

Review

Recent Advances in Hydrothermal Oxidation Technology for Sludge Treatment

Hang Yu ^{1,*} , Yuanyuan Liu ¹, Nana Guo ¹, Weiling Piao ², Zonglin Pan ¹, Bin Zhu ¹ , Yimin Zhu ¹, Libo Wu ^{3,4}, Jinling Wan ^{3,4} and Huangzhao Wei ^{2,*}

- ¹ Collaborative Innovation Center for Vessel Pollution Monitoring and Control, Dalian Maritime University, Dalian 116026, China; lyy17838797206@163.com (Y.L.); guonana0921@163.com (N.G.); zonglinpan@dmlu.edu.cn (Z.P.); binzhu@dmlu.edu.cn (B.Z.); ntp@dmlu.edu.cn (Y.Z.)
- ² Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116026, China; piaoweiling@dicp.ac.cn
- ³ Research Center of Supercritical and Subcritical Fluid, Zhejiang University of Technology, Hangzhou 310014, China; libo.wu@sr-water.cn (L.W.); jinling.wan@sr-water.cn (J.W.)
- ⁴ Hangzhou Sunrise Environment Co., Ltd., Hangzhou 310000, China
- * Correspondence: yuhang891@126.com or yuhang@dmlu.edu.cn (H.Y.); whzhdicpwtg@dicp.ac.cn (H.W.); Tel./Fax: +86-411-8472-4357 (H.Y.)

Abstract: With the rapid development of urbanization and the widespread adoption of wastewater treatment facilities, the volume of sludge produced has steadily increased. Hydrothermal oxidation (HTO) technology offers an effective solution for sludge reduction, harmless disposal, and resource recovery, making it a highly promising method for sludge treatment. In recent years, HTO has attracted significant attention due to its efficiency and environmental benefits. This paper provides a detailed explanation of the fundamental principles of HTO in sludge treatment, with a focus on the removal of organic pollutants, nitrogen transformation, and phosphorus recovery. The influence of key operational parameters, such as reaction temperature, time, initial oxygen pressure, and pH, on the performance of HTO treatment is also explored. In addition, the research status of HTO sludge treatment and an example of product recovery after treatment are also discussed. It examines the challenges associated with scaling up HTO for large-scale sludge treatment, along with potential research directions for future work. Special attention is given to the innovation of catalysts, with the goal of achieving self-catalysis in sludge treatment. Moreover, considering that ammonia nitrogen ($\text{NH}_3\text{-N}$) is a major intermediate product in HTO, its removal, as well as the prediction and planning of other unintended products, remains a key issue. Further areas of interest include improving sludge dewatering performance and enhancing the production of valuable single carboxylic acids, which can boost resource recovery efficiency. This paper also highlights the diversification of sludge applications after HTO treatment. By providing insights into future development trends, this review offers valuable references for further research and practical applications. The ultimate goal is to support the development of HTO as a sustainable and efficient solution for sludge treatment, addressing environmental concerns while maximizing resource recovery opportunities.

Keywords: sludge; hydrothermal oxidation technology; principle; influencing factors; optimization scheme; resource utilization



Citation: Yu, H.; Liu, Y.; Guo, N.; Piao, W.; Pan, Z.; Zhu, B.; Zhu, Y.; Wu, L.; Wan, J.; Wei, H. Recent Advances in Hydrothermal Oxidation Technology for Sludge Treatment. *Appl. Sci.* **2024**, *14*, 11827. <https://doi.org/10.3390/app142411827>

Academic Editors: Haoqi Yang, Ganyu Zhu and Jun-Ye Zhang

Received: 18 October 2024

Revised: 9 December 2024

Accepted: 16 December 2024

Published: 18 December 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

With the rapid development of industry, the number of wastewater treatment plants has increased significantly. Currently, the main wastewater treatment methods include biological treatment [1]; adsorption [2]; advanced oxidation processes such as UV/ H_2O_2 , Fenton, and photo-Fenton [3]; UV/ $\text{S}_2\text{O}_8^{2-}$ and UV/ HSO_5^- [4]; plasma degradation processes [5,6]; photocatalysis [7]; coagulation–flocculation [8]; electrochemical treatment [9];

and membrane filtration [10]. Although these methods can effectively treat wastewater, another problem that arises after treatment is the residual sludge. Wastewater contains many suspended solids, and most of these solids form sludge through adsorption or sedimentation. Sludge is the main byproduct of wastewater treatment plants, and its production has been increasing year by year. According to the Ministry of Housing and Urban–Rural Development of China, the sludge produced by urban areas and wastewater treatment facilities exceeded 60 million tons in 2022 (based on an 80% moisture content), showing a rapid growth trend compared to 50 million tons in 2020. It is estimated that by 2025, the sludge discharge will reach 90 million tons. Therefore, sludge treatment and disposal have become the primary potential source of secondary pollution in the wastewater treatment process [11]. Research indicates that most sludge consists of microorganisms, organic and inorganic components, water-soluble substances, proteins, pathogens, polysaccharides, difficult-to-degrade organic pollutants, heavy metals, and salts [12]. Consequently, sludge generally has a high organic content, complex composition, and high moisture and ash content. Improper management of harmful substances in sludge can pose a serious environmental threat.

To effectively manage sludge generated from wastewater treatment plants and other sources, researchers have made considerable efforts and conducted in-depth studies. Currently, there are four main traditional sludge treatment methods, as shown in Table 1: landfilling, aerobic composting, anaerobic digestion, and sludge drying and incineration [13]. The results in the Table 1 clearly show that the frequency of use of sludge treatment methods in China is landfill > anaerobic digestion > dry incineration > aerobic composting; The frequency of use in other developed countries is sorted as follows: anaerobic digestion > dry incineration > aerobic composting > landfill. It can be seen that the domestic method of landfill sludge treatment is still extensive, while foreign countries focus on anaerobic digestion due to environmental restrictions. A summary of the costs and advantages/disadvantages of these methods reveals that landfilling is simple and cost-effective, making it widely used in sludge management. However, it occupies substantial land and poses risks of leaching toxic substances due to high moisture content and heavy metal concentrations, potentially contaminating soil and groundwater. Biochemical techniques like anaerobic digestion and aerobic composting exhibit selectivity toward harmful substances but have limited applicability. On the other hand, drying and incineration face constraints due to lengthy processes and high costs, and they may generate secondary pollutants like dioxins [13–15]. In summary, traditional sludge treatment methods face multiple challenges, including land use, high costs, and the potential for secondary pollution.

Table 1. Comparison of technical investment, operating cost, advantages and disadvantages, and development trends of sludge treatment at this stage.

Treatment Method	Investment, Operating COST	Advantages	Disadvantages	Development Trend	
				China	Other Developed Countries
Landfilling	Low, Low	Low treatment cost, simple operation	Occupies large land area, potential groundwater contamination, not sustainable in the long term	Usage is high, declining in recent years, but still common (small urban and rural)	Restricted by environmental laws, the use of the European Union and other countries has gradually declined
Aerobic Composting	Medium, Medium	Enables resource recovery, produces fertilizers	Requires large space, long treatment cycle, specific requirements for sludge properties	Mostly used in urban sewage treatment plants	It is one of the main treatment methods used by sewage treatment plants in developed countries such as Europe

Table 1. Cont.

Treatment Method	Investment, Operating COST	Advantages	Disadvantages	Development Trend	
				China	Other Developed Countries
Anaerobic Digestion	High, Medium	Generates biogas as energy, reduces volume	High investment cost, requires rigorous management, specific requirements for sludge solid content	Mostly used in agricultural areas for small-scale treatment	Mainly used in some agricultural developed countries, such as the United States, Canada, France, etc.
Drying and Incineration	High, High	Thorough treatment, high degree of volume reduction	High investment and operating costs, high energy consumption, potential for secondary pollution	Use less frequently than landfills and anaerobic digestion	Mostly used in some countries with tight land resources (such as the Netherlands, Germany and other countries with high incineration rates)

To overcome these drawbacks, hydrothermal oxidation technology (HTO) has garnered increasing attention. As a novel sludge treatment method, as shown in Figure 1, HTO offers high treatment efficiency, effective detoxification, and potential resource recovery. It is well known that “hydrothermal (HT)” refers to homogeneous or heterogeneous chemical reactions occurring in aqueous solutions within closed systems at temperatures above 100 °C and pressures exceeding 1 bar (1 bar = 0.1 MPa). Hydrothermal oxidation, as a subset of hydrothermal technologies, involves thermochemical reactions in the presence of an oxidizing agent during the hydrothermal process. HTO can be classified based on the state of water into subcritical water oxidation (120–370 °C, 2–20 MPa) and supercritical water oxidation (above 574.2 °C and 22.1 MPa). Under subcritical conditions, such as in wet oxidation (WO) or catalytic wet oxidation (CWO), organic matter is partially oxidized, producing small organic molecules like acetic acid as the main byproducts. In contrast, during supercritical hydrothermal oxidation, organic matter is typically mineralized into carbon dioxide and water, with a mineralization efficiency that can reach as high as 99.999% [11,14,15].

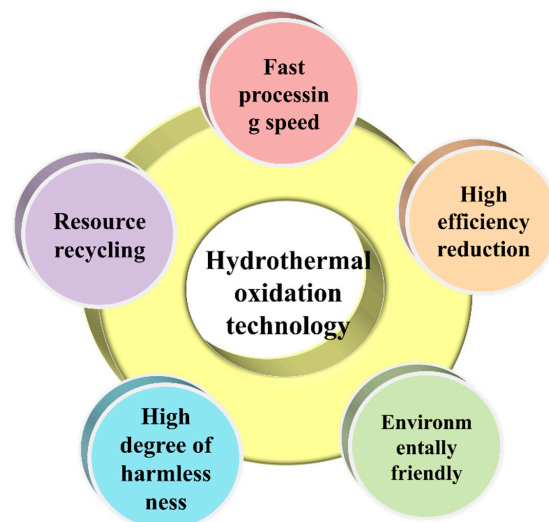


Figure 1. Advantages of hydrothermal oxidation technology for sludge treatment.

Researchers both domestically and internationally have conducted extensive studies on hydrothermal oxidation for sludge treatment. For example, Chu et al. designed a Cu-Ce/ γ -Al₂O₃ catalyst to assist in wet oxidation of antibiotic-laden sludge, achieving a chemical oxygen demand (COD) removal rate of 81.2% and a volatile suspended solids (VSS) removal rate of 93.8%. The resulting carboxylic acids included acetic and propionic acids, which can serve as carbon sources [15]. Similarly, Fang et al. applied wet oxidation technology to pharmaceutical sludge and found that the concentration of volatile fatty acids (including acetic, propionic, isobutyric, and isoamyl acids) increased to 4819 mg/L (mg/L in this paper is equivalent to mg/dm³ in the SI standard) at a pH of 12.56. This suggests that optimizing wet oxidation can enhance the quality of the sludge solution as a potential carbon source [16]. These studies strongly indicate that HTO is a promising sludge treatment method characterized by its high efficiency, effective detoxification, and ability for resource recovery.

In summary, HTO, as a novel sludge treatment method, has significant development potential. A thorough exploration of research advancements in hydrothermal oxidation for sludge treatment is crucial for promoting innovation and development in sludge management and achieving detoxification, volume reduction, and resource recovery. This study focuses on the following key aspects: firstly, the principles of HTO for sludge treatment; secondly, the control of temperature, time, and pressure in the HTO process, which has an impact on sludge treatment; thirdly, optimization strategies to improve the efficiency of HTO; fourthly, the optimization of reactors used in HTO; and lastly, the products generated from sludge after HTO and their related applications. The study summarizes these aspects and addresses the challenges faced in this field, as well as future research directions. This review provides a theoretical foundation for utilizing hydrothermal oxidation technology in sludge treatment, with the hope of achieving sustainable development in this area.

2. Results and Discussion

2.1. Introduction of Sludge

As is shown in Figure 2, sludge, as an inevitable byproduct of domestic wastewater and industrial effluent treatment processes, is a viscous substance composed of solid impurities, suspended solids, and colloidal materials [17]. Essentially, it represents the solid fraction of wastewater. Depending on its source, sludge can mainly be categorized into two types:

- (1) Municipal sludge: This type is derived from urban wastewater treatment plants and primarily generated from domestic sewage. It contains a certain amount of organic matter, nitrogen, phosphorus, and other nutrients, which can potentially be utilized as resources under specific conditions. However, municipal sludge also inevitably contains harmful substances such as pathogens, which, if not properly treated, can pose significant risks to the environment and human health [17,18].
- (2) Industrial sludge: This sludge is produced during various industrial processes, including those in the chemical, pharmaceutical, dyeing, papermaking, and metallurgy sectors. Due to the diverse raw materials and processes used in different industries, industrial sludge has a highly complex composition. It may contain heavy metals and toxic substances, significantly increasing the challenges associated with its treatment [18].

In-depth research reveals that sludge possesses several key characteristics [19–22]: first, sludge typically has an extremely high moisture content, often exceeding 95%. Such a high water content significantly increases the sludge volume, posing substantial challenges for subsequent treatment and escalating transportation costs and complexity. The water in sludge exists in four forms: free water, surface water, interstitial water, and bound water. Among these, the non-free water (surface, interstitial, and bound water) is tightly bound to sludge particles, making it difficult to separate using conventional methods. This further contributes to the large volume of sludge, complicating treatment and dewatering efforts. Second, sludge is rich in organic matter, containing a large number of microorganisms,

bacteria, parasite eggs, and heavy metal ions. The presence of these components makes sludge prone to decomposition and odor, which can negatively impact the surrounding environment if not properly managed. Third, the particles in sludge are very small, resulting in a large specific surface area and strong adsorptive properties. This characteristic complicates the treatment process, as sludge can easily adsorb other substances. Finally, sludge has a relatively low specific gravity, generally less than that of water, which makes it readily suspend in water, further complicating treatment efforts.

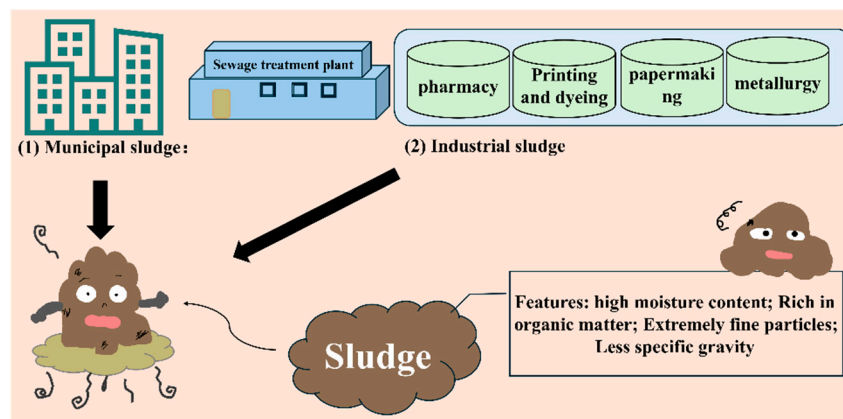


Figure 2. Source and characteristics of sludge.

Given the composition and characteristics of sludge, several key aspects should be emphasized during treatment. On one hand, research should focus on volume reduction, particularly addressing the significant volume caused by the high moisture content. On the other hand, it is essential to remove residual organic pollutants and heavy metals from the sludge to achieve environmentally friendly resource recovery. Therefore, the search for efficient and sustainable sludge treatment technologies is of critical practical significance.

2.2. The Application and Disadvantages of HT in Sludge

To achieve the goals of sludge reduction, harmlessness, and resource recovery, researchers have conducted extensive studies. Findings suggest that hydrothermal technology (HT), as an emerging sludge treatment method, has attracted significant attention in recent years. This technology operates under specific temperature and pressure conditions to treat sludge. Through HT reactions, the organic matter in sludge can be decomposed and transformed, thereby reducing its organic content and overall volume [23]. Additionally, HT technology promotes the stabilization of heavy metals in sludge, mitigating potential environmental hazards. However, literature reviews indicate that the effectiveness of standalone hydrothermal treatments is limited. For example, research by Chen et al. found that the addition of tannic acid (TA) could assist in HT treatment by lowering the effective HT temperature for deep dewatering of sludge proteins. Nonetheless, this approach faces significant economic challenges and has limited effectiveness in removing antibiotics and protein binding [24].

As the development of technology, HT technology has been continuously optimized, and the three commonly used methods at this stage mainly include hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), and hydrothermal gasification (HTG). Despite their respective advantages, these technologies still face challenges in practical applications, as shown in Table 2. Among the three commonly used technologies, HTC is the most widely applied. It operates at temperatures between 180 °C and 250 °C, producing a solid byproduct that can be used as biochar or a soil amendment. However, the treated sludge may still contain high levels of organic matter, particularly large organic molecules, and requires further dewatering. In addition, HTC has limited effectiveness in removing heavy metals from the sludge, which constrains its potential for safe disposal and resource recovery. As noted by Kossinska et al., the hydrochar produced from HTC

contains higher concentrations of heavy metals and has low energy value, limiting its use in agriculture and energy applications. To address this, their study optimized the process by using co-hydrothermal carbonization to improve the performance in these areas [25]. HTL, on the other hand, operates at higher temperatures (250 °C–350 °C) and produces liquid fuels such as bio-oil. However, the efficiency of HTL varies significantly depending on the types of organic materials present in the sludge, and the resulting liquid phase often requires further treatment to meet discharge standards. For example, Thomsen et al. found that the liquid phase from HTL-treated sludge did not meet regulatory standards, necessitating additional treatment using wet oxidation technology [26]. Moreover, persistent organic pollutants and heavy metals may still remain in the treated sludge, affecting the quality and usability of the final product. Compared to HTC and HTL, HTG is less frequently applied. HTG converts sludge into gaseous products, such as methane, at higher temperatures (350 °C–600 °C), achieving significant reduction in sludge volume. However, this process is energy-intensive and requires complex equipment. As noted by Qiu et al., supercritical water gasification (SCWG) and supercritical water oxidation (SCWO) still face technical challenges in achieving high efficiency. For instance, initiating and sustaining the reaction requires preheating the feedstock to supercritical temperatures, typically using direct heating via fuel combustion or electric heaters (EH). Furthermore, coking and salt precipitation during preheating reduce the efficiency of the EH and heat exchangers (HX), potentially leading to blockages and system shutdowns [27].

In summary, while these common hydrothermal technologies have achieved varying degrees of success in sludge treatment, they still face challenges such as difficulty in controlling reaction conditions, inconsistent product quality, and limited removal efficiency of organic pollutants and heavy metals. Therefore, further optimization of hydrothermal technology is necessary to enhance its effectiveness in sludge treatment.

2.3. Hydrothermal Oxidation Technology

2.3.1. Comparison with Common Hydrothermal Techniques

As shown in Table 2, the summary and discussion of traditional hydrothermal technologies indicate that they mainly focus on promoting the physical and chemical transformation of sludge components by adjusting reaction conditions. However, a significant amount of macromolecular organic substances may still remain in the treated sludge [24]. To address this issue, researchers have introduced hydrothermal oxidation, a process that incorporates oxygen or oxidants into the hydrothermal reaction to further oxidize organic matter. This technology breaks down macromolecular organic compounds into smaller molecules such as carbon dioxide and water, significantly improving the removal efficiency of organic pollutants [26,28,29]. Therefore, HTO demonstrates clear advantages over traditional HT methods, particularly in terms of sludge detoxification and reduction. For example, a study by Pola et al. compared the effectiveness of hydrothermal and hydrothermal oxidation methods in removing heavy metals from sludge. The results showed that, during hydrothermal treatment, the presence of oxygen had a significant impact on most heavy metals (Hg, Cr, Ni, Cu, Zn, and Fe), and oxidation promoted greater dissolution of these metals. Notably, the most significant differences were observed in the behavior of Hg, Ni, and Cu. For Hg, in the presence of oxygen, the percentage of total Hg in the liquid phase decreased from 40% to 21% after 210 min at 200 °C. In contrast, under anoxic conditions, the concentration of Hg could only be reduced to 30%. The study also found that Hg was almost completely removed in less than 30 min, but after that, at the lowest temperature (160 °C), Hg began to re-dissolve. After further treatment, its concentration could only be reduced to a minimum of 30%. For Ni and Cu, under WO conditions, low temperatures were sufficient for their removal. At 160–170 °C, the content of Ni and Cu in the liquid phase accounted for only 1.5% (0.42 ± 0.07 mg/kg DM) and 0.2% (0.34 ± 0.01 mg/kg DM) of the total Ni and total Cu, respectively. In contrast, during the HT process, these two metals were almost entirely retained in the solid phase, which was the opposite trend to that observed during wet oxidation [30]. This advantage positions hydrothermal oxidation

as a promising method for sludge treatment, offering efficient detoxification and effectively addressing the challenges of resource recovery. By comparing HTC, HTL, and HTG with hydrothermal oxidation, it becomes evident that HTO provides distinct benefits in sludge treatment. It not only achieves more thorough decomposition of organics but also efficiently removes heavy metals, reducing the environmental risks associated with sludge.

Table 2. Comparison of commonly used hydrothermal technology and hydrothermal oxidation technology for sludge treatment [31–33].

Comparison Item	Hydrothermal Carbonization (HTC)	Hydrothermal Liquefaction (HTL)	Hydrothermal Gasification (HTG)	Hydrothermal Oxidation (HTO)
Temperature Conditions	180 °C–250 °C	250 °C–400 °C	350 °C–600 °C	125 °C–320 °C
Pressure Conditions	2–6 MPa	10–25 MPa	20–30 MPa	0.5–10 MPa
Decomposition of Organic Matter	Limited decomposition: large molecules may remain (the removal rate of COD: 68–75%)	Moderate decomposition, mainly producing bio-oil (the removal rate of COD: 50–85%)	High decomposition into gases, leaving little organic residue	Very efficient organic matter decomposition into small molecules (CO ₂ , H ₂ O) (the removal rate of COD: more than 78%)
Dehydration Effect	Moderate dehydration, solid product still retains moisture (reduction around 50–70%)	Produces liquid products, so dehydration is moderate (reduction around 60–80%)	High dehydration, little solid residue	High dehydration efficiency, leading to effective sludge volume reduction (reduction around 80–90%)
Resource Recovery Potential	Produces solid hydrochar (HHV is 24.0–31.5 MJ/kg) for fuel or soil improvement	Produces bio-oil for energy, some nutrient recovery possible (HHV is 30–40 MJ/kg bio-oil)	Gaseous products like methane can be used as energy sources	High potential for heat recovery, metals and other resources are more easily recoverable
Advantages	Low temperature, easy to operate, solid product for energy use	Produces valuable liquid fuels, higher energy recovery potential	High energy yield in the form of gases, efficient organic conversion	Significant reduction and harmless treatment effects, high pollutant decomposition efficiency, and great resource recovery potential
Disadvantages	Large molecules remain, requires post-processing	Complex system, high pressure and temperature needed	Expensive setup, complex reaction control	Overall treatment efficiency: high, but improvements are needed in cost efficiency

2.3.2. Principle of HTO Technology

The principle of HTO in treating sludge primarily relies on the degradation or transformation of organic pollutants and harmful substances through oxidation reactions under high-temperature and high-pressure conditions. This technology takes advantage of the unique physical and chemical properties of water in subcritical or supercritical states, particularly its solubility and the accelerated rate of oxidation reactions, to achieve sludge reduction, detoxification, and resource recovery. Both subcritical (WO, CWO) and supercritical conditions in hydrothermal oxidation share common features, where the process involves two main steps: pyrolysis and oxidation.

In the pyrolysis step, the floc structure of the sludge is disrupted, releasing macromolecular organic compounds into the liquid phase. Subsequently, during the oxidation step, these macromolecules are oxidized into smaller organic molecules, with organic nitrogen and phosphorus being converted into inorganic nitrogen (e.g., N₂, NH₃, NO_x) and inorganic phosphorus (e.g., phosphates). The key difference between the two conditions lies

in the oxidation mechanism. In subcritical conditions (WO, CWO), the oxidation process follows a traditional free-radical chain reaction, which may leave behind small molecular compounds like acetic acid in the final products [26,28,29]. In contrast, the SCWO process exhibits a higher efficiency in organic matter mineralization. Due to the extremely high temperature and pressure, oxidation is not limited to the conventional free-radical chain reactions; instead, direct oxidation between oxygen molecules and organic compounds occurs in the supercritical state, leading to complete mineralization into carbon dioxide and water. Therefore, the reaction mechanisms involved in the oxidation process include the oxidation and mineralization of organic matter, the transformation of organic nitrogen, and the transformation of organic phosphorus, as shown in Figure 3.

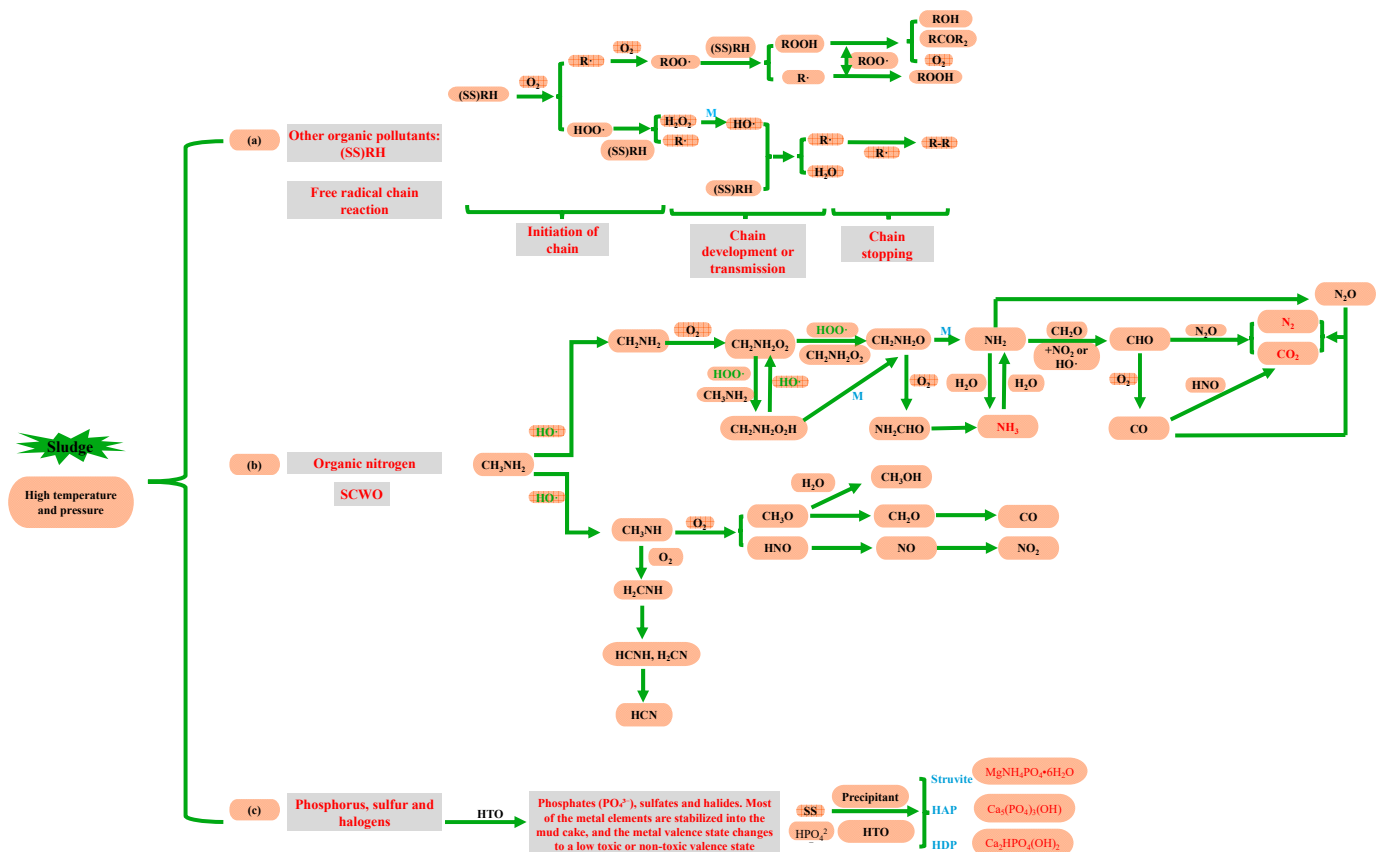
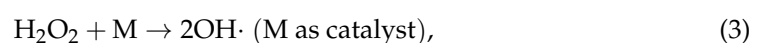
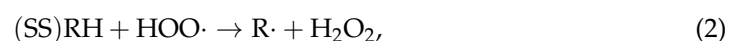
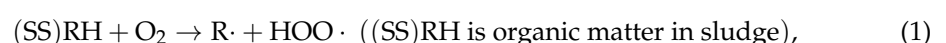


Figure 3. Reaction mechanism of sludge treatment by hydrothermal oxidation technology (including (a) free radical reaction, (b) organic nitrogen conversion, (c) phosphorus conversion).

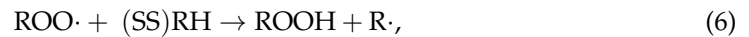
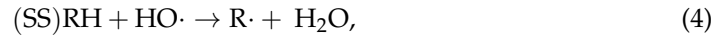
First is oxidation and mineralization of organic matter: Under subcritical conditions in HTO, the process mainly involves the traditional free-radical chain reactions, as shown in Figure 3a, which can be divided into three stages: chain initiation, chain propagation and development, and chain termination [34,35].

(1) Chain initiation: the process by which reactant molecules generate free radicals. In this process, the organic matter in the sludge will produce HO· through thermal reaction with oxygen, as follows (1)–(3):

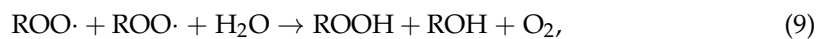


(2) Chain development or transfer: Free radicals interact with molecules, alternately making the number of free radicals increase rapidly. As shown in the following Formulas (4)–(6),

due to its high electron affinity (568 kJ), $\text{HO}\cdot$ can oxidize all hydrogen-containing organic compound RH in the sludge to generate organic free radical $\text{R}\cdot$, while organic free radical $\text{R}\cdot$ reacts with O_2 to form organic peroxyradical $\text{ROO}\cdot$, which further removes hydrogen atoms from RH. The organic hydroperoxide ROOH and another organic radical $\text{R}\cdot$ are formed.



(3) The termination of the chain (7)–(9): Free radicals collide with each other to generate stable molecules, and the growth process of the chain is interrupted.

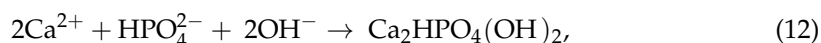
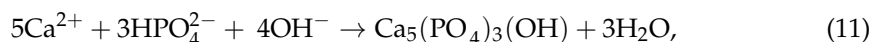


From the above reaction mechanism, it can be seen that the concentration of free radicals ($\text{HO}\cdot$, $\text{HOO}\cdot$, $\text{R}\cdot$, $\text{ROO}\cdot$), as the intermediate transfer of the whole chain reaction, plays a decisive role in enhancing the efficiency of the hydrothermal oxidation technology. In order to improve the application of hydrothermal oxidation technology in practice, it is necessary to comprehensively consider and optimize according to the characteristics of sludge, treatment requirements, and economic costs. In the supercritical state, the mineralization process is a simple direct oxidation of oxygen molecules and organic matter to produce carbon dioxide and water [36].

Second is transformation of organic nitrogen [36]. A comparison between subcritical and supercritical conditions reveals differences in the transformation of organic nitrogen. In subcritical conditions, due to the relatively mild reaction environment, the conversion of organic nitrogen is often incomplete, and the main products include ammonia (NH_3), nitrites (NO_2^-), and nitrates (NO_3^-). In contrast, under supercritical conditions, the conversion efficiency is significantly faster, and the residual nitrogen oxides (NO_x) are minimal. Ammonia nitrogen ($\text{NH}_3\text{-N}$) can be further oxidized to small molecules like N_2 under appropriate conditions. As illustrated in Figure 3b, Li et al. summarized the transformation of organic nitrogen in the SCWO process, finding that the primary products are formamide, $\text{NH}_3\text{-N}$, CO_2 , and formic acid, with $\text{NH}_3\text{-N}$ primarily originating from the hydrolysis of formamide. Furthermore, $\text{NH}_3\text{-N}$ can be oxidized into N_2O and N_2 under suitable conditions. The yield of $\text{NH}_3\text{-N}$ increases with rising temperature. When dimethylamine and trimethylamine are used as reactants, $\text{NH}_3\text{-N}$ primarily originates from the intermediate dimethylamine, while the concentrations of NO_x , N_2O , and N_2 remain relatively low. Similar conclusions apply to aromatic organic compounds containing amino groups. For instance, aniline, under the action of hydroxyl radicals ($\text{HO}\cdot$), generates intermediates such as phenol and $\text{NH}_3\text{-N}$. Under the influence of metal catalysts, phenol and $\text{NH}_3\text{-N}$ are further converted into final products like N_2 , N_2O , and NO_3^- , as reaction temperature, oxygen availability, and retention time increase.

Third is transformation of organic phosphorus [37]. Phosphorus in sludge is typically converted from organic phosphorus compounds (R-PO_4) to inorganic phosphate (PO_4^{3-}) during the oxidation process. Following this, dissolved phosphorus can be recovered by adding appropriate precipitating agents, usually magnesium (Mg^{2+}) or calcium (Ca^{2+}), along with available ammonium (NH_4^+). Magnesium phosphate precipitates primarily in the form of magnesium ammonium phosphate (struvite), while calcium phosphate (CaP) can form a broader range of compounds. The most common forms are hydroxyapatite (HAP) and dicalcium phosphate (HDP), but other forms, like amorphous calcium phos-

phate (ACP), brushite, or octa calcium phosphate, are also possible. The main reaction processes are represented by the following Equations (10)–(12):



2.4. Research on Influencing Factors of Sludge Treatment by HTO

In order to improve the treatment efficiency of sludge by HTO technology, researchers have conducted a large number of explorations of process optimization. Summarizing the research in recent years, it is found that the factors affecting the treatment of sludge by HTO technology include reaction temperature, time, pressure, pH value, etc. Comparing the performances of various influencing factors in improving the efficiency of HTO technology, it is found that the change in reaction temperature has a more significant improvement on the treatment effect of various sludges. This is because high temperatures can accelerate the dissolution and mineralization of sludge and promote the reaction. In contrast, reaction time and pressure have relatively less influence. The following section will discuss these factors and their impacts on the treatment of various sludges in detail.

(1) Reaction temperature

The reaction temperature of HTO technology is the most important parameter affecting the HTO process. Studies have shown that reaction temperature directly affects the reaction rate and the distribution of products. Generally, a higher temperature can increase the reaction rate of various sludge treatments and promote the degradation of organic matter, thus affecting the removal efficiency of COD and VSS [38]. In addition, it also has a certain influence on the generation of volatile fatty acids. Next, this article will conduct relevant discussions and summaries on the impact of temperature changes on the results when HTO is used to treat two types of sludge, municipal sludge and industrial sludge.

The study on municipal sludge treatment found that the change in the reaction temperature of HTO technology is crucial to sludge treatment, and the increase in reaction temperature is conducive to enhancing the removal ability of organic pollutants and the recovery of materials that can be used as carbon sources. For example, Chen et al. studied the treatment effect of wet oxidation technology on sewage plant sludge after the addition of a catalyst and compared the primary and secondary relationships of three influencing factors: temperature > concentration of $\text{Ca}(\text{ClO})_2$ > molar ratio of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} / \text{Ca}(\text{ClO})_2$. The results prove that reaction temperature is an important factor affecting the sludge dewatering performance. The concentration of $\text{Ca}(\text{ClO})_2$ and the molar ratio of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} / \text{Ca}(\text{ClO})_2$ have less influence. And they simultaneously used SPSS software to analyze the Pearson correlation coefficients of 18 operating parameters on sludge dewaterability (CST, SRF, and W_c). The results show that temperature is the main influencing factor [39]. Fang et al. studied the effects of temperature and oxygen pressure on HTO reaction and the basic properties of dissolved organic matter (DOM). The results show that, at 260 °C and an oxygen pressure of 0.9 MPa, the removal rates of total chemical oxygen demand (TCOD) and VSS reach the maximum values of 72% and 99%, respectively. And it is concluded that the influence of reaction temperature on the removal of TCOD and VSS is usually more significant in the operation of hydrothermal oxidation technology. An increase in temperature leads to an increase in the removal rates of TCOD and VSS. In addition, formic acid is generally present at lower temperatures, while acetic acid accumulates with the increase in temperature and oxygen pressure [40]. Núñez et al. also found that an increase in the reaction temperature of HTO technology is beneficial to the formation of volatile fatty acids such as acetic acid after municipal sludge treatment. Among them, the concentration at 160 °C for 180 min is 1.28 ± 0.07 g/L (g/L in this paper is equivalent to g/dm³ in the SI standard), and the concentration at 180 °C for 180 min is 1.65 times. However, the

degradation rates of non-volatile fatty acids such as oxalic acid, pyruvic acid, and formic acid accelerate with the increase in temperature, while the degradation rate of formic acid is not so obvious. But the decrease in the maximum concentration of short-chain fatty acids (SCFAs) due to excessive temperature can be attributed to the greater mineralization of organic matter. At higher temperatures, the oxidation pathway leading to the formation of CO_2 is more favorable than the oxidation pathway leading to the formation of acetic acid [41]. Zhang et al. also found that, under optimal conditions, as the reaction temperature increases, the acetic acid concentration increases from 1220 mg/L to 3250 mg/L, and the contribution of protein decreases from 26.7% to 2.3%. The content of carbohydrates also decreases with the increase in temperature due to the oxidation of carbohydrates and the loss of carbonyls related to the “caramel” or Maillard reaction. This study proves that the change in temperature has an important influence on the content changes of some components in sludge [42]. In addition, Wang et al. found that when persulfate and sludge are co-treated hydrothermally, higher temperatures and solid contents will also lead to the melting and deformation of microplastics (MPs), exacerbating the aging of polypropylene MPs, resulting in a rough surface, an increase in the carbonyl index, and a change in crystallinity [43].

For industrial sludge, the reaction temperature of HTO technology also has a significant impact on the removal of pollutants and resource recovery treatment. For example, Qin et al. discussed the influence of reaction conditions on the wet oxidation of excess sludge in the treatment process of caprolactam wastewater. The results show that, as the reaction temperature increases from 180 to 260 °C, the removal of COD and VSS is accelerated because a higher reaction temperature means higher reaction energy, which is beneficial to the increase in COD and VSS removal rates. It is worth noting that when the reaction temperature is too high, the removal rate of COD will not increase significantly because it may induce corrosion and is not conducive to equipment maintenance [35]. Wang et al. designed an improved CWO method for treating excess activated sludge in the process of coal chemical wastewater treatment. The results prove that, as the temperature increases, the solubility of oxygen increases, which increases the removal of organic pollutants in the solution. In addition to enhancing the removal efficiency of organic pollutants, an increase in reaction temperature can also increase the concentration of volatile fatty acids [38]. Chu et al.’s study also found the same conclusion. As the reaction temperature increases, the removal rates of COD and VSS increase significantly, and an increase in reaction temperature can also promote the production of volatile fatty acids [15].

Combining all these results with the results of the impact of temperature changes on sludge treatment by hydrothermal oxidation technology sorted out in Table 3 shows that reaction temperature is a key reaction parameter in the reaction and can significantly affect the relevant treatment effects of sludge, mainly in the following aspects: (1) The higher the reaction temperature, the removal rate of organic pollutants in sludge, and the removal rates of COD and VSS are all significantly enhanced. However, too high a temperature may reduce or stabilize the removal rate. (2) An increase in reaction temperature is beneficial to enhancing the dewatering performance of sludge. This is because the sludge particles become smaller and the pores increase significantly after treatment by HTO technology, which is conducive to the release of intercellular water, so the dewatering performance is improved. (3) As the reaction temperature continues to increase, the concentration of volatile fatty acids in the treated sludge is higher than that of non-volatile fatty acids, and most research results show that the concentration of acetic acid is significantly increased because a higher temperature can promote the solubilization and mineralization of these organic substances. (4) In addition to the above three common conclusions, researchers have also found that as the reaction temperature increases, the generation of $\text{NH}_3\text{-N}$ will also increase significantly, gaseous carbon w_{CO_2} will rise, and liquid carbon w_{aqueous} and w_{solid} will decrease, proving that an increase in temperature is conducive to the conversion of carbon from liquid to gaseous.

Table 3. Influence of reaction temperature change on sludge treatment by HTO in recent years.

Sludge Type	Treatment Process	Optimal Temperature (°C)	Impact of Temperature (T) Change	Change in Efficiency/Yield (mg/L)	References
Urban Sludge	HTO-Alkaline Hydrolysis	214	T increases, SCOD yield significantly increases then stabilizes, NH ₃ -N generation significantly increases	(T: 130–210–290 °C) SCOD: 25,000–35,000–30,000; NH ₃ -N: 400–1200–1800	[11]
Urban Sludge	Thermal hydrolysis -HTO	180	T increases, TOC removal rate significantly improves, carbohydrates and proteins increase then decrease, the concentration of NH ₃ -N and acetic acid significantly increases	(T: 140–180 °C) TOC: 1400–2500; carbohydrates: 700–900–600; NH ₃ -N: 50–500	[29]
Municipal Sludge	CWPO	230	T increases, potential toxicity of Pb increases, potential toxicity of Cd increases then decreases (still lower than raw material), the concentration of acetic acid increased, and the concentration of propionic acid, isobutyric acid, and n-butyric acid decreased gradually, the concentration of ammonia nitrogen also increased first and then decreased	(T: 100–250 °C) SCOD: 25,000–35,000–30,000; NH ₃ -N: 500–2600–2200; Acetic acid: 600–2900–1100	[44]
Urban Sludge	HTO	160	T increases, and it is beneficial to the formation of acetic acid. Volatile fatty acids are produced more than non-volatile fatty acids (the concentration of propionic acid increases with increasing temperature, while oxalic acid, pyruvate, and formic acid are degraded)	SCFA: 6.07 g/L (acetic acid accounted for 28.2%, VFA: 70%); (160–200 °C) oxalic acid: 1300–243; pyruvate: 700–200; formic: 1190–700	[41]
Municipal Sludge	HTO/Thermal hydrolysis	200	T increases, the dissolution of EPS and the release of heavy metals are accelerated; the removal rates of Cu decrease first and then increase, and the removal rate of Zn decrease with the increase in temperature	(160–180–200 °C) Cu: 0.2–56–26.1%; Zn: 11.2–0.8%	[30]
Urban Sludge	HTO	240	T increases, the removal of SCOD decreases, the increase in temperature promotes the conversion of organic nitrogen to NH ₃ -N and phosphorus from organophosphates and phosphates to non-hydroxyl phosphates, the concentration of humic acid, protein, and polysaccharide increases first and then gradually decreases	(T: 180–260 °C) SCOD: 25,000–10,000; NH ₃ -N: 1735–2800 mg/L, accounted for 58.3–69.5% of TN, organic nitrogen: 650–778; accounted for 13.3–26.1%, nitrate nitrogen and nitrite nitrogen: 30–40	[45]
Pharmaceutical Sludge	CWO	260	T increases, the removal rates of COD and VSS are significantly increased	(T: 180–260 °C) The removal rate of COD: 20–72.6%; and VSS: 50–87.3%	[22]
Pharmaceutical Sludge	CWO	260	T increases, the removal rates of TCOD and VSS are significantly increased, and the concentration of VFAs is first significantly increased and then stabilizes	(T: 180–260 °C) The removal rate of TCOD: 40–76.5%; and VSS: 60–93.6%; VFA: 1500–5000	[46]

Table 3. Cont.

Sludge Type	Treatment Process	Optimal Temperature (°C)	Impact of Temperature (T) Change	Change in Efficiency/Yield (mg/L)	References
Pharmaceutical Sludge	CWO	260	T increases, the removal rate of COD accelerates obviously, the removal rate of VSS increases little, the concentration of acetic acid increases, and the concentration of formic acid and oxalic acid begins to decrease	(T: 180–260 °C) The removal rate of COD: 10–60%; and VSS: 70–97%	[47]
Pharmaceutical Sludge	CWO	260	T increases, COD and VSS removal rates significantly improve	(T: 180–260 °C) The removal rate of COD: 43–81.2%; and VSS: 61–93.8%	[15]
Pharmaceutical Sludge	CWO	260	T increases, the removal rates of TSS and VSS are significantly increased, the removal rates of SCOD and TCOD are significantly increased, the concentration of VFAs rises sharply and then plummets	(T: 200–260 °C) The removal rate of TSS: 72.5–90.1%; and VSS: 80–98.4%; The removal rate of SCOD: 70–81.6%, and TCOD: 43–78.7%; VFA: 1700–4000–3600	[16]
Oilfield Sludge	SCWO	450	T increases, the concentration of TOC and COD decrease first and then became stable, gaseous carbon w_{CO_2} rises while liquid carbon $w_{aqueous}$ and w_{solid} decrease, indicating carbon transitions from liquid to gas, with negligible impact on methane ratio	(T: 390–450 °C) The concentration of TOC: 3000–2600 and COD: 9000–6300; w_{CO_2} : 20–30%, and $w_{aqueous}$: 40–30%; w_{solid} : 20–15%	[48]
Mechanical Processing Wastewater Sludge	CWO	80	T increases, the dewatering performance of sludge is improved	81.41% fell to 42.92%	[39]
Coal Chemical Sludge	CWO	260	T increases, the degradation efficiency of COD, SCOD, and TOC is significantly improved, VFA concentration sharply increases (especially acetic acid)	(T: 180–260 °C) The removal rate of COD: 40–80%; SCOD: 725–83%, and VSS: 61–93%; VFA: 2500–4750 (Acetic acid: 4000)	[38]
Coal Chemical Sludge	HTO	260	T increases, COD removal rate significantly increases then decreases, acetic acid concentration increases, while formic and oxalic acid concentrations decrease	(T: 180–260 °C) The removal rate of COD: 25–78.6%; and VSS: 68–89.3%	[35]

Note: temperature changes, other things being equal. TSS: total suspended solids, VSS: volatile suspended solids, TOC: total organic carbon, COD: chemical oxygen demand, TCOD: total chemical oxygen demand, EPS: extracellular polymers, SCOD: dissolved organic matter, VFA: volatile fatty acids, thermal hydrolysis, HTO: hydrothermal oxidation technology, CWO: catalytic wet oxidation technology, CWPO: catalytic hydrothermal oxidation technology (different oxidants), SCWO: supercritical water oxidation technology.

It is worth noting that if the reaction temperature is too high, excessive acetic acid generated in the reaction is not easily oxidized, which will lead to no significant increase in the COD removal rate. On the other hand, excessive reaction temperature will cause more serious corrosion, which will increase the construction cost of the reaction system [35]. Therefore, considering the impacts of cost and energy saving, it is necessary to find an optimal temperature to make the degradation performance or the performance of recovering substances reach the best. In addition, inevitably, a high temperature will increase the construction and operation costs of the reaction system. Therefore, in the industrial utilization of HTO technology, the reaction temperature should be considered together with the reaction efficiency and the cost of the reaction system.

(2) Reaction time

Aside from reaction temperature, adjusting the reaction time also has a significant impact on the process. Reaction time refers to the duration for which the sludge undergoes oxidation under specific temperature and pressure conditions. This time directly affects the treatment efficiency. Generally, as reaction time increases, the removal rates of COD and VSS gradually improve. The main reason for this is that, during the hydrothermal oxidation process, the sludge undergoes hydrolysis, causing the VSS in the solid phase to quickly dissolve into the liquid phase. Over time, degradable organic matter accumulates in the liquid, and through the action of hydroxyl radicals and other reactive species, it is converted into intermediate products that are harder to oxidize further, such as carboxylic acids like acetic and formic acids [38]. The accumulation of these intermediates may adversely affect COD removal rates. Therefore, determining the optimal reaction time, considering both oxidation efficiency and economic cost, is crucial for enhancing sludge treatment performance. In current research on industrial sludge, notable examples include a study by Shang et al., which optimized conditions at a reaction temperature of 260 °C, with a duration of 60 min, an initial oxygen pressure of 1.0 MPa, and a catalyst concentration of Cu/ γ -Al₂O₃ at 5.0 g/L. This setup achieved the highest removal rates for VSS at 93.6% and TCOD at 76.5%. The results indicate a linear relationship between the increase in removal rates and reaction time [46]. Similarly, Qin et al. investigated the effects of reaction conditions on the hydrothermal oxidation of excess sludge during the treatment of caprolactam wastewater. They found that at 260 °C, with an initial oxygen pressure of 1.3 MPa and a duration of 60 min, the removal rates of COD and VSS were 78.6% and 89.3%, respectively. Additionally, the accumulation of carboxylic acids resulting from sludge degradation increased with extended reaction time. Both the removal rates of COD and VSS also exhibited gradual increases over time, showing a similar trend. Notably, the VSS removal rate was already high within a short timeframe, likely because the solid-phase organic matter in the sludge transfers to the liquid phase, thereby enhancing VSS removal [35].

For municipal sludge, the effects of varying reaction time in HTO technology are similar, highlighting the need to determine an optimal reaction time for effective sludge treatment. For example, Gong et al. investigated the impact of various HTO conditions in the presence of NaOH on the treatment of urban sludge. They found that a reaction time of 30 min resulted in the highest SCOD yield at 21.67%. As reaction time increased, SCOD yield initially decreased before stabilizing. The concentrations of NH₃-N and NO₃-N gradually declined with extended reaction time. During the wet oxidation process, soluble proteins are degraded, leading to the formation of new organic compounds such as peptides and amino acids. Microbial cells also decompose over time, resulting in a gradual increase in the total phosphorus (TP) concentration. This study demonstrated that changes in reaction time significantly influence the harmlessness and resource recovery of sludge [11]. Additionally, Zhang et al. found that, at temperatures of 200 °C or higher, most organic matter dissolves within 10 min. With prolonged treatment time, the mineralization rate gradually increases due to sustained oxygen supply. The pattern of SCOD in sludge from 0 to 30 min shows an initial increase followed by a decrease, indicating rapid dissolution of organic matter from the solid phase, followed by gradual mineralization [42].

The current research on the effects of varying reaction time on the HTO of sludge reveals several key conclusions, which are summarized in Table 4: (1) the commonly used reaction time is typically around 60 min. (2) Longer reaction times are beneficial for increasing COD removal rates, but there exists a threshold beyond which removal rates plateau. (3) VSS removal rates are generally higher than COD removal rates and can reach their peak in a shorter timeframe. This is because COD removal primarily results from the oxidation of organic matter by soluble oxidants, such as gaseous oxygen, which is more affected by gas–liquid mass transfer, while VSS removal mainly occurs through rapid thermal hydrolysis of sludge. (4) Changes in reaction time also influence ammonia nitrogen concentrations, facilitating the conversion of carbon from liquid to gas. NH₃-N and NO₃-N

concentrations initially increase with extended reaction time before gradually declining. These findings indicate that the impact of a changing reaction time is not as significant as that of a changing reaction temperature. Identifying an appropriate reaction time is essential for optimizing sludge treatment efficiency, highlighting the necessity of selecting suitable reaction times to enhance the effectiveness of hydrothermal oxidation technology.

Table 4. Influence of reaction time change on sludge treatment by HTO technology in recent years.

Sludge Type	Treatment Process	Optimal Time	Effect of Time (t) Change	Change in Efficiency/Yield (mg/L)	Reference
Urban Sludge	HTO-Alkaline Hydrolysis	30 min	t increases, the yield of SCOD decreases first and then stabilizes, and the concentrations of $\text{NH}_3\text{-N}$ and $\text{NO}_3\text{-N}$ decreases slowly with the extension of reaction time	(t: 10–30–120 min) SCOD: 24,600–26,100–24,900; $\text{NH}_3\text{-N}$: 350–360–300	[11]
Urban Sludge	Thermal hydrolysis-HTO	60 min	t increases, the concentration of ammonia nitrogen also increase, the removal rate of carbohydrates, TOC, and protein concentration first increases and then decreases (not significant)	(t: 0–60 min, 180 °C) TOC: 1500–2750–2000; protein: 1000–1500–100; $\text{NH}_3\text{-N}$: 200–600	[29]
Coal Chemical Sludge	HTO	60 min	t increases, the removal rate of COD increases gradually, while the removal rate of VSS does not change much	(t: 20–60 min) The removal rate of COD: 43–78.6%; and VSS: 80–89.3%	[35]
Coal Chemical Sludge	CWO	60 min	t increases, the removal rate of COD and VSS increases at the same time, and the increase in removal rate is linear with the reaction time, but there is a node value	(t: 20–60 min) The removal rate of COD: 55–78%; and VSS: 85–93%	[38]
Pharmaceutical Sludge	CWO	60 min	t increases, the removal rate of COD and VSS increases with the increase in temperature, and the removal rate of VSS (which is very high in a short time) is much higher than that of COD	(t: 20–60 min) The removal rate of COD: 43–60%; and VSS: 78–87.3%	[22]
Pharmaceutical Sludge	CWO	60 min	t increases, the removal rate of TCOD and VSS increases with the increase in reaction time; even in a short time, the removal effect of VSS is high, and the increase in the removal rate is linear with the reaction time	(t: 20–60 min) The removal rate of TCOD: 50–75%; and VSS: 85–93.6%	[46]
Pharmaceutical Sludge	CWO	60 min	t increases, the removal rate of VSS and COD increases, and the removal rate of VSS is changed little compared with the removal rate of COD	(t: 20–60 min) The removal rate of COD: 20–60%; and VSS: 80–97%	[47]
Pharmaceutical Sludge	CWO	60 min	t increases, the removal rate of initial VSS is higher, the removal rate of COD increases gradually with the increase in time	(t: 20–60 min) The removal rate of COD: 55–81.2%; and VSS: 85–93.8%	[15]
Oilfield Sludge	SCWO	20 min	t increases, the removal rate of TOC and COD increases, gaseous carbon w_{CO_2} increases, liquid carbon w_{aqueous} , w_{solid} decreases, w_{CO} first increases and then decreases	(t: 5–30 min) The concentration of TOC: 3500–1500 and COD: 6500–4300; w_{CO_2} : 25–53%, and w_{aqueous} : 40–20%; w_{solid} : 35–18%	[48]

Note: time changes, other things being the same.

(3) Initial oxygen pressure

The principles of hydrothermal oxidation technology indicate that oxygen supply significantly affects sludge treatment. As oxygen supply increases, the contact opportunities between oxygen and organic matter in the sludge are enhanced, accelerating the reaction

rate. Under these conditions, higher oxygen concentrations can provide more reactive oxygen species, facilitating the oxidative decomposition of organic matter and generating various beneficial free radicals, such as hydroxyl radicals, which play a crucial role in removing organic pollutants. The oxygen supply is primarily determined by the initial oxygen pressure.

Research on common industrial sludge treatment has shown that, at elevated temperatures, increasing the initial oxygen pressure is beneficial for the removal of organic pollutants. For instance, Shang et al. demonstrated that the additional oxygen supply plays a vital role in the wet oxidation of pharmaceutical sludge, significantly increasing the TCOD removal rate as oxygen levels rise. This is likely due to the increased production of hydroxyl radicals, which have strong oxidative capabilities. They concluded that the highest TCOD removal rate occurs when the oxygen addition is at 1.0 MPa [46]. Qin et al. explored not only the effects of reaction temperature and time, but also the impact of oxygen supply on hydrothermal oxidation. Their results confirmed that higher oxygen supply effectively accelerates the oxidation reaction rate, thereby facilitating the removal of organic compounds, including COD and VSS [35]. Wang et al. found that the COD removal rate is significantly influenced by the amount of oxygen added; as the initial oxygen pressure increases, the wet oxidation process becomes more favorable. In contrast, the VSS removal rate is only slightly affected by variations in oxygen supply. This may be attributed to the hydrolysis of the sludge, as VSS removal remains above 80% even when the initial oxygen pressure is at 0.2 MPa [38]. Chu et al. also observed that COD removal significantly increases with changes in oxygen pressure, while VSS removal rates show little change, consistent with the findings of previous studies [15].

For municipal sludge, increasing the initial oxygen pressure affects the TOC removal rate and acetic acid generation during HTO. For instance, Fang et al. investigated the effects of reaction temperature and oxygen pressure on dissolved organic matter in the hydrothermal treatment of urban sludge. Their results indicated that the optimal TCOD and VSS removal rates occur at an initial oxygen pressure of 0.9 MPa, with both rates increasing as the reaction temperature and oxygen pressure rise [40]. However, changes in oxygen pressure do not always influence sludge treatment. Malhotra et al. studied the effects of HTO on sludge and found that, while the TOC dissolution rate rapidly increased in the initial reaction stage with rising temperatures, variations in oxygen pressure did not significantly enhance TOC dissolution rates. Notably, at high temperatures, increasing oxygen pressure leads to a significant rise in acetic acid concentration, while changes in other VFAs remain minimal [29]. In summary, based on the discussions from the studies and the results in Table 5, it is evident that changes in initial oxygen pressure have a greater impact on COD removal rates compared to VSS removal rates. Additionally, the effect of oxygen pressure becomes more pronounced with increasing temperature.

Table 5. Influence of initial oxygen pressure (IOP) change on sludge treatment by HTO technology in recent years.

Sludge Type	Treatment Process	Optimal IOP	Effect of Oxygen Pressure (P) Change	Change in Efficiency/Yield (mg/L)	Reference
Urban Sludge	Thermal hydrolysis-HTO	OC: 1	P increases, the change in oxygen pressure does not significantly improve the solubilization rate of TOC but leads to a significant increase in acetic acid concentration	(P: 0.2–1 MPa) TOC: increased by 900	[29]
Coal Chemical Sludge	HTO	1.3 MPa	P increases, the removal rate of COD increases significantly, while the removal rate of VSS increases gradually	(P: 0–1.2 MPa) The removal rate of COD: 10–78.6%; and VSS: 78–89.3%	[35]

Table 5. Cont.

Sludge Type	Treatment Process	Optimal IOP	Effect of Oxygen Pressure (P) Change	Change in Efficiency/Yield (mg/L)	Reference
Coal Chemical Sludge	CWO	1 MPa	P increases, the removal rate of COD is greatly affected by the amount of oxygen added, and the removal rate of VSS is only slightly affected by the change in oxygen amount (the possible reason for the removal of VSS is the hydrolysis of sludge)	(P: 0.2–1 MPa) The removal rate of COD: 43–78%; and VSS: 82–93%	[38]
Pharmaceutical Sludge	CWO	1 MPa	P increases, the removal rate of COD increases with increasing oxygen pressure (an increase in the concentration of oxidants usually leads to an increase in the oxidation rate)	(P: 0.2–1 MPa) The removal rate of COD: 30–60%; and VSS: 73–87.3%	[22]
Pharmaceutical Sludge	CWO	1 MPa	P increases, the removal rate of TCOD increases significantly, while the removal rate of VSS increases slightly	(P: 0.2–1 MPa) The removal rate of TCOD: 40–75%; and VSS: 80–93.6%	[46]
Pharmaceutical Sludge	CWO	1 MPa	P increases, the removal rates of VSS and COD increase slowly	(P: 0.2–1 MPa) The removal rate of COD: 30–60%; and VSS: 82–97%	[47]
Pharmaceutical Sludge	CWO	1 MPa	P increases, the removal rate of COD increases significantly, while the removal rate of VSS does not change significantly	(P: 0.2–1 MPa) The removal rate of COD: 43–81.2%; and VSS: 80–93.8%	[15]
Oilfield Sludge	SCWO	OC: 1	P increases, the higher oxidation coefficient OC is conducive to the increase in the TOC removal rate, and the trend is first increased and then decreased; in addition, it is conducive to the existing CH ₄ being oxidized into CO ₂	(P: 0.2–1 MPa) The concentration of TOC: 4000–1000 and COD: 10,500–4000; w _{CO₂} : 15–60%, and w _{aqueous} : 40–20%; w _{solid} : 30–10%	[48]

(4) The effect of pH

In addition to factors such as reaction temperature, time, and initial oxygen pressure that directly affect reaction efficiency, pH also significantly influences the HTO process for various types of sludge or the treatment of industrial sludge, particularly pharmaceutical sludge. HTO under alkaline conditions enhances the potential for resource recovery. Fang et al. found that, when the pH of the process was adjusted to 12.56, the concentration of volatile fatty acids (including acetic acid, propionic acid, isobutyric acid, and isovaleric acid) increased to 4819 mg/L. This suggests that adjusting the pH through the addition of reagents can improve the quality of HTO sludge solution as a potential carbon source [16]. Additionally, the addition of alkaline reagents promotes the removal of organic pollutants and the conversion of ammonia nitrogen during HTO. For example, Hušek et al. discovered that, after adding NaOH, the soluble chemical oxygen demand (SCOD) yield increased initially and then decreased as the NaOH concentration rose. The trends in NH₃-N and NO₃-N levels in the solution were consistent with the SCOD yield. This indicates that the addition of an appropriate amount of alkali promotes ammonia nitrogen conversion and organic pollutant removal from the sludge [14].

For municipal sludge, Guo et al. studied Fe (II)-activated persulfate-assisted hydrothermal conversion of waste-activated sludge (WAS) and found that, without pH adjustment (initial pH is 6.5), Fe²⁺-activated PMS oxidation led to a 6.14-fold increase in standardized-capillary suction time (SCST) after 2 min of conditioning, a 58.3% increase in centrifuged weight reduction (CWR), and a reduction in moisture content (MC) to 57.5%, which was nearly equal to the value at pH 8. This result demonstrates that an excellent dewatering

performance can be achieved under acidic conditions without pH adjustment [21]. Furthermore, Zamisa et al. found that adding NaOH enhanced the removal rates of VSS and COD, indicating that alkaline conditions favor the removal of organic pollutants [47].

In summary, acidic conditions may accelerate reaction rates and facilitate the oxidation of some organic compounds, but they also increase the risk of equipment corrosion. Alkaline conditions reduce oxygen solubility and reactivity, slightly slowing reaction rates, but they promote the removal of organic pollutants from the sludge. A neutral pH allows for moderate reaction rates with less equipment corrosion. Moreover, pH can affect sludge dewatering performance, ammonia nitrogen conversion, and subsequent resource recovery. Therefore, treating sludge under optimal pH conditions can improve both dewatering performance and resource recovery efficiency.

2.5. Issues and Optimization Strategies in HTO of Sludge

2.5.1. Challenges in HTO for Sludge Treatment

Although hydrothermal oxidation can enhance treatment efficiency through process optimization, its effectiveness in sludge treatment remains suboptimal, and several issues need addressing:

- (1) Pollution risks: Sludge may contain harmful substances, and improper treatment can pose threats to the environment and public health.
- (2) Low resource recovery: Current recovery rates for sludge resources are still low, with much sludge being disposed of through landfilling or incineration.
- (3) Outdated equipment: Many reactors involved in HTO are outdated and unable to withstand the high temperatures and pressures required for effective processing over extended periods.
- (4) The cost is too high: Hydrothermal oxidation technology requires oxygen assistance and is carried out in a high-temperature and -pressure environment, which inevitably generates some equipment costs and high energy consumption. To improve the efficiency of HTO for sludge treatment, researchers must continue to explore optimization methods to achieve more effective and environmentally friendly sludge management. Currently, various strategies are being implemented to address these three challenges, which will be summarized and discussed in the following sections.

2.5.2. Optimizing the Solution of HTO Technology

(1) Oxidizer assisted HTO technology to treat sludge

As is well known, oxygen is the most commonly used oxidant in sludge HTO. However, controlling oxygen pressure and other parameters can be quite complex. To address this issue, researchers have found that H_2O_2 can serve as an alternative oxidant. Its addition can replace oxygen, eliminating the need for air separation equipment, reducing gas–liquid mass transfer resistance, and accelerating the reaction rate. Moreover, oxidants like H_2O_2 have the advantages of being non-toxic, harmless, and highly oxidative. Additionally, H_2O_2 can react with organic pollutants to generate $\cdot\text{OH}$ radicals, which possess strong oxidative power (with a redox potential of 2.8 eV) and high selectivity, making them effective in removing harmful substances. In addition to H_2O_2 , persulfates (PMS), such as potassium peroxydisulfate and potassium peroxymonosulfate, have also garnered significant attention due to their higher oxidation potential. These oxidants can react with organic pollutants to generate $\cdot\text{SO}_4^{2-}$ radicals, which also positively impact sludge treatment [4]. By adjusting the dosage of the oxidant, the redox potential of the reaction can be controlled, subsequently influencing temperature and pressure. For municipal sludge, the addition of oxidants can improve dewatering performance. For example, Guo et al. studied the effect of PMS on sludge dewatering in hydrothermal oxidation processes. As the amount of PMS increased, both the SCST and CWR initially increased and then decreased with increasing PMS dosage, while the MC first decreased and then increased [21]. For instance, Zhang et al. investigated the effects of HTO temperature and H_2O_2 concentration on the product distribution of municipal sludge, including solid-phase moisture content, heavy metal migration behavior,

VFAs, $\text{NH}_3\text{-N}$ levels, and pH. The results indicated that increasing the amount of H_2O_2 and HTO temperature significantly improved sludge dewaterability. However, the potential toxicity fraction of solid residues containing Pb and Cd increased with higher H_2O_2 concentrations yet remained lower than that of the original material. Additionally, both VFAs and $\text{NH}_3\text{-N}$ concentrations showed an increasing trend, facilitating further resource recovery from sludge [44]. Moreover, sodium persulfate (SPS) can also serve as an oxidant to assist hydrothermal technology in treating municipal sludge. Xiong et al. found that the active persulfate oxidation method is an effective deep treatment technology for improving sludge dewaterability. Under optimal conditions—a hydrothermal temperature of 145°C , a reaction time of 2 h, and a persulfate concentration of 150 mg/g DS —the CST reduction efficiency reached a maximum of 90.5%. Furthermore, over 90% of phosphorus and heavy metals remained in the sludge cake after hydrothermal treatment, and the addition of sodium persulfate can convert phosphorus into more stable forms while removing heavy metals, thereby reducing environmental risks [49]. In summary, the incorporation of oxidants into hydrothermal oxidation technology shows tremendous potential and advantages in sludge treatment. Their application not only enhances treatment efficiency, but also improves sludge dewaterability and the degree of harmlessness.

(2) Treatment of sludge with catalyst-assisted HTO

In addition to the fact that the addition of oxidants can improve the treatment of sludge by HTO technology, the addition of catalysts can as well. In recent years, the development of CWO technology has aimed to achieve safe and efficient sludge treatment [46]. By incorporating catalysts into the reaction system, this method effectively lowers the reaction temperature and pressure, enhances the oxidation efficiency, and shortens the reaction time, thus accelerating the oxidative decomposition of organic substances in sludge. This approach allows for harmless treatment while reducing operational costs. The CWO technology is particularly useful for treating sludge contaminated with organic pollutants and heavy metals, offering advantages such as rapid reaction speed, effective treatment, and low energy consumption. In this technology, catalysts play a crucial role, and selecting an appropriate catalyst is essential for improving sludge treatment efficiency. Catalysts can be categorized into two types based on their phase: homogeneous and heterogeneous. Homogeneous catalysts, including soluble transition metal salts, are characterized by high activity and low cost. Among them, Cu-based catalysts are the most widely used; however, they exhibit biotoxicity and are challenging to recover. In contrast, heterogeneous catalysts can be reused and primarily include noble metal catalysts, transition metal catalysts, rare earth element catalysts, and carbon-based catalysts. The following section will introduce the catalysts used in CWO technology in recent years and their catalytic efficiencies, as shown in Table 6.

Table 6. Comparison of catalysts used in CWO technology in recent years.

Catalyst	Original Sludge Type	Reaction Condition	Treatment Results	Reference
Cu-Ce/ $\gamma\text{-Al}_2\text{O}_3$	Antibiotic-laden sludge	260°C , 60 min, 1 MPa, 5 g/L (catalyst dosage)	The removal rate of COD: 81.2% The removal rate of VSS: 93.8%	[15]
Cu-loaded Al_2O_3	Maleic acid (500 mg/L)	70°C , 60 min, 5 g/L (catalyst dosage), H_2O_2 : 0.09 mol/L	The removal rate of TOC: 98%	[50]
Cu/ Al_2O_3	Phenol (280 mg/L)	70°C , 60 min, 5 g/L (catalyst dosage), H_2O_2 : 0.09 mol/L	The removal rate of TOC: 96.8%	[51]
Cu-Ce/ $\gamma\text{-Al}_2\text{O}_3$	Pharmaceutical sludge	260°C , 60 min, 1 MPa, 10 g/L (catalyst dosage)	The removal rates of COD and VSS: 62.5%, 86.8%	[22]
Cu-Ce/ $\gamma\text{-Al}_2\text{O}_3$	Coal chemical sludge	260°C , 60 min, 1 MPa, 7 g/L (catalyst dosage)	The removal rate of VSS: 93.2%	[38]
Cu/ $\gamma\text{-Al}_2\text{O}_3$	Pharmaceutical sludge	260°C , 60 min, 1 MPa, 5 g/L (catalyst dosage)	The removal rate of COD and VSS: 76.5%, 93.6%	[46]

Table 6. Cont.

Catalyst	Original Sludge Type	Reaction Condition	Treatment Results	Reference
Cu/g-C ₃ N ₄ @AC	Phenol	120 °C, 60 min, 0.5 MPa	The removal rate of COD: 92.6%	[52]
FeOCl/Montmorillonite	Fuchsin (200 mg/L)	60 °C, 210 min, 1 g/L (catalyst dosage), H ₂ O ₂ : 0.38 mol/L	The removal rate of COD: 70.8%	[53]
CuO doped with Ce	Quinoline (100 mg/L)	75 °C, 85 min, 1 g/L (catalyst dosage), H ₂ O ₂ : 196 mmol/L, pH = 7.3	The removal rate of Quinoline and TOC: 98.1%, 86.1%	[54]
Cu/TiO ₂	Cresol (1000 mg/L)	140 °C, 120 min, 2 MPa, 10 g/L (catalyst dosage)	The removal rate of COD: 79.1%, the degradation of cresol: 100%	[55]
Ce-modified Cu-based carbon	Phenol (1000 mg/L)	160 °C, 330 min, 3 MPa, 40 mg (catalyst dosage), pH = 9	The removal rate of COD: 89%	[56]
N-La ₂ CuO ₄	Phenol (8000 mg/L)	140 °C, 30 min, 1 MPa, 1 g/L (catalyst dosage), pH = 9	The removal rate of COD: 87.1%	[57]
Fe ₃ C@NCNT/PSSF	Phenol (1000 mg/L)	80 °C, 7 h, H ₂ O ₂ : 5.1 g/L	The removal rate of TOC: 41%, phenol conversion: 90%	[58]
PrFe _x Co _{1-x} O ₃ /Mt	2-Hydroxybenzoic acid	80 °C, 210 min, 0.5 g/L (catalyst dosage), H ₂ O ₂ : 20.56 mmol/L, pH = 5.5	Degradation rate 97.6%, the removal rate of COD: 75.23%	[59]
CoFe ₂ O ₄ @SiO ₂	Chlorobenzenes	110 °C, 40 min, 0.3 g/L (catalyst dosage), PS: 15 mM	The removal rate of TOC: 41%	[60]
CuO/γ-Al ₂ O ₃	Reactive Red X-3B (0.3 g/L)	80 °C, 150 min, 5.5 g/L (catalyst dosage), H ₂ O ₂ : 0.39 mol/L, pH = 8	Degradation rate 90.72%, the removal rate of TOC: 45.26%	[61]
FeSO ₄ /Ca(ClO) ₂	Mechanical processing wastewater sludge	180 °C, FeSO ₄ ·7H ₂ O/Ca (ClO) ₂ : 1.25, Ca(ClO) ₂ : 0.04, pH: 5.9 ~ 7.4	Moisture content: 51.72% (initial sludge: 76.30%)	[20]

Recent research indicates that non-homogeneous catalysts dominate current studies, reflecting their increasing importance. These catalysts serve diverse functions, enabling the treatment of sludge as well as the removal of organic pollutants from wastewater. Notably, catalysts composed of the same element can yield varying removal efficiencies for different types of sludge. For instance, when comparing the VSS removal rates of Cu-Ce/γ-Al₂O₃ for antibiotic sludge, pharmaceutical sludge, and coal chemical sludge, it was found that the catalyst performed best with antibiotic sludge [15,22,38]. Therefore, selecting an appropriate catalyst is crucial for enhancing the efficiency of catalytic hydrothermal oxidation in sludge treatment.

In addition, the related effects of the addition of catalysts on the treatment of sludge by HTO technology were summarized. The study found that the effects of the addition of catalysts on the treatment of sludge by HTO technology mainly included the following aspects: The first was enhanced removal of pollutants. For instance, Wang et al. utilized a synthesized Cu-Ce/γ-Al₂O₃ catalyst in a CWO process to treat excess activated sludge from coal chemical wastewater. The results showed that, under conditions of 7.0 g/L catalyst, 1.0 MPa initial oxygen pressure, 260 °C temperature, and a reaction time of 60 min, the removal rate of volatile suspended solids reached 93.2%, while the COD removal rate was 78.3% [38]. Xu et al. compared the efficiency of sludge treatment using HTO with and without catalysts, finding that the use of a homogeneous catalyst improved COD removal efficiency by over 10%. This enhancement is attributed to the ability of the catalyst to lower operational temperatures, increase reaction rates, and shorten retention times. Furthermore, when comparing different catalysts, it was observed that using Cu-Ce/γ-Al₂O₃ at 260 °C, 1.0 MPa, and 10 g/L for 60 min yielded the highest removal rates for VSS and COD, reaching 87.3% and 72.6%, respectively [22]. The second was an improved dewatering performance: Li et al. studied the interaction between peroxydisulfate, zero-valent iron (ZVI), and reaction time on sludge dewatering. Under optimal experimental conditions, the moisture content of the sludge was reduced to 54%, enhancing the dewatering performance of the hydrothermal oxidation technology. Additionally, when using the SC-M catalyst, the removal rates for metacresol and TOC were 98.1% and 84.2%, respectively [62]. The

third was increased resource utilization of sludge as a carbon source: Shang et al. found that adjusting catalysts and temperature during hydrothermal oxidation promotes the production of VFA from sludge. These VFAs can serve as an organic carbon source, thus reducing the overall costs associated with hydrothermal oxidation technology [46]. It is important to note that the regulation of catalyst dosage also has a significant impact on sludge treatment. Table 7 illustrates the effect of varying additive dosages on the hydrothermal oxidation of sludge in current studies. The research indicates that an appropriate number of additives can enhance COD and VSS removal rates and promote ammonia nitrogen generation. However, excessive additive amounts can lead to reduced dewatering performance or lower SCOD removal rates. Therefore, it is crucial to determine an optimal dosage to avoid secondary pollution caused by excessive additions.

Table 7. Influence of additive content (AC) change on sludge treatment by HTO technology in recent years.

Original Sludge Type	Treatment Process	Optimal AC	Effect of Additive Concentration (C) Change	References
Pharmaceutical Sludge	CWO	5.0 g/L Cu-Ce/ γ -Al ₂ O ₃	C increases, the removal rate of COD and VSS remain basically unchanged after increasing gradually	[15]
Machining Wastewater Sludge	CWO	FeSO ₄ ·7H ₂ O/Ca(ClO) ₂ : 1.25	C increases, the dewatering property increased first and then decreased	[20]
Coal Chemical Sludge	CWO	7.0 g/L Cu-Ce/ γ -Al ₂ O ₃	C increases, the removal rate of COD is significantly increased, while the effect of VSS is slight	[38]
Municipal Sludge	CWPO	H ₂ O ₂ : 15%	C increases (H ₂ O ₂ from 0% to 15%); with the increase in H ₂ O ₂ mass fraction, lower solid yield and higher liquid gas yield can be achieved, which can improve the dehydration performance; the concentration of ammonia nitrogen increases first, then stabilizes and then increases, and the concentration of acetic acid increases	[44]
Urban Sludge	CWPO	0.2M K ₂ S ₂ O ₈	C increases, the concentration of TP in liquid products increases rapidly from 103.85 to 422.87 mg/L, an increase of 307.19%	[63]
Pharmaceutical Sludge	CWO	10 g/L Cu-Ce/ γ -Al ₂ O ₃	C increases, the removal rate of COD is significantly increased, while the removal efficiency of COD is only slightly increased compared with that of VSS	[22]
Pharmaceutical Sludge	CWO	5 g/L Cu/ γ -Al ₂ O ₃	C increases, the removal rate of TCOD increases significantly, but the removal rate of VSS does not change much	[46]
Oilfield Sludge	SCWO	20 wt% Ni/Al ₂ O ₃	C increases, the removal rate of TOC increases, the CO ₂ production rate increases, and the production of CO and CH ₄ decreases	[48]

Overall, the addition of catalysts significantly enhances the effectiveness of HTO for sludge treatment, leading to improved pollutant removal, better dewatering, and greater resource recovery. In summary, CWO demonstrates unique advantages in sludge treatment. Compared to traditional hydrothermal oxidation, it achieves higher reaction efficiency, enabling deep oxidative decomposition of organic matter in sludge in a shorter time frame, significantly reducing processing time and energy consumption. Moreover, this technology is environmentally friendly, converting organic substances in sludge into harmless materials and facilitating resource recovery, thereby minimizing environmental pollution and treatment costs. As environmental protection standards continue to rise,

CWO has substantial development potential. It can be integrated with other methods to further enhance sludge treatment efficacy. In the future, ongoing optimization of catalysts and processes is expected to establish this technology as one of the mainstream approaches for sludge treatment, providing robust support for the harmless, reduced, and resource-efficient management of sludge.

Moreover, oxidants and catalysts can work synergistically in HTO technology to achieve more significant treatment effects on sludge containing high levels of antibiotics. For instance, Yang et al. studied the use of acidified red mud (ARM) in a catalytic wet peroxide oxidation (CWPO) system to degrade antibiotic-laden sludge and produce the hydrogen carrier formic acid. In their experiments, under conditions of 90 °C, a reaction time of 30 min, H₂O₂ concentration of 20 mL/L, ARM dosage of 0.8 g/L, pH = 7, and stirring at 500 rpm, the yield of formic acid reached 792.38 mg/L [32]. Similarly, Ning et al. investigated the use of Fe (II)-activated persulfate-assisted hydrothermal treatment (Fe (II)-PS-HT) to enhance nitrogen removal efficiency from sewage sludge (SS) under relatively mild conditions (150 °C, 20 min). Their findings revealed that the nitrogen removal rate from SS treated under these optimal conditions was 35.0% higher than that of SS subjected to conventional high-temperature treatment [64]. These studies demonstrate that the incorporation of oxidants and catalysts enables HTO technology to achieve excellent sludge treatment outcomes without the need for high temperatures. This approach offers new insights into the degradation and resource recovery of sludge.

(3) Supercritical water oxidation sludge treatment

Subcritical water (100 °C < T ≤ 373.946 °C), also known as superheated water, thermal pressurized water, or pressurized hot water (PHW), is a liquid with pressure above its saturated vapor pressure (SVP). Chen et al. concluded that, in the presence of air, subcritical water at relatively high temperatures (200–325 °C) and pressures (5–15 MPa) can generate large amounts of highly reactive hydroxyl radicals with high oxidation potential. As a result, subcritical water oxidation has demonstrated excellent performance as an advanced oxidation process (AOP) for degrading refractory wastewater and sludge [65]. Based on this example and the above-mentioned content, it was found that the previous optimization efforts were all subcritical; although the treatment effect of sludge was enhanced, the reaction times were not fast, all of them being around 1 h or even longer. In order to speed up the reaction rate, researchers also discovered the supercritical water oxidation technology for sludge treatment. It has been reported that, at pressures and temperatures above the critical point (P = 22.064 MPa, T = 373.946 °C), water behaves as a typical fluid known as supercritical water. SCWO offers advantages over conventional hydrothermal oxidation, including faster reaction rates, thorough treatment, and no secondary pollution. It can convert heteroatoms such as chlorine, sulfur, and phosphorus into their respective inorganic acids or salts, and it can also mineralize heavy metals, depositing them as stable solid residues [36]. Li et al. reviewed the treatment effects and kinetic parameters of various nitrogen-containing organic compounds and NH₃-N in the SCWO environment, analyzing the transformation pathways of organic nitrogen in different nitrogen groups to understand its degradation mechanisms. Their results indicated that nitro-containing organic compounds primarily convert nitrogen into nitrogen oxides (NO_x[−]) in the form of nitrogenous intermediates, while the main intermediate for amino-containing or nitrogen-heteroatom organic compounds is NH₃-N. For organic compounds containing both amino and nitro groups, the generated NO_x[−] can react with NH₃-N through redox processes to form N₂. Furthermore, supercritical water oxidation, when coupled with conventional oxidants like H₂O₂ or O₂ under relatively mild SCWO conditions, enhances the synergistic removal efficiency of COD or TOC and NH₃-N while avoiding the generation of NO_x, NO₃[−], and NO₂[−], converting organic nitrogen into environmentally friendly products such as N₂ and N₂O [36]. Yan et al. investigated the effect of adding a Ni/Al₂O₃ catalyst in the SCWO process, with reaction conditions set at 450 °C for 20 min, achieving TOC removal and carbon conversion to gas phase efficiency of 95.2% and 68.2%, respectively [48]. The study revealed that the advantage of SCWO technology lies in its ability to achieve efficient

conversion of organic matter in a short time, far surpassing traditional hydrothermal oxidation in treatment efficiency. Additionally, SCWO does not produce harmful by-products such as dioxins, and inorganic salts can be recovered in solid form, reducing the complexity and cost of subsequent treatment processes.

2.5.3. Optimization Measures for the Reactor

In addition to the optimization of the hydrothermal oxidation process itself, improvements in reactor design and process flow are also crucial for enhancing sludge treatment efficiency. Traditional HTO technologies operate at high temperatures and pressures, leading to expensive equipment costs and safety concerns. Therefore, optimizing reactors and refining process designs can significantly increase treatment efficiency, reduce operational costs, and promote the widespread application of HTO in sludge treatment. WO technology is an early form of HTO. Initially, reactors were designed as high-pressure vessels where the organic matter in sludge reacts with oxygen under controlled temperatures (150–374 °C) and pressures (2–15 MPa). The Zimpro wet oxidation reactor is a classic example of this technology; it efficiently removed organic pollutants from sludge. However, its high energy consumption and equipment costs limited its widespread use [66]. As demand grew, reactor designs evolved from simple high-pressure vessels to catalytic wet oxidation reactors, where metal catalysts were introduced to lower reaction temperatures and pressures, improving efficiency. Later, SCWO technology marked a significant breakthrough. The unique properties of supercritical water enabled the effective decomposition of organic matter at higher temperatures and pressures, although issues such as equipment cost and material corrosion remained [36]. For instance, Fidel A. Mato and colleagues proposed a novel energy recovery method based on injecting reactor effluents into gas turbines, utilizing ultrafiltration and evaporation units for front-end concentration while employing SCWO reactors as the main treatment unit. This method was found to be more efficient compared to simpler direct-use methods [67].

In recent years, further advancements in HTO technology have included the development of tubular reactors, fixed-bed reactors, and continuous-flow reactor designs, all aimed at making the process more efficient. For example, the Vertech wet oxidation reactor significantly reduced energy consumption through heat recovery [68]. The introduction of multiphase reactors, which incorporate solid catalysts in liquid-phase reactions, has notably increased the reaction rate between oxygen and organic matter. The latest wet peroxide oxidation reactors (WPO) utilize hydrogen peroxide as a strong oxidizing agent, achieving high removal efficiencies for organic matter at lower temperatures and pressures [69]. Consequently, researchers have increasingly focused on reactor optimization. For instance, Yamasaki et al. proposed a hydrothermal catalytic plasma reactor to expand the treatment capacity for water-soluble volatile organic compounds (VOCs), such as toluene, acetaldehyde, acetic acid, and ammonia. They also installed a manganese dioxide catalytic unit downstream to remove ozone, further improving efficiency. Mato et al. developed an energy recovery system utilizing gas turbines to optimize the entire process flow by recovering energy from reactor effluents [67,70]. Additionally, Qiu et al. designed a dual-shell reactor using hydrothermal flames as an internal heat source, effectively avoiding corrosion, salt blockages, and overheating while demonstrating advantages in both economic and energy efficiency [27].

Overall, reactors used in wet oxidation and HTO technologies have evolved from simple high-pressure vessels to more advanced, environmentally friendly designs that incorporate catalysts, supercritical conditions, and energy recovery innovations. These developments have greatly enhanced sludge treatment efficiency while reducing costs. As these optimizations continue, the potential for HTO technology in sludge treatment will expand significantly.

2.6. Comparison of Sludge Before and After HTO Treatment

In order to study the changes before and after the reaction of sludge treated by hydrothermal oxidation technology, including its treatment efficiency of organic pollutants and dewatering performance of sludge and product composition, the following summary was made, as shown in Table 8:

Table 8. Comparison of sludge changes before and after hydrothermal oxidation treatment of sludge.

Original Sludge Type	Treatment Process	Before Treatment	After Treatment	Reference
Pharmaceutical Sludge	CWO	COD: 15,000–16,000	COD and VSS removal rates: 81.2%, 93.8%	[15]
Municipal Sludge	HTO-Alkaline Hydrolysis	TCOD: 12,000, COD: 285–320, TP: 25.52, pH: 6.52	COD: 69,500, TP: 1145, pH: 11.8, TN: 2150 (NH ₃ -N: 1080, NO ₃ -N: 693)	[11]
Municipal Sludge	HT-HTO	Soluble TOC and COD: 65, 164; total TOC and COD: 3880, 13,000 ± 260; TSS, VSS: 14,448 ± 28.3, 9310 ± 12.5, ammonium nitrogen and protein (liquid phase): 14 and 0.5	Total COD and VSS removal rate 55%, 90%, TOC: 2750, soluble COD, protein, carbohydrate concentration: 5800, 2250, 900, NH ₄ ⁺ -N concentration is 600, acetic acid, propionic acid, butyric acid and isobutyric acid concentration: 400, 100, 10–15.	[29]
Coal Chemical Sludge	HTO	Total COD: 20,000–25,000, pH: 7.42–8.56	COD and VSS removal rates: 78.6%, 89.3%, acetic acid, formic acid, and oxalic acid concentrations: 7000, about 1500	[35]
Mechanical Processing Wastewater Sludge	CWO	Initial sludge with particle size 100–200 µm, moisture content 76.30%	Sludge particle size significantly reduced, moisture content 51.72%	[20]
Coal Chemical Sludge	CWO	COD: 16,500–17,500, VSS/SS 81.3%, pH: 8.47	COD, VSS, and SCOD removal rates: 78.3%, 93.2%, 83%; acetic and VFAs concentrations: 4000, 4750	[38]
Municipal Sludge	CWPO	Moisture content: 95.5%, TN: 12.5, NH ₄ ⁺ : 10.3, CST: 163.5	Moisture content: 38.5%, SCST: 8.74, CWR: 89.2%, TOC: 285.6, TN: 153.4, NH ₄ ⁺ : 52.3	[21]
Municipal Sludge	CWPO	N: 4.24%, volatile: 45%, fixed carbon: 9%	Denitrification rate: 76.2%, protein: 4184	[64]
Municipal Sludge	CWPO	Ammonia nitrogen: 1230, moisture content: 46.41%	Acetic acid: 2923.41, moisture content: 45.70%, ammonia Nitrogen: 2100	[44]
Urban Sludge	HTO	TCOD: 22,030 ± 40, SCOD: 350 ± 150, TOC: 6100 ± 800, TSS: 33,000 ± 1000, VSS: 26,800 ± 400	SCFA: 6070, acetic acid accounts for 28.2%, 2830 ± 80, non-volatile lactic acid: 750 ± 20, lactic acid bacteria, malic acid, oxalic acid, pyruvate and formic acid concentration: 160 ± 50, 110 ± 10, 1300 ± 100, 700 ± 6, 1190 ± 80	[41]
Municipal Sludge	HTO/HT	Ni, Cu, Hg, Cr, Zn: 28, 150, 0.6, 19, 340 mg/g	Ni, Cu, Hg, Cr, Zn removal rates: 86.7%, 56.1%, 35.7%, 14%, 11.2%	[30]
Urban Sludge	CWPO	Organic matter content: 44.22%, TN: 18.89 mg/g, TP: 18.36 mg/g	98% phosphorus recovery in liquid phase (solid recycling water: 9.47% ± 0.21%), liquid TOC removal rate: 376.45–744.80 mg/L, solid TP: 0.96 ~ 5.02 mg/g	[63]
Urban Sludge	HTO	TCOD: 53,540–60,677, TN: 2976–3255, TP: 1733–1955, Soluble Ammonia Nitrogen: 45–50	COD and TOC removal rates: 60–70%, 68.1%; amino acids, proteins, humic acid derivatives, VFAs, acetic acid concentrations: 3000, 5151, 2400, 4199, 3900; SCOD: 10,000, TN: 5000	[45]

Table 8. Cont.

Original Sludge Type	Treatment Process	Before Treatment	After Treatment	Reference
Pharmaceutical Sludge	CWO	COD: 15,000–16,000, VSS: 13,500–13,800, VSS/SS ratio: 39–40%, pH: 7.5–8.0	COD and VSS removal rates: 72.6%, 87.3%	[22]
Pharmaceutical Sludge	CWO	TCOD: 16,500–18,000, TSS: 16,300–17,800, VSS: 13,200–14,100, pH: 7.3–7.8	TCOD and VSS removal rates: 76.5%, 93.6%	[46]
Pharmaceutical Sludge	CWO	TCOD: 19,000–20,000 g/L; VSS: 15,500–15,800 g/L, pH: 7.5–8.5	COD and VSS removal rates: 57.3%, 95.2%; acetic, formic, and oxalic acid concentrations: 8000, 2000, 2250	[47]
Oilfield Sludge	SCWO	Volatile: 7.3 wt%, fixed carbon: 73.84 wt%, C: 48.18 wt%, N: 0.36 wt%, S: 0.28 wt%	TOC removal rate: 95.2%, TOC concentration: 1368.5, COD: 3832.5; carbon conversion rate (CE): 68.2%, w_{CO_2} : 53.6%, $w_{aqueous}$: 29.7%, w_{CH_4} : 6.7%, w_{CO} : 10.8%	[48]
Pharmaceutical Sludge	CWO	VSS: 160.6 g/L; TSS: 192.3 g/L; VSS/TSS: 83.5%; pH: 8.17; TCOD: 206.3 g/L	TSS: 90.1%, VSS: 98.4%, TCOD: 78.7%, COD: 81.6%, volatile fatty acids: 4819	[16]
Urban Sludge	HTO	TS: $1.7 \pm 0.1\%$; VS/TS: $58.5 \pm 0.5\%$; pH: 7.8 ± 0.1 ; TCOD: 12.0 ± 0.3 g/L; SCOD: 7.1 ± 0.3 g/L; TN: 3.3 ± 0.2 g/L	Ammonia nitrogen: 3609, amino acids, humic acid derivatives, acetic acid concentrations: ~3000, 2400, 3900	[42]

Note: The above ununit data use a unit of uniform concentration—mg/L.

From Table 8, it is evident that sludge undergoes significant changes after treatment with hydrothermal oxidation technology, which is reflected in several key aspects: first, the dewatering performance of the sludge improves, leading to a reduction in moisture content. Second, the removal rates of TOC and VSS increase, enhancing the removal of organic pollutants from the sludge. Finally, the products after treatment are mainly volatile fatty acids (acetic acid content is the most), nitrogen (ammonia nitrogen content is the most), phosphorus, carbon dioxide, etc.

The development of the above optimization measures can be summarized as follows: first, HTO technology uses oxidants to replace oxygen, avoiding the safety risks brought by oxygen injection. Second, the addition of catalysts reduces the operating temperature of the equipment while enhancing the degradation of organic matter in sludge. Third, supercritical oxidation technology further improves the harmless disposal of sludge. Finally, advancements in reactor design and upgrades play a crucial role. In addition to these optimization methods, pretreatment techniques such as ultrasonic processing or acid/alkali pretreatment can also enhance the efficiency of HTO in sludge treatment. However, due to the complex composition of sludge, some byproducts are inevitably generated after treatment. To reduce processing costs, resource recovery from these byproducts can be employed to improve economic viability.

2.7. Resource Recycling

From the literature reviewed, it is evident that the sludge treated by hydrothermal oxidation contains rich nutritional components such as proteins, nitrogen (N), and phosphorus (P). Below, we summarize several potential and common applications of the products obtained from treated sludge, categorized into three main aspects: solid products, liquid products, and gaseous products, as shown in Figure 4.

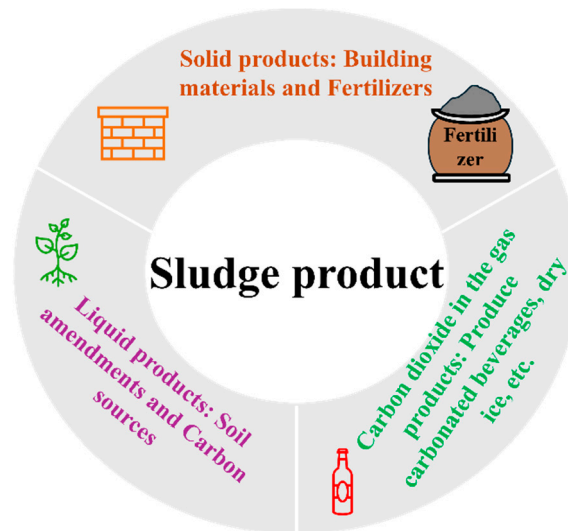


Figure 4. Application of sludge-treated products.

2.7.1. Solid Products

The solid products obtained from the hydrothermal oxidation of sludge typically possess the following characteristics: first, the pollutants, mostly inorganic substances, are effectively removed; second, they contain essential nutrients such as nitrogen, phosphorus, potassium, calcium, and magnesium. Based on these characteristics, the solid products can be utilized in several ways.

(1) Construction Materials

After hydrothermal oxidation treatment, the sludge demonstrates not only an improved dewatering performance, but also significantly reduced organic pollutants. The inorganic content of the solid products is relatively high and stable. Therefore, these solid products can be further processed for use as construction materials, such as brick-making raw materials. Their particle size and composition characteristics can meet the strength requirements for bricks, facilitating resource recovery from sludge and reducing the need for natural raw materials. For example, Zeng et al. demonstrated that, after catalyst treatment, the COD and VSS of sludge were reduced to a certain extent, and the resulting inorganic residues could be used for the production of construction materials [22]. Wang et al. found that, following hydrothermal oxidation, the sludge particles decreased in size and showed increased porosity, which aided in the release of intercellular moisture, thereby enhancing dewatering performance. The solids can be used to produce ceramic aggregates or permeable bricks. Additionally, these materials can serve as fillers for wastewater treatment, effectively utilizing waste [38].

(2) Fertilizers and Soil Conditioners

The treated solid products contain certain amounts of nutrients and minerals, such as nitrogen, phosphorus, potassium, calcium, and magnesium, allowing for their use as fertilizers. For instance, Cañas et al. studied phosphorus recovery from wastewater sludge treated by hydrothermal oxidation. Under high-temperature (up to 300 °C) and high-pressure (up to 200 bar) conditions, the process achieved high removal rates of organic matter (up to 85% COD) and total solids (up to 75%). Liquid and solid fractions recovered from the effluent contained significant amounts of recoverable phosphorus. In the liquid effluent, phosphorus was recovered as struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), a slow-release fertilizer, reaching concentrations of up to 90 mg P/L. The recovered struvite can be utilized as fertilizer [37]. Similarly, Liu et al. found that high reaction temperatures converted organic phosphorus and phosphate into non-hydroxyl phosphorus. The sludge cake enriched with non-hydroxyl phosphorus post-hydrothermal oxidation can serve as a soil conditioner. Notably, researchers also validated this hypothesis using seed germination

tests, finding that the effluent from treated sludge promoted plant germination and growth, although different seeds required varying concentrations. The results indicated that the effluent had a beneficial effect on seed growth [45].

2.7.2. Liquid Phase Products

The liquid products consist of partially oxidized organic substances and dissolved inorganic salts, mainly volatile fatty acids (mainly acetic acid, formic acid, propionic acid, etc.), ammonia nitrogen, etc. These liquids can be further processed to recover energy and nutrients, with several main applications as follows:

(1) Soil Amendments

The liquid products obtained from hydrothermal oxidation contain essential nutrients. After appropriate treatment and purification, they can be used as liquid fertilizers for agricultural irrigation, providing nutrients to crops and promoting growth while reducing reliance on freshwater resources. For instance, Liu et al. proposed a resource recovery method, revealing that, after treatment at 240 °C, phosphorus, potassium, and heavy metals remained in the solid phase. The effluent contained ammonium nitrogen at 2800 mg/L, amino acids near 3000 mg/L, humic acid derivatives at 2400 mg/L, and acetic acid at 3900 mg/L. Acetic acid aids in seed germination, while the other components are crucial for root growth. Thus, the solid products from sludge treatment have potential as soil amendments. Applying these products to impoverished soils can enhance organic matter content and promote plant growth. Their study demonstrated that diluted effluent significantly improved germination and development of three plant species, especially scallions, with a germination index exceeding 200% [42]. It is important to strictly control pollutant levels during application, employing methods such as filtration, sedimentation, and biological treatment to remove harmful substances and ensure compliance with standards.

(2) Carbon Source

Under hydrothermal conditions, sludge undergoes hydrolysis and oxidation, generating small organic acids such as acetic acid, formic acid, and oxalic acid as primary products, which can serve as carbon sources in wastewater treatment. Xu et al. noted that using a Cu-Ce/ γ -Al₂O₃ catalyst at an initial oxygen pressure of 1.0 MPa and 10 g/L of catalyst allowed the exothermic wet oxidation reaction to sustain itself. The produced low molecular weight carboxylic acids have potential commercial applications as organic carbon sources in biological wastewater treatment [22]. Similarly, Qin et al. found that hydrothermally treated coal chemical sludge yielded primarily acetic acid, formic acid, and oxalic acid, which can also serve as carbon sources in wastewater treatment. Therefore, wet oxidation can facilitate the resource recovery of organic carbon [35]. Additionally, research by Chu et al. indicates that sludge treated via catalytic hydrothermal oxidation has potential as a carbon source, as the degradation products mainly include acetic acid and propionic acid. Biological treatment experiments showed that the degradation liquid after catalytic wet oxidation has the potential to meet the carbon source requirements for biological treatment, aiding in the removal of COD and TN [15]. This work confirms the effectiveness of the catalyst in treating antibiotic-laden sludge, providing new insights for the rational disposal of such sludge.

2.7.3. Gaseous Phase Products

The gaseous products primarily consist of carbon dioxide (CO₂), nitrogen (N₂), and other small molecular gases, possibly including trace amounts of combustible gases such as methane and hydrogen. These gases can be collected and purified for various applications. For instance, the produced carbon dioxide can be utilized for greenhouse gas management, as a resource in the production of carbonated beverages, or dry ice, or to enhance plant photosynthesis. Nitrogen, being an inert gas, finds use in packaging, metal processing, and the electronics industry. Additionally, the gases generated during hydrothermal oxidation can be harnessed for thermal energy recovery, providing energy for electricity

generation and heating within the plant, thereby reducing overall energy consumption while generating economic benefits. For example, Zhang et al. found that, during wet air oxidation (WAO) of digested sludge, insoluble organic matter is converted into volatile fatty acids (VFAs), ammonia, nitrates, nitrites, organic nitrogen, and carbon dioxide. The study also indicated that the WAO method can decompose digested sludge, with subsequent anaerobic digestion (AD) further producing methane [42].

Overall, the solid-phase products of sludge treated with HTO technology are primarily inorganic compounds. The liquid-phase products mainly include non-volatile fatty acids (with acetic acid as the main component), aldehydes, ketones, and aromatic compounds, while the gas-phase products consist mostly of carbon dioxide and nitrogen. Under ideal reaction conditions, these intermediate products can eventually be converted into acetic acid and carbon dioxide. However, in engineering practice, excessively pursuing organic conversion can significantly increase energy consumption and operational costs, making it impractical for real-world production needs. As a result, achieving the ideal outcomes may not always be feasible.

This highlights the necessity of predicting the products of sludge treatment under different conditions, designing well-planned treatment schemes, and preventing the formation of unexpected byproducts. For example, Arrian Prince-Pike developed a detailed kinetic model for the wet oxidation of municipal sludge. This model can predict the concentrations of intermediate products that are critical to the biological nutrient removal (BNR) process under various reaction conditions, providing insights into the concentration of key intermediates during wet oxidation [71].

Therefore, to successfully apply HTO technology in industrial settings, continuous experimental research is essential to further refine and optimize the technology.

3. Conclusions and Prospect

Hydrothermal oxidation technology shows remarkable promise in the field of sludge treatment. Current research indicates that this technology offers a highly potential solution to various sludge disposal challenges. On one hand, hydrothermal oxidation effectively achieves sludge reduction and harmless treatment. By conducting reactions under optimized conditions, it rapidly decomposes organic pollutants in the sludge and enhances dewatering performance, thereby addressing land occupation issues associated with sludge. The removal of harmful substances from the sludge also mitigates risks for subsequent disposal and utilization, transforming sludge from waste into useful materials—an essential consideration in today's increasingly strained land resources. On the other hand, resource recovery stands out as a significant advantage of hydrothermal oxidation in sludge treatment. The products recovered after treatment can be repurposed as building materials, carbon sources, or fertilizers, contributing to successful waste utilization and promoting resource recycling.

However, hydrothermal oxidation technology is not without its challenges. Several issues remain: (1) Cost: The implementation costs of these emerging technologies are currently high, particularly for industrial applications, which require substantial investment in equipment and operational expenses, potentially limiting widespread adoption. (2) Technological maturity: Compared to traditional wastewater treatment technologies, hydrothermal oxidation is still in a developmental stage, lacking sufficient long-term industrial application data to support its broader use. (3) Byproduct management: During the HTO process, the addition of certain additives may lead to the formation of toxic intermediate products. Additionally, some catalysts contain heavy metals that can leach into the products due to losses during use. These byproducts can hinder the subsequent resource recovery and utilization of the treated sludge.

In light of the future development of this research, several prospects and key areas of focus are proposed:

(1) Achieving sludge self-catalysis: Given the excellent performance of CWO, future research should focus on developing new catalysts that promote the hydrothermal oxidation

of sludge. Beyond enhancing the catalyst's function, it is also crucial to explore whether the catalyst can enable the sludge to self-catalyze during the CWO process. This would allow the sludge itself to promote the removal of harmful substances, such as organic pollutants and heavy metals.

(2) Prediction, planning, and control of products: Developing precise techniques for detecting product composition, such as advancements in liquid and gas chromatography, is essential. Alternatively, new kinetic models can be designed to accurately analyze the treated products. Furthermore, when utilizing these products as resources, it is necessary to test relevant parameters to ensure they meet usage standards. For example, the concentration of heavy metals must remain below the acceptable thresholds.

(3) Elimination of ammonia nitrogen: At present, there is a large amount of ammonia nitrogen in the liquid phase of sludge treated by hydrothermal oxidation process, so it is very important to solve the issue regarding the potential harm of ammonia nitrogen. Future efforts should focus on further eliminating ammonia nitrogen and potentially converting it into nitrogen gas. This would improve the safety of sludge treatment and enhance the decontamination process.

(4) Improving sludge dewatering performance: While hydrothermal oxidation technology can improve sludge dewatering, the results are not yet optimal. Future research should investigate how to enhance the dewatering efficiency to achieve more effective sludge reduction.

(5) Producing a single carboxylic acid: A key finding of this study is that hydrothermal treatment of sludge can produce various volatile fatty acids such as acetic acid and propionic acid, along with non-volatile acids like lactic acid. This raises the question of whether it is possible to regulate the sludge treatment process to produce a single type of carboxylic acid. For example, if only acetic acid were produced, it could be entirely used as a carbon source. Moreover, the detection technology for different acids in the sludge effluent requires further optimization. Advanced chromatographic techniques could be employed to distinguish and separate these acids more effectively.

(6) Cost reduction: Successfully treated sludge products can be utilized for resource recovery, generating economic benefits and reducing overall costs. Additionally, using inexpensive oxidants and catalysts, as well as developing new technologies to enhance treatment efficiency, can further lower costs.

(7) Diversifying applications: Currently, the applications of treated sludge are somewhat limited, mainly focused on construction materials or soil conditioners. Further exploration is needed in areas such as electricity generation, hydrogen production, and methane production. Expanding the applications of sludge products and forming a comprehensive industrial chain would maximize the utility of treated sludge.

Additionally, equipment innovation and improvement will be a key focus of future research to enhance stability, reliability, and cost-efficiency. Looking ahead, hydrothermal oxidation technology has the potential to play an increasingly important role in sludge treatment. As the technology continues to evolve, costs will decrease, and efficiency will improve. Furthermore, combining this technology with other advanced methods could open new possibilities for sludge treatment. In the near future, hydrothermal oxidation is expected to become a mainstream technology in sludge management, contributing significantly to environmental protection and sustainable development.

Author Contributions: Conceptualization, H.Y. and Y.L.; methodology, H.Y., Y.L. and N.G.; software, Z.P. and W.P.; validation, J.W., L.W. and B.Z.; formal analysis, B.Z. and Y.Z.; investigation, J.W. and Y.Z.; resources, L.W.; writing—original draft preparation, H.Y., Y.L. and N.G.; writing—review and editing, W.P., H.Y. and H.W.; visualization, Z.P.; supervision, H.Y.; project administration, H.W.; funding acquisition, H.Y. and H.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (No. 52370127), Young Elite Scientists Sponsorship Program by China Association for Science and Technology (No. 2022QNRC001), Project LJ222410151015, supported by Fundamental Research Funds of

higher education Department of Liaoning Province (Program for Liaoning Innovative Research Team in University), and Fundamental Research Funds for the Central Universities (No. 3132023518). This work was financially supported by the National Key R&D Program of China (2023YFE0101000) and Innovation Research Fund of Dalian Institute of Chemical Physics (DICP I202320).

Data Availability Statement: The authors confirm that the data supporting the findings of this study are available from the authors upon reasonable request.

Conflicts of Interest: There are no conflicts to declare.

References

1. Khalidi-Idrissi, A.; Madinzi, A.; Anouzla, A.; Pala, A.; Mouhir, L.; Kadmi, Y.; Souabi, S. Recent advances in the biological treatment of wastewater rich in emerging pollutants produced by pharmaceutical industrial discharges. *Int. J. Environ. Sci. Technol.* **2023**, *20*, 11719–11740. [\[CrossRef\]](#) [\[PubMed\]](#)
2. Filipovic, K.; Petrovic, M.; Najdanovic, S.; Velinov, N.; Hurt, A.; Bojic, A.; Kostic, M. Highly efficient nano sorbent as a superior material for the purification of wastewater contaminated with anthraquinone dye RB19. *J. Water Process Eng.* **2024**, *67*, 106118. [\[CrossRef\]](#)
3. Radovic, M.D.; Mitrovic, J.Z.; Kostic, M.M.; Bojic, D.V.; Petrovic, M.M.; Najdanovic, S.M.; Bojic, A.L. Comparison of ultraviolet radiation/hydrogen peroxide, Fenton and photo-Fenton processes for the decolorization of reactive dyes. *Hem. Ind.* **2015**, *69*, 657–665. [\[CrossRef\]](#)
4. Mitrovic, J.; Vučić, R.M.; Kostic, M.; Velinov, N.; Najdanovic, S.; Bojic, D.; Bojic, A. Sulfate radicals-based degradation of anthraquinone textile dye in a plug flow photoreactor. *J. Serbian Chem. Soc.* **2019**, *84*, 1041–1054. [\[CrossRef\]](#)
5. Petrović, M.; Rančev, S.; Đorđević, M.P.; Najdanović, S.; Velinov, N.; Vučić, M.R.; Bojić, A. Electrochemically synthesized Molybdenum oxides for enhancement of atmospheric pressure non-thermal pulsating corona plasma induced degradation of an organic compound. *Chem. Eng. Sci.* **2021**, *230*, 116209. [\[CrossRef\]](#)
6. Petrović, M.; Jovanović, T.; Rančev, S.; Kovač, J.; Velinov, N.; Najdanović, S.; Kostić, M.; Bojić, A. Plasma modified electrosynthesized cerium oxide catalyst for plasma and photocatalytic degradation of RB 19 dye. *J. Environ. Chem. Eng.* **2022**, *10*, 107931. [\[CrossRef\]](#)
7. Najdanović, S.M.; Petrović, M.M.; Slipper, I.J.; Kostić, M.M.; Prekajski, M.D.; Mitrović, J.Z.; Bojić, A.L. A New Photocatalyst Bismuth Oxo Citrate: Synthesis, Characterization, and Photocatalytic Performance. *Water Environ. Res.* **2018**, *90*, 719–728. [\[CrossRef\]](#) [\[PubMed\]](#)
8. Liang, C.-Z.; Sun, S.-P.; Li, F.-Y.; Ong, Y.-K.; Chung, T.-S. Treatment of highly concentrated wastewater containing multiple synthetic dyes by a combined process of coagulation/flocculation and nanofiltration. *J. Membr. Sci.* **2014**, *469*, 306–315. [\[CrossRef\]](#)
9. Haque, M.M.; Smith, W.T.; Wong, D.K.Y. Conducting polypyrrole films as a potential tool for electrochemical treatment of azo dyes in textile wastewaters. *J. Hazard. Mater.* **2015**, *283*, 164–170. [\[CrossRef\]](#) [\[PubMed\]](#)
10. Liu, P.; Zhang, Y.; Tang, H.; Wang, Y.M.; Sun, X.D. Prevalence of *Streptococcus suis* in pigs in China during 2000–2021: A systematic review and meta-analysis. *One Health* **2023**, *16*, 100513. [\[CrossRef\]](#)
11. Gong, W.J.; Huang, L.; Ji, Y.; Lv, J.J.; Guo, L.A.; Li, Y.; Li, J.X.; Ren, Y.L.; Zhang, J.J. Study on the reuse of municipal sludge treated with wet oxidation coupled with alkali hydrolysis. *Desalination Water Treat.* **2023**, *294*, 40–50. [\[CrossRef\]](#)
12. Hou, J.C.; Hong, C.; Ling, W.; Hu, J.S.; Feng, W.B.; Xing, Y.; Wang, Y.J.; Zhao, C.W.; Feng, L.H. Research progress in improving sludge dewaterability: Sludge characteristics, chemical conditioning and influencing factors. *J. Environ. Manag.* **2024**, *351*, 119863. [\[CrossRef\]](#)
13. Ding, A.; Zhang, R.R.; Ngo, H.H.; He, X.; Ma, J.; Nan, J.; Li, G.B. Life cycle assessment of sewage sludge treatment and disposal based on nutrient and energy recovery: A review. *Sci. Total Environ.* **2021**, *769*, 144451. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Hušek, M.; Moško, J.; Pohořelý, M. Sewage sludge treatment methods and P-recovery possibilities: Current state-of-the-art. *J. Environ. Manag.* **2022**, *315*, 115090. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Chu, S.Y.; Lin, H.; Zeng, X. The Treatment of Antibiotic Excess Sludge via Catalytic Wet Oxidation with Cu-Ce/ γ -Al₂O₃ and the Production of a Carbon Source. *Water* **2024**, *16*, 1249. [\[CrossRef\]](#)
16. Fang, K.Y.; Zeng, X.; Yao, G.D.; Xia, S.Q.; Zhao, J.F.; Zhou, Y.Y.; Zhu, Y.T.; Li, X.J.; Qu, C.J. Wet Oxidation of Pharmaceutical Sludge for the Treatment and Production of Value-Added Materials. *Processes* **2023**, *11*, 2747. [\[CrossRef\]](#)
17. Bertanza, G.; Galessi, R.; Menoni, L.; Salvetti, R.; Slavik, E.; Zanaboni, S. Wet oxidation of sewage sludge: Full-scale experience and process modeling. *Environ. Sci. Pollut. Res.* **2015**, *22*, 7306–7316. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Liu, Z.M.; Yin, D.N.; Ge, H.J.; Zhou, G.; Song, T. Techno-economic analysis of municipal sludge co-combustion power generation with different fuels. *J. Environ. Chem. Eng.* **2023**, *11*, 111593. [\[CrossRef\]](#)
19. Guo, Y.Q.; Gong, H.; Shi, W.J.; Fang, N.; Tan, Y.Q.; Zhou, W.Q.; Huang, J.L.; Dai, L.L.; Dai, X.H.; Guo, Y.L. Insights into multisource sludge distributed in the Yangtze River basin, China: Characteristics, correlation, treatment and disposal. *J. Environ. Sci.* **2023**, *126*, 321–332. [\[CrossRef\]](#) [\[PubMed\]](#)
20. Chen, D.D.; Dou, Y.H.; Tang, Q.; Huang, Y.J.; Song, M.; Peng, F.R. New Insight on the Combined Effects of Hydrothermal Treatment and FeSO₄/Ca(ClO)₂ Oxidation for Sludge Dewaterability Improvement: Moisture Distribution and Noncovalent Interaction Calculation. *ACS OMEGA* **2020**, *5*, 15891–15900. [\[CrossRef\]](#)

21. Guo, J.Y.; Zhou, Y.L. Transformation of heavy metals and dewaterability of waste activated sludge during the conditioning by Fe^{2+} -activated peroxymonosulfate oxidation combined with rice straw biochar as skeleton builder. *Chemosphere* **2020**, *238*, 124628. [\[CrossRef\]](#)
22. Zeng, X.; Liu, J.; Zhao, J. Wet oxidation and catalytic wet oxidation of pharmaceutical sludge. *Sci. Rep.* **2023**, *13*, 2544. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Duan, Y.H.; Gao, N.B.; Sipra, A.T.; Tong, K.; Quan, C. Characterization of heavy metals and oil components in the products of oily sludge after hydrothermal treatment. *J. Hazard. Mater.* **2022**, *424*, 127293. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Chen, R.J.; Dai, X.H.; Dong, B. Mechanism insights into hydrothermal-activated tannic acid (TA) for simultaneously sewage sludge deep dewatering and antibiotics removal. *Water Res.* **2024**, *256*, 121619. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Kosińska, N.; Grosser, A.; Kwapińska, M.; Kwapiński, W.; Ghazal, H.; Jouhara, H.; Krzyżyńska, R. Co-hydrothermal carbonization as a potential method of utilising digested sludge and screenings from wastewater treatment plants towards energy application. *Energy* **2024**, *299*, 131456. [\[CrossRef\]](#)
26. Thomsen, L.B.S.; Anastasakis, K.; Biller, P. Wet oxidation of aqueous phase from hydrothermal liquefaction of sewage sludge. *Water Res.* **2022**, *209*, 117863. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Qiu, Y.; Zhang, F.; Yuan, Y.; Zhao, Y.; Liu, Y.; Rong, W. Thermodynamic and economic comparisons of supercritical water oxidation and gasification of oily sludge under hydrothermal flames. *Int. J. Hydrogen Energy* **2024**, *85*, 571–585. [\[CrossRef\]](#)
28. Jiang, G.Y.; Xu, D.H.; Hao, B.T.; Liu, L.; Wang, S.Z.; Wu, Z.Q. Thermochemical methods for the treatment of municipal sludge. *J. Clean. Prod.* **2021**, *311*, 127811. [\[CrossRef\]](#)
29. Malhotra, M.; Garg, A. Characterization of value-added chemicals derived from the thermal hydrolysis and wet oxidation of sewage sludge. *Front. Environ. Sci. Eng.* **2021**, *15*, 13. [\[CrossRef\]](#)
30. Pola, L.; Fernández-García, L.; Collado, S.; Oulego, P.; Díaz, M. Heavy metal solubilisation during the hydrothermal treatment of sludge. *J. Environ. Manag.* **2021**, *286*, 112120. [\[CrossRef\]](#)
31. Zhang, X.; Li, X.X.; Li, R.; Wu, Y.L. Hydrothermal Carbonization and Liquefaction of Sludge for Harmless and Resource Purposes: A Review. *Energy Fuels* **2020**, *34*, 13268–13290. [\[CrossRef\]](#)
32. Leng, L.J.; Zhang, W.J.; Leng, S.Q.; Chen, J.; Yang, L.H.; Li, H.L.; Jiang, S.J.; Huang, H.J. Bioenergy recovery from wastewater produced by hydrothermal processing biomass: Progress, challenges, and opportunities. *Sci. Total Environ.* **2020**, *748*, 142383. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Wang, L.P.; Chang, Y.Z.; Li, A.M. Hydrothermal carbonization for energy-efficient processing of sewage sludge: A review. *Renew. Sustain. Energy Rev.* **2019**, *108*, 423–440. [\[CrossRef\]](#)
34. Huber-Benito, D.; Martín-Martínez, M.; Larriba, M.; Agueda, I.; García, J. Enhanced prednisone removal by catalytic wet air oxidation using sewage sludge derived catalyst. *Process. Saf. Environ. Prot.* **2024**, *190*, 475–485. [\[CrossRef\]](#)
35. Qin, S.L.; Wang, Z.Q.; Zheng, W.C.; Zeng, X. Effects of reaction conditions on the wet oxidation of excess sludge from the caprolactam wastewater treatment process. *Water Sci. Technol.* **2023**, *88*, 2491–2498.
36. Li, J.N.; Wang, S.Z.; Li, Y.H.; Jiang, Z.H.; Xu, T.T.; Zhang, Y.S. Supercritical water oxidation and process enhancement of nitrogen-containing organics and ammonia. *Water Res.* **2020**, *185*, 116222. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Xu, H.; He, P.; Gu, W.; Wang, G.; Shao, L. Recovery of phosphorus as struvite from sewage sludge ash. *J. Environ. Sci.* **2012**, *24*, 1533–1538. [\[CrossRef\]](#)
38. Wang, Z.Q.; Qin, S.L.; Zheng, W.C.; Lou, X.D.; Zeng, X.; Wu, T.H. The Catalytic Wet Oxidation of Excess Activated Sludge from a Coal Chemical Wastewater Treatment Process. *Catalysts* **2023**, *13*, 1352. [\[CrossRef\]](#)
39. Chen, D.D.; Dou, Y.H.; Tang, Q.; Huang, Y.J.; Song, M.; Zhou, J.; Fu, L.C. New insight on the combined effects of hydrothermal treatment and $\text{FeSO}_4/\text{Ca}(\text{ClO})_2$ oxidation for sludge dewaterability improvement: From experimental to theoretical investigation. *Fuel Process. Technol.* **2020**, *197*, 106196. [\[CrossRef\]](#)
40. Fang, K.Y.; Yao, G.D.; Zhou, Y.Y.; Zhao, J.F.; Xia, S.Q. Effects of reaction temperature and oxygen pressure on dissolved organic matter in hydrothermal reactions of municipal sludge: A comprehensive analysis. *Chem. Eng. J.* **2024**, *495*, 153279. [\[CrossRef\]](#)
41. Núñez, D.; Zabatta, M.; Oulego, P.; Collado, S.; Riera, F.A.; Díaz, M. Production and purification of organic acids from partially oxidised waste activated sludge. *Sep. Purif. Technol.* **2024**, *343*, 126815. [\[CrossRef\]](#)
42. Zhang, Y.; Li, H.; Li, D. Maximize methane recovery from sludge anaerobic digestion by combining an optimal wet air oxidation process. *Renew. Energy* **2021**, *179*, 359–369. [\[CrossRef\]](#)
43. Wang, Y.; Shi, Y.F.; Fang, L.Y.; Wang, Z.P.; Wu, P.; Yang, X.; Shi, X.; Pi, K.W. Characteristics and aging of microplastics in waste activated sludge under persulfate and hydrothermal co-treatment: Impact of solid content and temperature. *Environ. Pollut.* **2024**, *358*, 124498. [\[CrossRef\]](#) [\[PubMed\]](#)
44. Zhang, Y.-F.; Zhang, S.-Y.; Li, H.; Wang, C.-W.; Jiang, F.-H.; Lyu, J.-F. Treatment of municipal sludge by hydrothermal oxidation process with H_2O_2 . *Chemosphere* **2020**, *257*, 127140. [\[CrossRef\]](#)
45. Liu, J.Y.; Wang, L.; Li, D.B.; Li, H. Nutritional ingredients and fertilizer potential of the dewatering effluent after sludge wet air oxidation. *Environ. Technol. Innov.* **2023**, *32*, 103443. [\[CrossRef\]](#)
46. Chu, S.Y.; Zeng, X.; Lin, H.; Zhu, Y.T. High-Performance Catalytic Wet Oxidation of Excess Activated Sludge Derived from Pharmaceutical Wastewater Treatment Process over a $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ Catalyst. *Water* **2023**, *15*, 3494. [\[CrossRef\]](#)
47. Zhu, Y.T.; Zeng, X.; Fang, K.Y. Enhanced Wet Oxidation of Excess Sludge from Pharmaceutical Wastewater Treatment by NaOH. *Catalysts* **2023**, *13*, 1070. [\[CrossRef\]](#)

48. Yan, M.; Chen, C.; Zhong, L.; Hantoko, D.; Kanchanapip, E. Experimental study on the catalytic supercritical water oxidation of oilfield sludge. *Process. Saf. Environ. Prot.* **2022**, *168*, 582–590. [\[CrossRef\]](#)
49. Xiong, Q.; Xia, J.; Wu, X.; Wu, X.; Hou, H.; Lv, H. Influence of persulfate on transformation of phosphorus and heavy metals for improving sewage sludge dewaterability by hydrothermal treatment. *Environ. Sci. Pollut. Res.* **2022**, *29*, 33252–33262. [\[CrossRef\]](#)
50. Zhang, W.M.; Guo, Y.; Ding, Q.Y.; Jin, J.X.; Xi, Y.Y.; Lin, X.F. The degradation of maleic acid with wet peroxide oxidation catalyzed by Al₂O₃-supported Cu catalyst: Effect of inorganic ions. *React. Kinet. Catal. Lett.* **2024**, *137*, 3175–3189. [\[CrossRef\]](#)
51. Zhang, W.; Zhuang, H.; Guo, Y.; Chi, H.; Ding, Q.; Wang, L.; Xi, Y.; Lin, X. Wet peroxide oxidation process catalyzed by Cu/Al₂O₃: Phenol degradation and Cu²⁺ dissolution behavior. *Environ. Sci. Pollut. Res.* **2024**, *31*, 26916–26927. [\[CrossRef\]](#) [\[PubMed\]](#)
52. Wei, W.X.; Cui, H.Y.; Zhao, J.Y.; Song, F.; Wang, J.H. g-C₃N₄ Coating Enhanced Cu@AC for Catalytic Wet Air Oxidation of Phenol under Mild Conditions. *Chemistryselect* **2024**, *9*, e202304800. [\[CrossRef\]](#)
53. Hun, T.C.; Zhao, B.X.; Zhu, T.T.; Liu, L.X.; Li, Z.L.; Sun, L. Catalytic wet peroxide oxidation degradation of magenta wastewater and preparation of FeOCl/montmorillonite. *Water Sci. Technol.* **2021**, *84*, 596–608. [\[CrossRef\]](#) [\[PubMed\]](#)
54. Jiao, Z.J.; Zhang, X.M.; Gong, H.F.; He, D.L.; Yin, H.; Liu, Y.Q.; Gao, X. CuO-doped Ce for catalytic wet peroxide oxidation degradation of quinoline wastewater under wide pH conditions. *J. Ind. Eng. Chem.* **2022**, *105*, 49–57. [\[CrossRef\]](#)
55. Feng, B.X.; Hao, L.N.; Deng, C.T.; Wang, J.Q.; Song, H.B.; Xiao, M.; Huang, T.T.; Zhu, Q.H.; Gai, H.J. A highly hydrothermal stable copper-based catalyst for catalytic wet air oxidation of m-cresol in coal chemical wastewater. *Chin. J. Chem. Eng.* **2023**, *57*, 338–348. [\[CrossRef\]](#)
56. Li, G.Q.; Chai, S.Q.; Zhang, G.J.; Liu, J.; Zhang, Y.F.; Lv, Y.K.; Wang, Y.; Zhao, Y.Q. Deactivation characteristics of Ce-modified Cu-based carbon materials for catalytic wet air oxidation of phenol wastewater. *J. Environ. Chem. Eng.* **2022**, *10*, 108228. [\[CrossRef\]](#)
57. Ding, Z.T.; Liu, C.; Yang, B.G.; Ding, C.; Mao, S.; Shi, M.X.; Hong, X.Y.; Wang, F.Y.; Xia, M.Z. The efficient degradation of high concentration phenol by Nitrogen-doped perovskite La₂CuO₄ via catalytic wet air oxidation: Experimental study and DFT calculation. *Sep. Purif. Technol.* **2023**, *322*, 124310. [\[CrossRef\]](#)
58. Huang, H.X.; Zhang, H.P.; Yan, Y. Preparation of novel catalyst-free Fe₃C nanocrystals encapsulated NCNT structured catalyst for continuous catalytic wet peroxide oxidation of phenol. *J. Hazard. Mater.* **2021**, *407*, 124371. [\[CrossRef\]](#)
59. Zhao, B.; Gao, Y.; Hun, T.; Fan, X.; Shao, N.; Chen, X. Preparation of PrFe_xCo_{1-x}O₃/Mt catalyst and study on degradation of 2-hydroxybenzoic acid wastewater by catalytic wet peroxide oxidation. *Chin. J. Chem. Eng.* **2024**, *65*, 286–297. [\[CrossRef\]](#)
60. Görmez, O. Mineralization of clofibric acid by persulfate-promoted catalytic subcritical water oxidation process using CoFe₂O₄@SiO₂ catalyst. *J. Mater. Sci.* **2024**, *59*, 12793–12811. [\[CrossRef\]](#)
61. Zhao, P.; Zhao, Y.W.; Guo, Y.P.; Guo, R.; Tian, Y.M.; Zhao, W.G. Preparation of CuO/γ-Al₂O₃ catalyst for degradation of azo dyes (reactive brilliant red X-3B): An optimization study. *J. Clean. Prod.* **2021**, *328*, 129624. [\[CrossRef\]](#)
62. Yu, L.; Chang, H.; Wu, S.; Zhu, J.; Zhao, Y.; Wang, L.; Wei, H. Efficient degradation of m-cresol during catalytic wet peroxide oxidation with biochar derived from the pyrolysis of persulfate-ZVI treated sludge. *J. Environ. Manag.* **2022**, *324*, 116388. [\[CrossRef\]](#) [\[PubMed\]](#)
63. Wang, R.C.; Zhu, W.; Zhao, S.; Cao, J. Hydrothermal oxidation-precipitation method for recovering phosphorus from dewatered sludge and the mechanisms involved. *Sep. Purif. Technol.* **2022**, *298*, 121580. [\[CrossRef\]](#)
64. Ning, H.; Zhai, Y.B.; Li, S.H.; Liu, X.M.; Wang, T.F.; Wang, B.; Liu, Y.L.; Qiu, Z.Z.; Li, C.T.; Zhu, Y. Fe(II) activated persulfate assisted hydrothermal conversion of sewage sludge: Focusing on nitrogen transformation mechanism and removal effectiveness. *Chemosphere* **2019**, *244*, 125473. [\[CrossRef\]](#) [\[PubMed\]](#)
65. Chen, Z.; Zheng, Z.; He, C.; Liu, J.; Zhang, R.; Chen, Q. Oily sludge treatment in subcritical and supercritical water: A review. *J. Hazard. Mater.* **2022**, *433*, 128761. [\[CrossRef\]](#)
66. Haering, K.C.; Daniels, W.L.; Evanylo, G.K. Soybean phytotoxicity from land-applied biosolids. *J. Residuals Sci. Technol.* **2008**, *5*, 1–12.
67. Mato, F.A.; Peña, M.; García-Rodríguez, Y.; Bermejo, M.-D.; Martín, A. Analysis of the Energy Flow in a Municipal Wastewater Treatment Plant Based on a Supercritical Water Oxidation Reactor Coupled to a Gas Turbine. *Processes* **2021**, *9*, 1237. [\[CrossRef\]](#)
68. Kolaczowski, S.T.; Plucinski, P.; Beltran, F.J.; Rivas, F.J.; McLurgh, D.B. Wet air oxidation: A review of process technologies and aspects in reactor design. *Chem. Eng. J.* **1999**, *73*, 143–160. [\[CrossRef\]](#)
69. Márquez, J.J.R.; Levchuk, I.; Sillanpää, M. Application of Catalytic Wet Peroxide Oxidation for Industrial and Urban Wastewater Treatment: A Review. *Catalysts* **2018**, *8*, 673. [\[CrossRef\]](#)
70. Yamasaki, H.; Kishimoto, K.; Shimada, T.; Kuroki, T.; Kang, J.Y.; Kim, D.; Yagi, T.; Okubo, M. Toward Ideal VOCs and Nanoparticle Emission Control Technology Using a Wet-Type Catalysis Nonthermal Plasma Reactor. *IEEE Trans. Ind. Appl.* **2022**, *58*, 6591–6598. [\[CrossRef\]](#)
71. Prince-Pike, A.; Wilson, D.I.; Baroutian, S.; Andrews, J.; Gapes, D.J. A kinetic model of municipal sludge degradation during non-catalytic wet oxidation. *Water Res.* **2015**, *87*, 225–236. [\[CrossRef\]](#) [\[PubMed\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.