adding H_2O_2 increased, which was inconsistent with the experimental results of lysis rate. This was due to the strong oxidizing properties of H_2O_2 at low pH [33]. In addition, hydrogen peroxide is relatively stable under acidic conditions, which can slowly release oxygen, enhance the cavitation effect of ultrasound, and effectively mineralize the organic matter in sludge [34]. Considering the lysing effect and reduction effect of sludge, pH 11.0 was selected as its optimal working condition.

3.2. The Effect of H_2O_2 Addition on Sludge Destruction

3.2.1. The Effect of H_2O_2 Addition on the Release of N and P

Figure A3a,b shows the effect of H_2O_2 addition on the release of nitrogen and phosphorus. It can be seen from Figure A3a that the release of TN was the highest when H_2O_2 addition was 0.5 mmol/L, with a release amount of 162.25 ± 23.3 mg/L. The hourly release of NH_3-N was 33.8 ± 1.77 mg/L when H_2O_2 addition was 2 mmol/L. The reason for the inconsistency of the optimal release effects of NH_3-N and TN was probably that the targets of H_2O_2 oxidation were different. At 0-0.5 mmol/L, the release of TN increased rapidly,

which was 23.1% ($p < 0.05$) higher than the release effect without adding H_2O_2, indicating that the main function of H_2O_2 at this time was to oxidize the sludge flocs and dissolve the sludge flocs. However, in the process of 0.5–2 mmol/L, the release efficiency of TN decreases. This was because high-level H_2O_2 could decompose itself, and the generated bubbles that might hinder the effect of ultrasonic cavitation. Non-vacuum cavitation bubbles are usually difficult to be broken; even if they can be broken by ultrasonic action, the energy produced would be much lower than that of vacuum cavitation bubbles [35]. Furthermore, the oxygen decomposed by H_2O_2 participates in the sonolysis could form ·OOH [36], and its existence would decrease the ·OH produced by ultrasound and H_2O_2. In addition, as there was more organic matter in the liquid phase that could react with H_2O_2, in particular, organic matter containing amino groups reacts with H_2O_2 to gradually release NH_4^+ during the oxidation process, thereby increasing the concentration of NH_3-N in the solution. In Figure A3b, the release effect of TP was maximum when the dosage of H_2O_2 was 0.5 mmol/L, which increased from 56.23 ± 0.1 mg/L to 63.78 ± 0.4 mg/L ($p < 0.05$) compared with none H_2O_2 addition. Although the release of total phosphorus had increased significantly, compared with the total phosphorus content of the sludge, the released proportion was still a much lower value.

3.2.2. The Effect of H_2O_2 Addition on the Release of Organic Matter

It can be seen from Figure A3c that when the addition of H_2O_2 was 0.5 mmol/L, the release of SCOD from sludge was significantly enhanced. Compared with none H_2O_2 addition, SCOD was increased by 385 mg/L, and the disintegration degree increased by 21.22% ($p < 0.05$), indicating that at the concentration from 0 to 0.5 mmol/L H_2O_2 addition could enhance lysis effect. However, H_2O_2 has a relatively mild effect on the treatment of sludge, which mainly affects the extracellular polymer (EPS) in the sludge floc [37]. When the dosage of H_2O_2 was higher than 0.5 mmol/L, the self-decomposition of H_2O_2 could decrease the sludge lysis. A similar phenomenon was found by Gao et al. [38] while using ultrasonic/H_2O_2 for the removal of bisphenol A. Even the release of SCOD could be enhanced at low-level H_2O_2 addition; the elevation of the release of SCOD was also a low value. A proper H_2O_2 dosing strategy would be undoubtedly essential if the current technology is considered for a subsequent industrial application.

3.2.3. The Effect of H_2O_2 Addition on Sludge Reduction

Under the treatment conditions of pH 11.0 and H_2O_2 dosage of 0.5 mmol/L, the ΔMLSS reached 2.13 ± 0.17 g/L. That means that H_2O_2 at this concentration could better improve the rate of sludge reduction ($p < 0.05$). Combined with the release curve of organic matter in the previous section, it can be found that the lysis efficiency and sludge reduction were not sufficient at H_2O_2 dosage of 5 mmol/L.

There might be two reasons: (1) the oxygen formed from the self-decomposition of H_2O_2 was absorbed by the sludge, which changed the sludge properties so the sludge become not conducive to destruction; (2) the oxygen bubbles from H_2O_2 decomposition could be adsorbed by the surface of sludge, which decreased the ultrasonic mass transfer.

3.3. Effect of Initial Sludge Concentration on Sludge Destruction

3.3.1. Effect of Initial Sludge Concentration on the Release of N and P

The initial sludge concentration could indicate the substrate concentration in the reaction system. The impact of initial sludge concentration on nitrogen and phosphorus release is shown in Figure A4a,b.

In Figure A4a, sludge concentration ranged from of 8 to 17 g/L, while the sludge concentration increased, the destruction gradually increased. The release of TN had been shifted from 64.90 ± 9.07 mg/L to 180.10 ± 5.88 mg/L (177.5% elevation) ($p < 0.05$), with the sludge concentration increased by 112.5%, which indicated that the lysis process would be facilitated at high sludge concentration. According to Figure A4b, it was found that the release of TP was basically consistent with that of TN, reaching maximum when the sludge

concentration was 17 g/L, with a release of TP at 65.73 ± 1.35 mg/L. Some studies have shown that the viscosity of the liquid could enhance the cavitation effect of ultrasound within a certain range, but high liquid viscosity may hinder the ultrasonic cavitation effect [39].

3.3.2. Effect of Initial Sludge Concentration on Organic Matter Release

The organic matter in the reaction system would increase along with the elevation of the initial sludge concentration. Higher organic matter concentration can boost the sludge solubilization efficiency of the ultrasonic/H_2O_2 system. The release of organic matter is displayed in Figure A4c.

It can be seen from Figure A4c that with the increase of sludge concentration, ΔSCOD increased steadily from 945.79 ± 3.69 mg/L to 2830.24 ± 89.06 mg/L ($p < 0.05$), which was nearly twice that of the original level (945.79 ± 3.69 mg/L), indicating that the higher sludge concentration can effectively enhance the ultrasonic/H_2O_2 lysis of sludge. However, when the sludge concentration was 20 g/L, the disintegration degree and SCOD release were slightly decreased compared with that at 17 g/L. This might be due to the elevation of liquid viscosity with the increase of sludge concentration, which would hinder the ultrasonic destruction effect. At the same time, the self-decomposition of H_2O_2 (at high H_2O_2 level) may weaken the oxidation effect of H_2O_2.

3.3.3. Effect of Initial Sludge Concentration on Sludge Reduction

The optimal sludge reduction was obtained when the initial sludge concentration was 14 g/L, and MLSS was reduced by 1.78 ± 0.11 g/L (Figure A4d). However, within the range of 14–20 g/L, both sludge reduction rate and ΔMLSS decreased slightly, which was possibly owing to the incomplete destruction of sludge by ultrasound/H_2O_2. However, at sludge concentration of 17 g/L, although the reduction efficiency decreased, the release of SCOD was significantly higher than that at sludge concentration of 14 g/L. As the main component of extracellular polymer is proteoglycan, at high sludge concentration, the high-level extracellular polymer might protect the cell from being crushed. As a result, the sludge concentration of 17 g/L was selected for the following experiments.

3.4. Effects of Ultrasonic Duration Time on Sludge Destruction

3.4.1. Effects of Ultrasonic Duration Time on the Release of N and P

Ultrasonic time had played an important role in the release of various substances from sludge, and its effect on nitrogen and phosphorus release is shown in Figure A5a,b.

The NH_3-N and TN release appeared to be a gradual increasing trend along with the increase of ultrasonic time. With the increase of ultrasonic time, the cavitation and thermal effects produced by ultrasound could improve the lysis of sludge and cause greater destruction. At 15 min, after adding H_2O_2, the release of TN increased from 257.79 ± 19.36 mg/L to 282.30 ± 24.06 mg/L, which was nearly 10% ($p < 0.05$), indicating that the presence of H_2O_2 could significantly promote the treatment performance of ultrasound. It can be seen from Figure A5b that the release rate of TP was relatively higher in the period of 0–15 min, which increased from 57.89 ± 2.40 mg/L to 105.69 ± 7.84 mg/L ($p < 0.05$). That indicates that the sludge was rapidly decomposed under the action of ultrasonic for 0–15min. Some studies have shown that the ultrasonic destruction of sludge can be divided into fast stage and slow stage. The fast stage is mainly due to the reduction of sludge particle size through destruction, and the extracellular polymer wrapped around the cells is rapidly dissolved in the liquid phase. The slow stage is mainly due to the reduction of easily soluble and decomposable substances in the sludge [40]. In this stage, ultrasound may disrupt exposed cells. Compared with the previous stage, the efficiency of the current stage is relatively slow.

3.4.2. Effect of Ultrasonic Time on Organic Matter Release

The effect of ultrasonic time on the release of organic compounds is shown in Figure A5c. With the increase of ultrasound time, more organic matter was released. The effect of ultrasound can effectively reduce the solid concentration of sludge, and the extracellular polymer and cell contents can be effectively dissolved out [41]. It can be seen that after adding H_2O_2, the sludge destruction was enhanced. When the reaction time was 15 min, adding H_2O_2 increased ΔSCOD from 3087.71 ± 223.58 mg/L to 3662.78 ± 239.21 mg/L, which was enhanced by 18.62% ($p < 0.05$). The release amount was similar to the effect of applying ultrasonic alone for 20 min, indicating that the addition of H_2O_2 can effectively improve the lysis efficiency of sludge and shorten the ultrasonic time. Active oxygen existed in H_2O_2 is the main factor that decomposes organic matter and promotes sludge compatibilization, where ·OH could play a pivotal role in the process [42]. Meanwhile, more ·OH can be produced under ultrasound, which would further enhance the solubilization of ultrasound on sludge.

3.4.3. Influence of Ultrasonic Time on Sludge Reduction

The effect of ultrasonic time on sludge reduction can be seen in Figure A5d, the improvement on sludge reduction reached maximum at 15 min. The sludge reduction rate increased from 16.16 ± 0.83% before adding H_2O_2 to 19.47 ± 0.82% after adding H_2O_2, while ΔMLSS was increased by 0.562 g/L ($p < 0.05$). The results indicated that there was more organic matter being dissolved, and ultrasonic sludge lysis had been significantly improved by H_2O_2.

3.5. Economic Analysis

An economic analysis was conducted to evaluate the prospect of the ultrasonic/H_2O_2 sludge pretreatment technology (Table 2). As shown in Table 2, a process coupling three stages, "the ultrasonic/H_2O_2 pretreatment", "sludge drying and incineration", and "recovering potential valuable by-products from the sludge supernatant", was considered.

In the pretreatment stage, the costs were mainly composed of the energy consumption of ultrasound and the chemical dosage (NaOH and H_2O_2), which was $259.90/ton DS in total. Considering a 20% sludge reduction by the ultrasonic/H_2O_2 treatment, the costs of the second stage drying and incineration could be reduced by around 20%, which was $311.20/ton DS.

The sludge supernatant obtained after 5–7 days of anaerobic acidification basically meets the preparation conditions of $MgNH_4PO_4{\cdot}6H_2O$, and more than 50% of TN could be converted to NH_3-N without adjusting the pH value. If $MgCL_2$ is used as the magnesium source, at least 90% of P could be recovered [43], with the $MgNH_4PO_4{\cdot}6H_2O$ recovery quantity of around 44.22 kg/ton DS. The organic matter has gradually decomposed into small-molecule organic matter, which is more valuable. Due to the low nitrogen removal efficiency of low C/N sewage, organic matter such as glucose and sodium acetate were usually used as additional carbon sources to enhance the removal effect of TN [44]. Volatile fatty acids produced by acidification of organic matter in sludge can also be used as alternative carbon sources [45]. The price of glucose is $278/ton COD (calculated by COD), the price of sodium acetate trihydrate is $564/ton COD (calculated by COD) [46], and the average value is $421/ton COD. After calculation, the final economic cost is $345.76/ton DS, which is slightly lower than the operating cost of only the cost of conventional drying and incineration ($389/ton DS) [47].

Table 2. Economic analysis of ultrasonic/H_2O_2 sludge pretreatment coupled with downstream by-products recovery.

Process	Item	Material Consumption	Market Average Price	Estimated Costs
I: Ultrasonic/H_2O_2 pretreatment	NaOH	0.8 kg/m^3	\$510/ton	\$24.00/ton DS
	H_2O_2 (30%)	0.5 mol/m^3	\$186/ton	\$0.62/ton DS
	Ultrasound	0.20 kW/L	\$0.08/kWh	\$235.28/ton DS
	Total			\$259.90/ton DS
II: Conventional drying and incineration	Total		\$389/ton DS [47]	\$311.20/ton DS
III: By-products recovery	$MgCl_2$	22.91 kg/ton DS	\$541/ton	\$12.39/ton DS
	COD	215.44 kg/ton DS	\$421/ton COD	\$−90.70/ton DS *
	$MgNH_4PO_4 \cdot 6H_2O$	44.22 kg/ton DS	\$3325/ton	\$−147.03/ton DS *
	Total			\$−237.73/ton DS *
I + II + III	Total			\$345.76/ton DS

*: Minus value represents that the corresponding item would reduce the cost.

4. Conclusions

(1) pH has an important impact on sludge destruction. Alkaline conditions can effectively promote the solubilization of internal substances in sludge, making the sludge structure loose, and make it easier for the oxidation of H_2O_2. In terms of sludge reduction, alkaline condition betters acid condition, while acid condition outcompetes neutral condition.

(2) Excess H_2O_2 cannot further enhance the sludge lysis effect; on the contrary, it will play an inhibitory role on sludge destruction. H_2O_2 can be used as the scavenger of ·OH to eliminate the ·OH produced by ultrasound/H_2O_2, and the decomposed oxygen will hinder the cavitation effect of ultrasound.

(3) When the initial pH is 11.0, the concentration of H_2O_2 is 0.5 mmol/L, the initial sludge concentration is 17 g /L, and the ultrasonic time is 15 min long, the ΔSCOD in the supernatant after the sludge destruction can reach 3662.78 ± 239.21 mg/L, the disintegration degree is as high as 28.61 ± 2.14%, the sludge reduction rate is 19.47 ± 0.82%, and the ΔMLSS is reduced by 3.31 ± 0.06 g/L. The release of TN, NH_3-N, and TP were 282.30 ± 24.06 mg/L, 25.68 ± 2.09 mg/L, and 105.69 ± 7.84 mg/L, respectively.

Author Contributions: Data curation, H.C., Y.H., Z.H., S.G., and Q.W.; formal analysis, H.C., W.D., and Q.W.; funding acquisition, W.J. and X.Z.; investigation, W.H. and Z.H.; methodology, W.D. and Q.W.; project administration, W.J., X.Z., and Q.W.; resources, Q.W.; software, Q.W.; supervision, W.J. and W.H.; validation, S.G.; writing—original draft, D.Y.; writing—review and editing, W.H. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Shenzhen Science and Technology Innovation Project (KJYY20171011144235970), the National Natural Science Foundation of China (No. 51878215), Natural Science Foundation of Guangdong Province, China (2018A030313185), Natural Science Foundation of Guangdong Province, China (2019A1515011740).

Informed Consent Statement: Informed consent was obtained from all subjects involved in the study.

Data Availability Statement: Data available in a publicly accessible repository.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

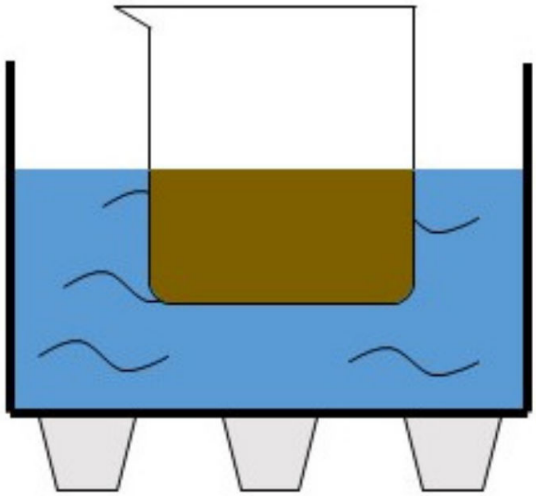

Figure A1. Schematic of the experimental set-up.

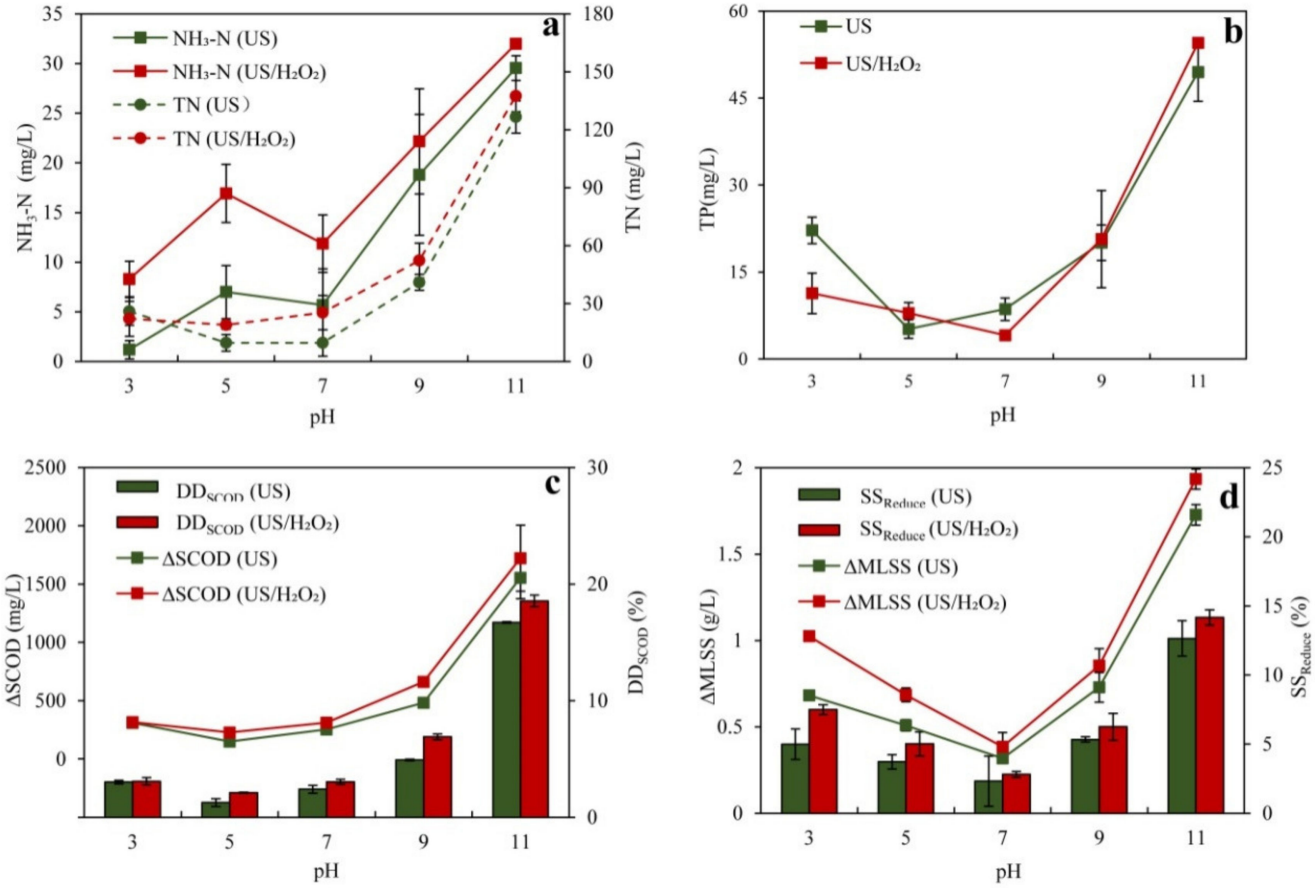

Figure A2. Effect of different initial pH on (**a**) NH_3-N and TN, (**b**) TP, (**c**) ΔSCOD and DD_{SCOD}, and (**d**) ΔMLSS and SS_{Reduce}. (Error bars represent the standard deviation, N = 2).

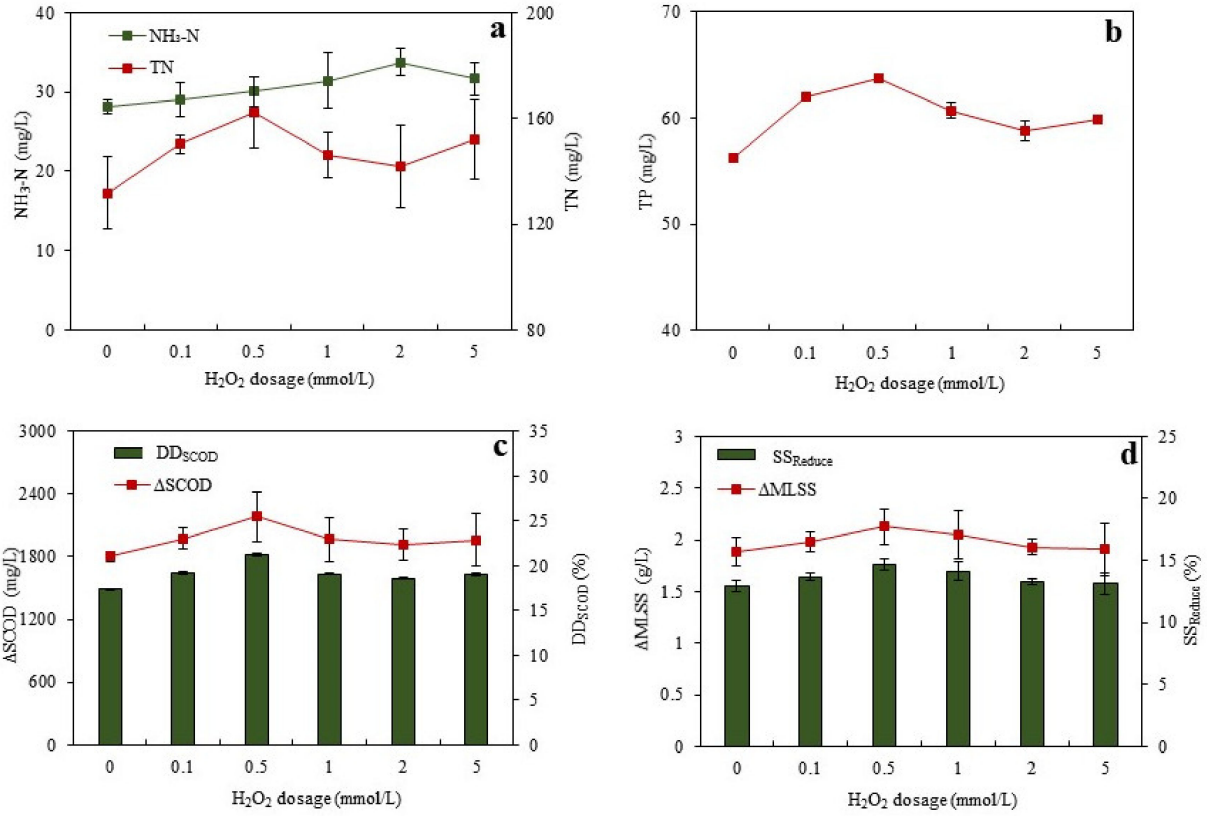

Figure A3. Effect of different H_2O_2 dosages on (**a**) NH_3-N and TN, (**b**) TP, (**c**) ΔSCOD and DD_{SCOD}, and (**d**) ΔMLSS and SS_{Reduce}. (Error bars represent the standard deviation, N = 2).

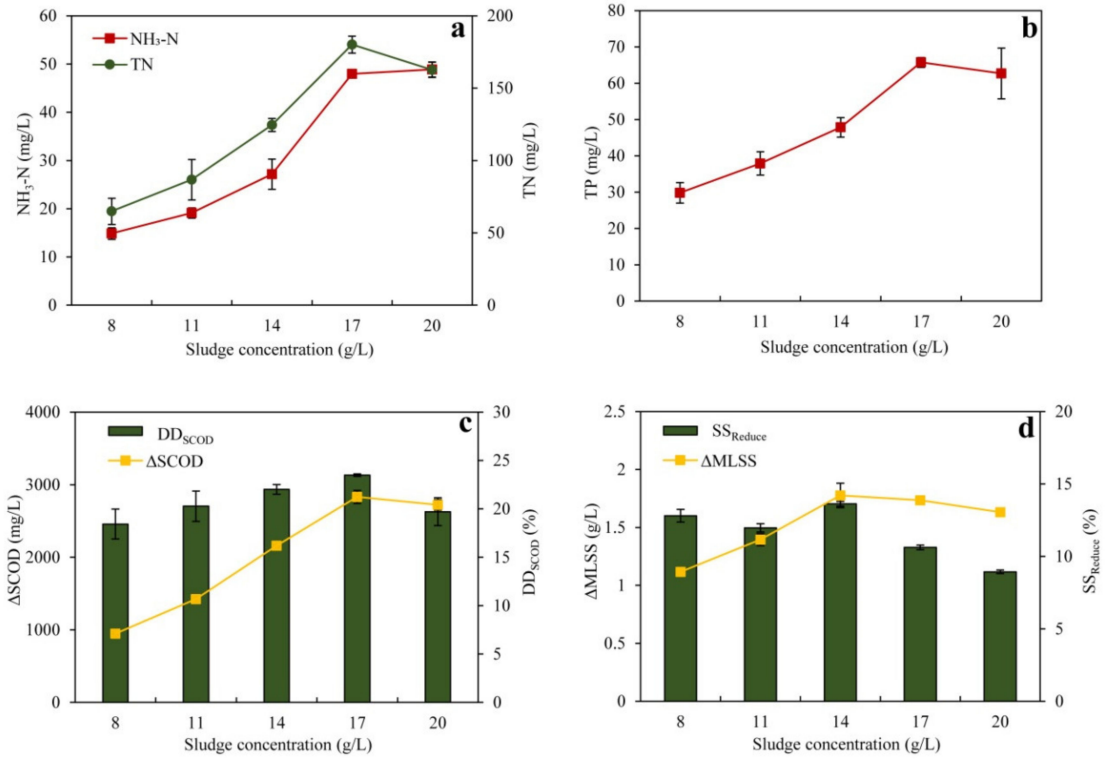

Figure A4. Effect of different initial sludge concentrations on (**a**) NH_3-N and TN, (**b**) TP, (**c**) ΔSCOD and DD_{SCOD}, and (**d**) ΔMLSS and SS_{Reduce}. (Error bars represent the standard deviation, N = 2).

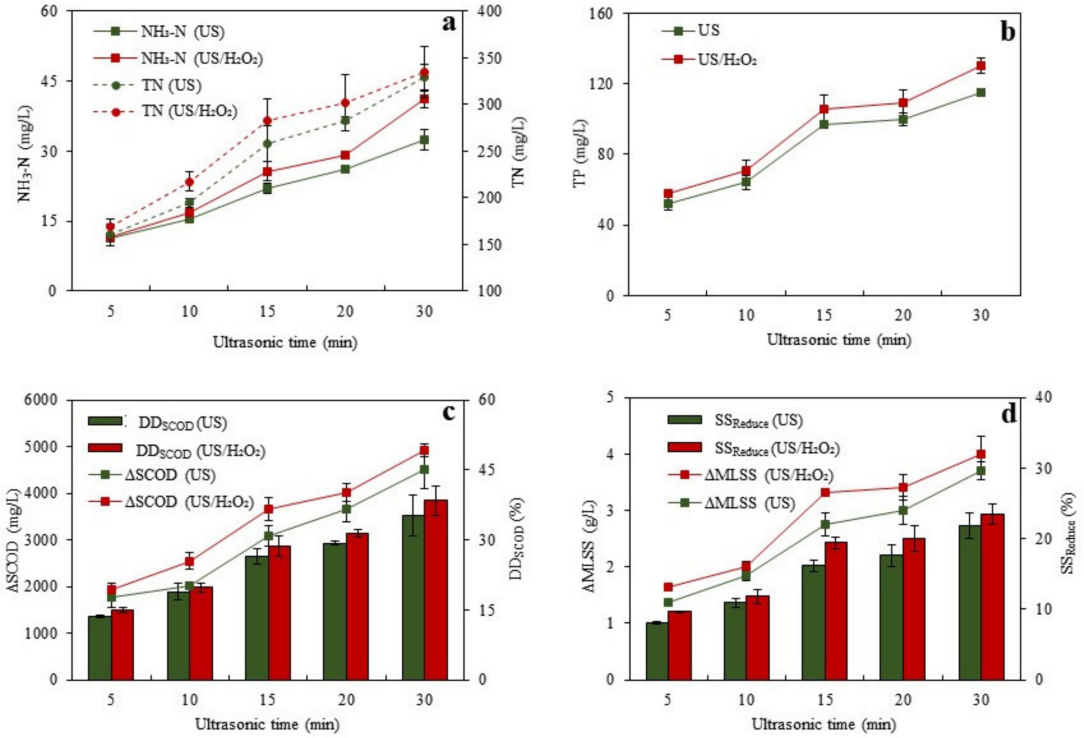

Figure A5. Effect of different ultrasonic times on (**a**) NH_3-N and TN, (**b**) TP, (**c**) ΔSCOD and DD_{SCOD}, and (**d**) ΔMLSS and SS_{Reduce}. (Error bars represent the standard deviation, N = 2).

References

1. Che, L.; Jin, W.; Zhou, X.; Cao, C.; Han, W.; Qin, C.; Tu, R.; Chen, Y.; Feng, X.; Wang, Q. Biological Reduction of Organic Matter in Buji River Sediment (Shenzhen, China) with Artificial Oxygenation. *Water* **2020**, *12*, 3592. [CrossRef]
2. Han, W.; Mao, Y.; Wei, Y.; Shang, P.; Zhou, X. Bioremediation of Aquaculture Wastewater with Algal-Bacterial Biofilm Combined with the Production of Selenium Rich Biofertilizer. *Water* **2020**, *12*, 2071. [CrossRef]
3. Ji, B.; Zhang, M.; Gu, J.; Ma, Y.; Liu, Y. A self-sustaining synergetic microalgal-bacterial granular sludge process towards energy-efficient and environmentally sustainable municipal wastewater treatment. *Water Res.* **2020**, *179*, 115884. [CrossRef]
4. Cheng, J.; Lu, X.; Kato, H.; Zhao, Y.; Cheng, J. Overview of pretreatment strategies for enhancing sewage sludge disintegration and subsequent anaerobic digestion: Current advances, full-scale application and future perspectives. *Renew. Sustain. Energy Rev.* **2017**, *69*, 559–577.
5. Egemen, E.; Corpening, J.; Nirmalakhandan, N. Evaluation of an ozonation system for reduced waste sludge generation. *Water Sci. Technol.* **2001**, *44*, 445–452. [CrossRef] [PubMed]
6. Ding, A.; Zhao, Y.; Ngo, H.H.; Bai, L.; Li, G.; Liang, H.; Ren, N.; Nan, J. Metabolic uncoupler, 3,3′,4′,5-tetrachlorosalicylanilide addition for sludge reduction and fouling control in a gravity-driven membrane bioreactor. *Front. Environ. Sci. Eng.* **2020**, *14*, 1–12. [CrossRef]
7. Rahmani, A.R.; Mousavi-Tashar, A.; Masoumi, Z.; Azarian, G. Integrated advanced oxidation process, sono-Fenton treatment, for mineralization and volume reduction of activated sludge. *Ecotoxicol. Environ. Saf.* **2019**, *168*, 120–126. [CrossRef]
8. Feng, X.-C.; Guo, W.; Yang, S.-S.; Zheng, H.-S.; Du, J.-S.; Wu, Q.-L.; Ren, N.-Q. Possible causes of excess sludge reduction adding metabolic uncoupler, 3,3′,4′,5-tetrachlorosalicylanilide (TCS), in sequence batch reactors. *Bioresour. Technol.* **2014**, *173*, 96–103. [CrossRef]
9. Song, U.; Lee, E.J. Environmental and economical assessment of sewage sludge compost application on soil and plants in a landfill. *Resour. Conserv. Recycl.* **2010**, *54*, 1109–1116. [CrossRef]
10. Sanger, M.J.; Werther, J.; Ogada, T. NO_x and N_2O emission characteristics from fluidised bed combustion of semi-dried municipal sewage sludge. *Fuel* **2001**, *80*, 167–177. [CrossRef]
11. Chiavola, A.; D'Amato, E.; Boni, M.R. Effects of low-dosage ozone pre-treatment on the anaerobic digestion of secondary and mixed sludge. *Environ. Sci. Pollut. Res.* **2019**, *26*, 35957–35967. [CrossRef] [PubMed]
12. Tokumura, M.; Katoh, H.; Katoh, T.; Znad, H.; Kawase, Y. Solubilization of excess sludge in activated sludge process using the solar photo-Fenton reaction. *J. Hazard. Mater.* **2009**, *162*, 1390–1396. [CrossRef] [PubMed]

13. Zheng, X.; Jiang, Z.; Ying, Z.; Ye, Y.; Chen, W.; Wang, B.; Dou, B. Migration and Transformation of Phosphorus during Hydrothermal Carbonization of Sewage Sludge: Focusing on the Role of pH and Calcium Additive and the Transformation Mechanism. *ACS Sustain. Chem. Eng.* **2020**, *8*, 7806–7814. [CrossRef]
14. Garg, A.; Stensel, H.D.; Bucher, B.; Sukapanpotharam, P.; Winkler, M.K. Effect of waste activated sludge pretreatment methods to mitigate Gordonia foaming potential in anaerobic digestion. *Water Environ. J.* **2020**, *0*, 1–9. [CrossRef]
15. Riau, V.; De La Rubia, M.A.; Pérez, M. Upgrading the temperature-phased anaerobic digestion of waste activated sludge by ultrasonic pretreatment. *Chem. Eng. J.* **2015**, *259*, 672–681. [CrossRef]
16. Wang, Y.; Xiao, Q.; Liu, J.; Yan, H.; Wei, Y. Pilot-scale study of sludge pretreatment by microwave and sludge reduction based on lysis–cryptic growth. *Bioresour. Technol.* **2015**, *190*, 140–147. [CrossRef]
17. Tian, Y.; Zuo, W.; Ren, Z.; Chen, D. Estimation of a novel method to produce bio-oil from sewage sludge by microwave pyrolysis with the consideration of efficiency and safety. *Bioresour. Technol.* **2011**, *102*, 2053–2061. [CrossRef]
18. Baier, U.; Schmidheiny, P. Enhanced anaerobic degradation of mechanically disintegrated sludge. *Water Sci. Technol.* **1997**, *36*, 137–143. [CrossRef]
19. Tyagi, V.K.; Lo, S.-L.; Appels, L.; Dewil, R. Ultrasonic Treatment of Waste Sludge: A Review on Mechanisms and Applications. *Crit. Rev. Environ. Sci. Technol.* **2014**, *44*, 1220–1288. [CrossRef]
20. Siddique, N.I.; Munaim, M.S.A.; Wahid, Z.B.A. The combined effect of ultrasonic and microwave pre-treatment on bio-methane generation from co-digestion of petrochemical wastewater. *J. Clean. Prod.* **2017**, *145*, 303–309. [CrossRef]
21. Packyam, G.S.; Kavitha, S.; Kumar, S.A.; Kaliappan, S.; Yeom, I.T.; Banu, J.R. Effect of sonically induced deflocculation on the efficiency of ozone mediated partial sludge disintegration for improved production of biogas. *Ultrason. Sonochem.* **2015**, *26*, 241–248. [CrossRef] [PubMed]
22. Wu, S.; Zheng, M.; Dong, Q.; Liu, Y.; Wang, C. Evaluating the excess sludge reduction in activated sludge system with ultrasonic treatment. *Water Sci. Technol.* **2018**, *77*, 2341–2347. [CrossRef] [PubMed]
23. He, J.; Wan, T.; Zhang, G.; Yang, J. Ultrasonic reduction of excess sludge from activated sludge system: Energy efficiency improvement via operation optimization. *Ultrason. Sonochem.* **2011**, *18*, 99–103. [CrossRef] [PubMed]
24. Liu, X.; Wang, C.A.; Zhu, T.; Lv, Q.; Che, D. Simultaneous removal of SO_2 and NO_x with (OH)-O-center dot from the catalytic decomposition of H_2O_2 over Fe-Mo mixed oxides. *J. Hazard. Mater.* **2021**, *404*, 123936. [CrossRef] [PubMed]
25. Nepa, C. *Water and Wastewater Monitoring Methods*, 4th ed.; Chinese Environmental Science Publishing House: Beijing, China, 2012.
26. Wang, J.; Wang, X.; Guo, P.; Yu, J. Degradation of reactive brilliant red K-2BP in aqueous solution using swirling jet-induced cavitation combined with H_2O_2. *Ultrason. Sonochem.* **2011**, *18*, 494–500. [CrossRef]
27. Zeronian, S.H.; Inglesby, M.K. Bleaching of cellulose by hydrogen peroxide. *Cellulose* **1995**, *2*, 265–272. [CrossRef]
28. Fang, J.M.; Sun, R.C.; Tomkinson, J. Isolation and characterization of hemicelluloses and cellulose from rye straw by alkaline peroxide extraction. *Cellulose* **2000**, *7*, 87–107. [CrossRef]
29. Hartmann, J.; Bartels, P.; Mau, U.; Witter, M.; Tümpling, W.; Hofmann, J.; Nietzschmann, E. Degradation of the drug diclofenac in water by sonolysis in presence of catalysts. *Chemosphere* **2008**, *70*, 453–461. [CrossRef]
30. Katafias, A.; Lipińska, M.; Strutyński, K. Alkaline hydrogen peroxide as a degradation agent of methylene blue—kinetic and mechanistic studies. *React. Kinet. Mech. Catal.* **2010**, *101*, 251–266. [CrossRef]
31. Mancuso, G.; Langone, M.; Andreottola, G.; Bruni, L. Effects of hydrodynamic cavitation, low-level thermal and low-level alkaline pre-treatments on sludge solubilisation. *Ultrason. Sonochem.* **2019**, *59*, 104750. [CrossRef]
32. Bao, H.; Yang, H.; Zhang, H.; Liu, Y.; Su, H.; Shen, M. Improving methane productivity of waste activated sludge by ultrasound and alkali pretreatment in microbial electrolysis cell and anaerobic digestion coupled system. *Environ. Res.* **2020**, *180*, 108863. [CrossRef]
33. Li, L.; Chen, P.; Gloyna, E.F. Generalized kinetic model for wet oxidation of organic compounds. *AIChE J.* **1991**, *37*, 1687–1697. [CrossRef]
34. Lu, X.; Zhao, J.; Wang, Q.; Wang, D.; Xu, H.; Ma, J.; Qiu, W.; Hu, T. Sonolytic degradation of bisphenol S: Effect of dissolved oxygen and peroxydisulfate, oxidation products and acute toxicity. *Water Res.* **2019**, *165*, 114969. [CrossRef] [PubMed]
35. Liu, L.; Yang, Y.; Liu, P.; Tan, W. The influence of air content in water on ultrasonic cavitation field. *Ultrason. Sonochem.* **2014**, *21*, 566–571. [CrossRef] [PubMed]
36. Nikfar, E.; Dehghani, M.H.; Mahvi, A.; Rastkari, N.; Asif, M.; Tyagi, I.; Agarwal, S.; Gupta, V.K. Removal of Bisphenol A from aqueous solutions using ultrasonic waves and hydrogen peroxide. *J. Mol. Liq.* **2016**, *213*, 332–338. [CrossRef]
37. Wei, H.; Tang, Y.; Shoeib, T.; Li, A.; Yang, H. Evaluating the effects of the preoxidation of H_2O_2, NaClO, and $KMnO_4$ and reflocculation on the dewaterability of sewage sludge. *Chemosphere* **2019**, *234*, 942–952. [CrossRef]
38. Zhang, K.; Gao, N.; Deng, Y.; Lin, T.F.; Ma, Y.; Li, L.; Sui, M. Degradation of bisphenol-A using ultrasonic irradiation assisted by low-concentration hydrogen peroxide. *J. Environ. Sci.* **2011**, *23*, 31–36. [CrossRef]
39. Manmi, K.; Wang, Q. Acoustic microbubble dynamics with viscous effects. *Ultrason. Sonochem.* **2017**, *36*, 427–436. [CrossRef]
40. Al Ramahi, M.; Keszthelyi-Szabó, G.; Beszédes, S. Improving biogas production performance of dairy activated sludge via ultrasound disruption prior to microwave disintegration. *Water Sci. Technol.* **2020**, *81*, 1231–1241. [CrossRef]
41. Kavitha, S.; Banu, J.R.; Kumar, G.; Kaliappan, S.; Yeom, I.T. Profitable ultrasonic assisted microwave disintegration of sludge biomass: Modelling of biomethanation and energy parameter analysis. *Bioresour. Technol.* **2018**, *254*, 203–213. [CrossRef]

42. Zhang, A.; Wang, J.; Li, Y. Performance of calcium peroxide for removal of endocrine-disrupting compounds in waste activated sludge and promotion of sludge solubilization. *Water Res.* **2015**, *71*, 125–139. [CrossRef]
43. Shaddel, S.; Grini, T.; Ucar, S.; Azrague, K.; Andreassen, J.-P.; Østerhus, S.W. Struvite crystallization by using raw seawater: Improving economics and environmental footprint while maintaining phosphorus recovery and product quality. *Water Res.* **2020**, *173*, 115572. [CrossRef] [PubMed]
44. Hu, H.; Ma, S.; Zhang, X.; Ren, H. Characteristics of dissolved organic nitrogen in effluent from a biological nitrogen removal process using sludge alkaline fermentation liquid as an external carbon source. *Water Res.* **2020**, *176*, 115741. [CrossRef] [PubMed]
45. Longo, S.; Katsou, E.; Frison, N.; Frison, N.; Renzi, D.; Fatone, F. Recovery of volatile fatty acids from fermentation of sewage sludge in municipal wastewater treatment plants. *Bioresour. Technol.* **2015**, *175*, 436–444. [CrossRef] [PubMed]
46. Xiong, Z.; Zheng, H.; Shang, J.; Jiang, J.; Zhong, Z.; Zhao, R.; Hu, Y. State-of-the art review of adding extra carbon sources to denitrification of wastewater treatment-in Chinese. *J. Civ. Environ. Eng.* **2020**, *2*, 34–36.
47. Hao, X.; Chen, Q.; Li, J. Ultimate Approach to Handle Excess Sludge: Incineration and Drying. *China Water Wastewater.* **2019**, *35*, 35–42.