Fenton oxidation as pretreatment for biomass gasification condensate: cost and biomass inhibition evaluation

Qiqi Zhang, Jonas Pluschke and Sven-Uwe Geißen*
Environmental Process Engineering, Technical University of Berlin, Berlin 10623, Germany
*Corresponding author. E-mail: sven.geissen@tu-berlin.de

ABSTRACT

Gasification transforming organic compounds into energy-rich pyrolytic gas, is a climate-friendly treatment option for biological solid wastes. The condensates arising from the pyrolytic gas valorization is owing to high concentrations of small molecular phenols, cyanides, nitrogen-heterocyclics, aromatics and ammonium, posing an environmental and health hazard. In this paper, the watery phase of the biomass gasification condensate from spent mushroom compost (SMC), with a chemical oxygen demand (COD) of 16.4 g/L and total nitrogen of 2.3 g/L, was pretreated by Fenton oxidation. The experiments were conducted at room temperature with an initial pH value of 3, 5 and 8.9, hydrogen peroxide (H₂O₂) dosages between 15 and 100% of the normalized stoichiometric ratio (NSR), and Fe²⁺ dosages corresponding to molar ratio of H₂O₂:Fe²⁺ between 10 and 30. Through respiration inhibition assays, the best operational condition for detoxification was determined at an initial pH 5 with 30% NSR H₂O₂ dosage and molar ratio of H₂O₂:Fe²⁺ at 15:1. The specific operational cost of the Fenton oxidation was calculated at 2.17 €/kg CODelimination. In respiration inhibition assay, the oxygen consumption of wastewater after Fenton oxidation was increased by 316% in three days. In a 20 days’ biogas production test, the biogas production was increased by 81%.

Key words: cost evaluation, detoxification, gasification condensate, pretreatment by Fenton oxidation, respiration inhibition assay

HIGHLIGHTS

- Detoxification of biomass gasification condensate via Fenton oxidation.
- Modification of respiration inhibition assays with utilization of WTW OxiTop®-C.
- Toxicity evaluation of treated wastewater by respiration inhibition assays.
- Operational parameter optimization based on detoxification capabilities and cost-efficiency.
- Toxicity increased by UV mediated Fenton oxidation.

1. INTRODUCTION

Gasification is an efficient technology to sustainably dispose of solid biomass (Farzad et al. 2016). During the gasification process, the feedstock undergoes a succession of thermal reactions, mainly drying, pyrolysis, combustion, and gasification. The high temperatures in the gasifier (1,100–1,500 °C) guarantee a thorough decomposition of the biomass, such as agriculture wastes, wood waste materials and sewage sludge (Liu et al. 2011; Sansaniwal et al. 2017; Widjaya et al. 2018).

Spent mushroom compost (SMC) is a waste stream from the industrial mushroom production. Considering a worldwide mushroom production of 35 million tons, an estimated 140–175 million tons of SMC is produced every year (Grimm & Wösten 2018; Umor et al. 2021). Due to slow decomposition rates, high content of water and ash as well as a potential pollution to underground and surface water by phosphorus and nitrogen, the SMC is not suitable to be treated by composting, anaerobic digestion, incineration or landfilling (Huang et al. 2018). However, the upper calorific value of dried SMC with a value of 11.95 MJ/kg, is comparable to dried sewage sludge, making it suitable for gasification. (Williams et al. 2001)

The watery phase of the condensate is produced during the drying of the pyrolytic gas, containing 82–93% water and 7–18% organic compounds (Muzyka et al. 2015). Independent of the feed substrate, organic acids, aldehydes, benzenes, ethers, furans, hydrocarbons, ketones and phenols are produced during gasification and pyrolysis processes (Zhang et al. 2019a). The recovery of valuable organic compounds from the condensate is limited by its complex composition and low individual...
concentrations. Moreover, these organic compounds show a moderate or high acute toxicity to the environment and a tendency for bioaccumulation (Ji et al. 2016; Huang et al. 2019).

Due to the inhibitory effects of the condensate to microorganisms, a conventional treatment of activated sludge processes observed a long lag phase and requires an extended hydraulic retention time, that leads to a higher operation cost (Muzyka et al. 2015; Mishra et al. 2021). Advanced oxidation processes (AOPs) were widely applied to abate the organic pollutants, such as pharmaceutics, phenols, formaldehyde, dye intermediate in wastewater. (Muzyka et al. 2015; Cetinkaya et al. 2018; Guo et al. 2018; Nidheesh et al. 2021). The Fenton oxidation relies on the in-situ production of hydroxyl radical from hydrogen peroxide through catalysis by Fe²⁺ at a low pH value. It is a homogeneous catalytic oxidation process. Owing to the wide availability, low costs and low toxicity, Iron(II) is typically used in form of iron sulfate as catalyst (Nidheesh et al. 2021). Due to a narrow working pH range, high chemical consumption and excessive iron sludge production, numerous optimized Fenton-based AOPs such as UV-Fenton oxidation, heterogeneous catalytic Fenton oxidation and electro-Fenton oxidation are being developed in recent years. However, the UV-Fenton oxidation is limited by light irradiation, rendering it unsuitable for wastewaters with high turbidity or deep color (Brillas 2020). Owing to complicated synthesis routes and high costs of heterogeneous catalysts, the heterogeneous Fenton oxidation was often limited to lab scale applications until now (Zhang et al. 2019b). The chemical consumption is lowered in electro-Fenton oxidation, but their overall costs are often increased due to the costly electrodes and high electricity demand. A relative COD elimination cost of 5.76 $/kg was achieved in textile wastewater treatment by electro-Fenton oxidation (Kaur et al. 2019).

The complete COD degradation by Fenton oxidation observed a high operation cost, the specific operation cost in biomass gasification wastewater treatment reached 8.7 $/kg COD elimination (Muzyka et al. 2015). Through coupling of Fenton oxidation with biological degradation, the treatment process is more cost-effective. (Tripathi et al. 2013; Zhu et al. 2018; Mishra et al. 2021). However, generated transformation products and intermediates of the Fenton process, may increase the toxicity of the feed (Babu et al. 2019). The overall biomass inhibition of wastewater is most efficiently assessed by toxicity assays. Identifying singular components, transformation products and intermediates and evaluate their inhibitory effects individually is inconclusive (Sharma et al. 2018).

In this paper, Fenton oxidation was investigated as a pretreatment for the watery phase of SMC gasification condensate. The operation conditions such as pH value, the dosage of H₂O₂ and Fe²⁺ were optimized in single-factor experiments with regards to detoxification efficiency through respiration inhibition assays (OECD/OCDE 2010; Babu et al. 2019). The corresponding removal rates of organic phenolic compounds, COD, ammonium after Fenton oxidation were also investigated. Moreover, biogas production tests were conducted as an additional evaluation tool for the detoxification effect of Fenton oxidation on the wastewater.

2. METHODS AND MATERIALS

2.1. Wastewater

The counterflow biomass gasification plant located in Westphalia, Germany is fed with SMC (periodically mixed with manure and forestry residues). The pyrolytic gas produced in the gasification process was dried before its valorization in a combined heat and power unit. In the drying process a condensate was segregated by a cyclone water trap. The condensate was separated into a sinking layer with tars and heavy oils, a floating layer and the watery phase (80-90% water content). The sinking and floating layers were reintroduced into the gasifier, as both mixtures have high calorific value. The remaining condensate of water-soluble components needs to be disposed before discharge. The overview of the wastewater's main composition is given in Table 1. The wastewater was stored at 6 °C, before experiments the wastewater was pretreated by centrifuge at 4,000 rpm for 20 min followed by a membrane filtration (0.45 μm).

2.2. Chemicals and utilities

The HCl (37%, 7647-01-0) from Merck & Co., NaOH (≥98%, 1310-73-2) from Carl Roth GmbH were utilized in adjustment of pH value during tests. The H₂O₂ (35%, 7722-84-1) from Carl Roth GmbH and FeSO₄·7H₂O (99.5%, 7782-63-0) from Merck & Co. were utilized in the Fenton oxidation tests. The aerobic and anaerobic activated sludge samples were collected from the local municipal wastewater treatment plant in Schönerlinde, Berlin. The aerobic activated sludge, with a dry matter concentration of 6.7 g/L, was collected directly from the aeration pool. It was further used in the respiration inhibition assays. The anaerobic sludge was used for the biogas production tests. Table 2 gives an overview of the physio-chemical properties of the activated sludges.
2.3. Experimental design

2.3.1. Fenton reaction

The Fenton experiments were conducted in batch reactors as shown in Figure 1 in supplemental material. 100 mL of the wastewater sample was treated in quartz stube with or without UV irradiation for 120 min. Single factor test series were conducted to isolate the effect of the initial pH value, Fe$^{2+}$ and H$_2$O$_2$ dosage on their detoxification efficiency and economic viability.

To estimate the most efficient pH value of Fenton oxidation, the initial pH value was set at 3, 5 and unchanged condition of pH 8.9. The H$_2$O$_2$ with 30% of the normalized stoichiometric ratio (NSR) to COD (275 mM H$_2$O$_2$) and Fe$^{2+}$ ions with a molar ratio of H$_2$O$_2$:Fe$^{2+}$ at 15:1 (18.3 mM of Fe$^{2+}$) were dosed as oxidant and homogeneous catalyst in feed. Subsequently, the most cost efficient Fe$^{2+}$ dosage was determined from tests at initial pH 5 and an initial H$_2$O$_2$ dosage of 30% NSR, among molar ratios of H$_2$O$_2$:Fe$^{2+}$ between 10 and 30. To estimate the optimal H$_2$O$_2$ dosage in range of 15–100% NSR, the tests with conditions of initial pH 5, molar ratio of H$_2$O$_2$:Fe$^{2+}$ at 15:1 were investigated.

To estimate the chemical costs of Fenton oxidation, the samples were neutralized to pH 7 $\pm$ 0.5 by NaOH. The iron hydroxide was precipitated through coagulating or adsorbing with humic substances and other organic compounds. To estimate the sludge production and organic content, the entire precipitated sludge was filtered by paper filter. The sludge production was quantified after overnight drying at 105 °C.

To prepare the Fenton oxidation treated samples for further analysis and experiments, 5 g/L MnO$_2$ were added into feed solution to remove residual oxidants. Due to adsorption effect of phenolic compounds onto MnO$_2$, the concentration of phenolic compounds was decreased by 34–38% in the blank control by this procedure. However, the concentration reduction of phenolic compounds by adsorption of MnO$_2$ was not subtracted.

2.3.2. Respiration inhibition assays

The respiration inhibition assays were conducted based on the modified OECD guideline 209. The experimental setup is depicted in Figure 2 in supplementary material. They were conducted with a total residence time of three days at 25 °C.

The OxiTop®-C works at absolute pressure of 1,000 $\pm$ 250 mbar. As the whole air in reactor was blown out by pure oxygen, the maximal reduction of partial oxygen pressure in this respiration assay is 0.25 bar. The dissolved oxygen in the feed

### Table 1 | Composition of wastewater

| Components                        | Value |
|-----------------------------------|-------|
| pH                                | 8.9   |
| Conductivity [mS/cm]              | 11.83 |
| Total Phenol index [g/L]          | 1.4   |
| COD [g/L]                         | 16.4  |
| DOC [g/L]                         | 5.3   |
| NH$_4^+$-N [g/L]                  | 1.5   |
| NO$_3^-$-N [mg/L]                 | 67.5  |
| TN [g/L]                          | 2.3   |

### Table 2 | Properties of the utilized activated sludge

| Components                  | aerobic sludge | anaerobic sludge |
|-----------------------------|----------------|------------------|
| Dry matter content [g/L]    | 6.7            | 24.5             |
| Organic dry matter [g/L]    | 5.4            | 17.4             |
| COD$_{\text{liquid}}$ [mg/L]| 97.5           | 523.6            |
| DOC$_{\text{liquid}}$ [mg/L]| 30.3           | 171.6            |
| Usage                       | Respiration inhibition assays | Biogas production |
Figure 1 | The removal rates of ammonium, COD, Phenol index as well as pH decrease after Fenton reaction for 120 min with or without UV irradiation. (a) pH = 3, 5 and 8.9, Fe$^{2+}$ = 18.3 mM, H$_2$O$_2$ = 275 mM; (b) UV = 15 W, pH = 5 and 8.9, Fe$^{2+}$ = 18.3 mM, H$_2$O$_2$ = 275 mM; (c) pH = 5, H$_2$O$_2$ = 275 mM, Molar ratio of H$_2$O$_2$:Fe$^{2+}$ = 10–30; (d) pH = 5, Molar ratio of H$_2$O$_2$:Fe$^{2+}$ = 15, H$_2$O$_2$ = 137.5–917 mM (NSR at 15–100%).

Figure 2 | The iron concentration in treated wastewater and its content in generated sludge after Fenton reaction.
samples is considered within 25% deviation. The 0.25 bar partial oxygen pressure corresponds to a biochemical oxygen consumption of 357 mg. Thus, considering the biological availability, the COD of samples was set at 550 mg.

During respiration inhibition assays, 100 mL feed samples were prepared through mixing of wastewater samples (85% COD), synthetic sewage (15% COD) and desalinated water. These prepared samples were mixed after that with 100 mL of aerobic activated sludge in a 1 Liter three-neck laboratory bottle, subsequently to adjust the pH to 7 ± 0.2. Before the bottles were airtightly closed, the air in bottles was totally purged out by pure oxygen. During the respiration assays, the produced CO₂ was totally absorbed by NaOH platelets in the gas phase of reactor. The pressure reduction in bottle was congruent to the total oxygen consumption. To decrease experimental error of pressure deviation from instable temperature, the respiration inhibition tests were stirred by magnetic stirrer under thermostable condition. The composition of the feed samples is shown in Table 3. The O₂ consumption was calculated by followed Equation (2)

\[ V_{O_2} = \Delta p \times V_{bottle} \]  

(2)

where the \( V_{O_2} \) is the consumption of O₂ (mL), \( \Delta p \) is the pressure change during tests (bar), \( V_{bottle} \) is the gas volume of 800 mL in bottle.

### 2.3.3. Biogas production test

To show the efficiency of the Fenton oxidation on wastewater detoxification, the original wastewater and the Fenton oxidation treated wastewater were provided in 20 days' biogas production tests. Before tests, all samples were adjusted to pH 7 ± 0.3. The composition of samples is described in Table 4. The experimental setup is depicted in Figure 3 in supplementary material.

### Table 3 | Composition of feed samples in respiration inhibition assays

| Sample | COD [g/L] | Volume [mL] | Total COD [mg] | \( V_{water} \) [mL] | \( V_{sewage} \) [mL] | COD_{sewage} [mg] | \( V_{sludge} \) [mL] |
|--------|-----------|-------------|----------------|------------------|-----------------|----------------|----------------|
| Blank  | 0         | 0           | 0              | 96.3             | 3.7             | 100            | 100            |
| Original | 16.4      | 33          | 550            | 62.7             | 3.7             | 100            | 100            |
| Optimal (5, 15, 30%) | 8.7 | 63.5 | 550 | 32.8 | 3.7 | 100 | 100 |
| pH     | pH 3      | 8.7         | 63.2           | 550              | 33.1            | 3.7            | 100            | 100            |
|        | pH 8.9    | 14.5        | 37.9           | 550              | 58.4            | 3.7            | 100            | 100            |
| UV-Fenton | pH 5 | 9.0 | 61.6 | 550 | 34.7 | 3.7 | 100 | 100 |
|        | pH 8.9    | 14.3        | 38.6           | 550              | 57.7            | 3.7            | 100            | 100            |
| \( \text{H}_2\text{O}_2\): Fe\(^{2+}\) | 10 | 8.4 | 62 | 550 | 34.3 | 3.7 | 100 | 100 |
|        | 20        | 8.9         | 62.3           | 550              | 34              | 3.7            | 100            | 100            |
|        | 30        | 9.2         | 60             | 550              | 36.3            | 3.7            | 100            | 100            |
| NSR of \( \text{H}_2\text{O}_2\) | 15% | 11.3 | 48.6 | 550 | 47.7 | 3.7 | 100 | 100 |
|        | 45%       | 7.4         | 75             | 550              | 21.3            | 3.7            | 100            | 100            |
|        | 60%       | 6.4         | 81.5           | 550              | 14.8            | 3.7            | 100            | 100            |
|        | 100%      | 6.4         | 86.1           | 550              | 10.1            | 3.7            | 100            | 100            |

### Table 4 | Samples for the biomethane assays

| Sample | \( V_{sample} \) [mL] | \( V_{sludge} \) [mL] | \( V_{water} \) [mL] | \( COD_{sample} \) [mg] | COD_{sludge} [mg] |
|--------|-------------------|-----------------|------------------|----------------|----------------|
| Original | 75.2             | 100             | 44.8             | 1,151          | 168            |
| Fenton  | 85.4             | 100             | 34.6             | 800            | 168            |
| Blank  | 0                 | 220             | 0                | 0              | 370            |
2.4. Analytical methods

The total phenol concentration was detected through a wet chemical color-spectrophotometric analysis method using the Folin-Ciocalteau reagent. The method was described in the supplementary material. The concentration of NH$_4^+$ was detected by flow injection analysis (FIA) FOSS FIA Star 5000. The concentration of dissolved organic carbon and total nitrogen in samples were measured by thermal catalytic oxidation process at 850 °C with Analytik Jena multi N/C 3100 CLD. The chemical oxygen demand (COD) was detected through a total combustion of sample at 1,200 °C by COD analyzer from company LAR process Analyzers AG. The iron concentration in wastewater samples were detected by AAS with model 900AA from Perkin Elmer-AAS-PinAAcle™.

3. RESULTS AND DISCUSSION

3.1. Influence of pH, H$_2$O$_2$ dosage and Fe$^{2+}$ dosage on degradation

The optimal pH was determined among the pH values 3, 5 and 8.9 (original pH). The tests were conducted with a 30% NSR H$_2$O$_2$ dosage (275 mM) and a molar ratio of H$_2$O$_2$:Fe$^{2+}$ at 15:1 (18.3 mM Fe$^{2+}$). After two hours' reaction, the pH values of the samples decreased from 3 to 2.48, 5 to 2.69 and 8.9 to 7.93 (Figure 1(a)). Similar removal rates of phenolic compounds, COD and NH$_4^+$ were observed in tests with initial pH 3 and 5. The sample without pH adjustment (pH 8.9) showed higher ammonium removal rate (30%). Two effects contribute to this phenomenon: lower concentration of ammonium was generated from nitrogen containing organic compounds by Fenton oxidation at pH 8.9; and higher escape rate of ammonia was achieved at alkaline condition of pH 8.9 (Gamaralalage et al. 2019).

Figure 3 | Total oxygen consumption of feed samples during respiration inhibition assays. (a) influence of initial pH on toxicity; (b) influence of UV irradiation on toxicity; (c) influence of molar ratio of H$_2$O$_2$:Fe on toxicity; (d) influence of H$_2$O$_2$ dosage on toxicity.
Due to the pH buffering system (such as humic substances), a further pH lowering from pH 5 to pH 3 deemed uneconomic in this application scenario. Owing to an obvious higher COD removal rate in comparison of pH 8.9, the optimal pH value of the Fenton oxidation was determined to be pH 5. This contrasts with other research and the theoretical basics of Fenton oxidation, that the most effective pH of Fenton oxidation was found at around 2.5 (Pignatello et al. 2006). The aqueous phase from hydrothermal carbonization process contains high concentration of humic substances (Usman et al. 2020). Humic substances building complex bonds to ionic iron, act as chelating agents in Fenton oxidation processes. Through applying of chelating agents in feed, the Fenton oxidation achieved also high efficiency at pH 5–8 (Zhang & Zhou 2019).

UV irradiation can regenerate Fe$^{2+}$ from Fe$^{3+}$, and improve the COD degradation efficiency in Fenton experiments (Hu et al. 2011; Nidheesh et al. 2021). A 15 W UV lamp was used to irradiate the wastewater in tests of initial pH 5 and 8.9. However, in comparison of Figure 1(a), the removal rate of COD and ammonium were not obviously improved in Figure 1(b). The COD removal rate was slightly increased from 33% to 38% under UV irradiation in test with an initial pH of 5. The wastewater in this work had an intense color, likely impeding the transfer of UV light. Compared with the initial Fe$^{2+}$ concentrations in referenced publication (40 mg/L), it is much higher (1,021 mg/L) in this work. Thus, the COD degradation was not obviously enhanced by regenerated Fe$^{2+}$.

The iron and H$_2$O$_2$ dosages are the two main operational parameters in Fenton oxidation. For the treatment of similar industrial wastewater (originating from e.g. petroleum refineries, pharmaceutical and antibiotic fermentation processes) the molar ratios of H$_2$O$_2$:Fe$^{2+}$ have been set in range of 8.2–20 (Ribeiro & Nunes 2021). Based on 275 mM H$_2$O$_2$ dosage (NSR value of 30%), the molar ratio of H$_2$O$_2$:Fe$^{2+}$ was set between 10 and 30 in this work. At these reaction conditions, the Fe$^{2+}$ concentration showed little influence on the removal rates of phenolic compounds and COD. Their removal rates ranged 67–72% and 34–38%, respectively. The pH value of feed was more obviously decreased at higher Fe$^{2+}$ dosage. With a molar ratio of H$_2$O$_2$:Fe$^{2+}$ of 10, 15, 20, 50, the pH values decreased from 5 to 2.57, 2.69, 2.76 and 2.91, respectively. Among these tests, the highest NH$_4^+$ removal (22%) was achieved at molar ratio of 15:1.

To investigate the correlation between H$_2$O$_2$ dosage and the degradation efficiency, H$_2$O$_2$ was dosed between 15 and 100% NSR with a molar ratio to Fe$^{2+}$ of 15:1. The drop of pH values after Fenton oxidation was increased by higher H$_2$O$_2$ dosage, correspondingly to final pH values between 3.08 and 2.44 (Figure 1(d)). The phenolic compounds and COD were degraded more efficiently by higher H$_2$O$_2$ dosage. After increasing the H$_2$O$_2$ dosage from 15% to 45% NSR, their removal rates increased from 54% to 82% and 15% to 45%. The removal rate of COD plateaued at 30% NSR and reached a maximum of 51% at H$_2$O$_2$ dosage of 60% NSR. The removal efficiency of COD by Fenton reaction was efficiently improved through a multistage neutralization-coagulation process with limestone (Guo et al. 2018). However, the precipitates must be treated as hazardous solid waste. Due to the increased sludge production yield from the lime and its secondary effect to organic compounds such as adsorption or agglomeration, larger amount of sludge should be managed (Gao et al. 2022). The solid waste management requirements limit the applicability of Fenton oxidation in industrial-scale utilization.

The NH$_4^+$ removal rates were comparably lower, ranging between 12 and 20% with H$_2$O$_2$ dosages of higher than 30% NSR. The nitrogen containing organic compounds shared around one third of the nitrogen source in the condensate, this is connected to the formation of ammonium as by-product from the decomposition of nitrogen containing organic compounds. Same phenomenon was observed in palm oil mill effluent treatment, a removal rate of NH$_4^+$ was achieved by 97% within 15 min, subsequently decreased to 35% after 90 min reaction time (Gamalalalage et al. 2019).

This work focused on the detoxification of wastewater by Fenton oxidation, in comparison to the mentioned paper, the dosage of H$_2$O$_2$ and Fe$^{2+}$ were reduced by 30 and 95%. (Gamalalalage et al. 2019). For a higher removal rate of NH$_4^+$, the electro-Fenton oxidation could be performed. As announced by Menon and coworkers, the NH$_4^+$ removal rate reached 59% in textile wastewater treatment (Menon et al. 2021).

### 3.2. Iron precipitation

To make a complete economic evaluation of pretreatment by Fenton oxidation, the chemical consumption and sludge production yield after neutralization of NaOH are summarized in Table 5. To further provide a sustainable reuse application of precipitates, the iron content in sludge was also determined.

With an initial dosage of H$_2$O$_2$ and Fe$^{2+}$ at 30% NSR and 1,021 mg/L, 7.5–9.5 kg sludge per ton wastewater was precipitated after neutralization. The iron content reached 9.9% in the sludge sample of pH 8.9, that was much higher than the content in the samples of pH 3 or pH 5. This is consequence of a lower solubility of iron hydroxide at neutral pH value, transferring most iron into the solid sludge. Su and coworkers researched the influence of the final pH on the sludge production.
With final pH of 3, the sludge production yield was higher than that at pH 5 ([Su et al. 2019]). However, the sludge in this work was collected after neutralization, the lower sludge production from test with initial pH 5 might be owing to a slight alkalization in neutralization step.

The sludge production yield and iron content of the sludge augmented along with the H2O2 and Fe2+ concentration in the sample. With a molar ratio of H2O2:Fe2+ at 15:1, the H2O2 was dosed in range of 15–100% NSR into the feed, increasing the sludge yield from 6.4 to 18.3 kg sludge/ton wastewater. The content of iron grew correspondingly from 3 to 16.8%. The highest sludge production yield reached to 18.3 kg/m3 with an iron content of 16.8%, in test with H2O2 dosage of 100% NSR. Under the operational condition of pH 5, molar ratio of H2O2 : Fe2+ of 15 and H2O2 dosage of 30% NSR, the sludge production reached 7.5 kg/ton with an iron content of 4.5%.

In comparison to initial wastewater, the content of toxic compounds such as polycyclic aromatic hydrocarbons is lower in Fenton sludge ([Wang et al. 2019]). The Fenton sludge could be processed in anaerobic digestion trials for biogas production. It was also found an enhancement on hydrolysis of macromolecular organic compounds in the hydrolysis or acidification process of wastewater treatment ([Wang et al. 2022]). Moreover, it was applied as source material for the production of magnetic adsorbent or catalysts ([Zhang et al. 2017; Gan et al. 2020; Tong et al. 2021]). In this work, the Fenton sludge could be introduced as feedstock into gasifier. Compared with other publications, the Fe2+ dosage is obviously lower in this work, the ash production of gasifier will not be seriously impacted by introduced Fenton sludge. ([Gamaralalage et al. 2019; Wu et al. 2021]).

In the experiment with 100% NSR H2O2 dosage, the Fe2+ concentration was set at 3,404 mg/L. The residual iron concentration in this sample was low at 83 mg/L. That corresponds to a 98 wt.% transfer of iron into the sludge. One reason for the near complete precipitation of the iron is the overdosed H2O2 at 100% NSR. The generated hydroxyl radicals oxidized the Fe2+ to Fe3+, wasting their oxidation potential on the iron. ([Nidheesh et al. 2021]). Due to the low solubility of Fe3+ hydroxides, the iron was more efficiently filtrated from feed, resulting a low iron ion concentration after neutralization ([Cravotta 2008]).

In the other samples, the iron ion concentrations kept between 187 and 713 mg/L. As shown in previous publications, the residual iron ions negatively impact the nitrogen removal in subsequent biological treatments ([Philips 2003]). With an iron ion concentration of 112 mg/L (Fe2+ or Fe3+), the nitrogen removal was 40% or 60% lower than the iron free blank sample. After adaption for 12 days, they were still 9% or 30% lower. Thus, the wastewater after Fenton oxidation may have inhibition on nitrification process.

### 3.3 Respiration inhibition assays

The total oxygen consumption of samples are drawn in Figure 3. The blank sample containing only activated sludge and synthetic sewage, showed a sharp increase of oxygen consumption within the first 8 hours and a flat curve with moderate constant over the remaining 64 hours in Figure 3(a). The highest oxygen consumption rate reached 7.2 mL/h in 5 hours. The total oxygen consumption was accounted at 100 mL. Compared with blank sample, the original sample showed a slightly higher oxygen consumption rate of 7.5 mL/h at 7 h. Owing to toxic compounds in wastewater, the highest oxygen consumption rate was 2 hours delayed, the total oxygen consumption reached lower at 56.8 mL in 72 hours.

#### Table 5 | Mass balance of Fe after Fenton reaction

| Sample | pH | NSR | H2O2 [%] | Fe2⁺input [mg/L] | Fe2⁺solution [mg/L] | wFe2⁺solution [%] | Sludge [kg/ton] | Fe in Sludge [m.-%] |
|--------|----|-----|----------|------------------|---------------------|-------------------|-----------------|-------------------|
| pH 3   | 3  | 30  | 1,021    | 601              | 59                  | 9.5               | 4.3             |
| pH 5   | 5  | 30  | 1,021    | 595              | 58                  | 7.5               | 4.9             |
| pH 8.9 | 8.9| 30  | 1,021    | 21               | 2                   | 9.4               | 9.9             |
| NSR of H2O2 | 15% | 5   | 15      | 511              | 309                 | 60                | 6.4             |
|        | 30%| 5   | 30      | 1,021            | 713                 | 70                | 7.5             |
|        | 45%| 5   | 45      | 1,531            | 187                 | 12                | 10.2            |
|        | 60%| 5   | 60      | 2,042            | 599                 | 29                | 11.2            |
|        | 100%| 5 | 100    | 3,404            | 83                  | 2                 | 18.3            |
| H2O2: Fe | 10 | 5   | 30      | 1,532            | 384                 | 25                | 10.6            |
|        | 15 | 5   | 30      | 1,021            | 713                 | 70                | 7.5             |
|        | 20 | 5   | 30      | 766              | 591                 | 77                | 8               |
|        | 30 | 5   | 30      | 511              | 494                 | 97                | 6.6             |

Water Science & Technology Vol 00 No 0, 8

Uncorrected Proof
After Fenton oxidation with an initial pH of 3 or 5, the toxic transformed organic compounds might be built in feed. At beginning of respiration assays, the oxygen consumption of sample pH 3 and pH 5 are underperform the sample of original (Figure 3(a)). Their oxygen consumption rates reached the highest value of 5.6 and 10.4 mL/h at residence time of 20 and 21 h. Compared with the sample of pH 3 (lag phase with 18 h), less amounts of toxic compounds were generated at pH 5 (lag phase with 14 h).

The toxic organic compounds were efficiently removed after Fenton reaction with an initial pH of 8.9, the lag phase of sample pH 8.9 is comparable to the blank sample, its highest oxygen consumption rate reached 11.2 mL/h in 5 hours. The total oxygen consumption reached among tests the highest with value of 180 mL, in the sample of pH 5. Considering the COD removal rate and total oxygen consumption, the optimal pH vale was indicated at pH 5.

Figure 3(b) shows a similar oxygen consumption for the wastewater samples at pH 8.9 with and without UV irradiation. However, the oxygen consumption rate of the sample UV-5 is much lower than sample without UV at pH 5. Although a slightly higher COD removal rate was achieved by UV-Fenton oxidation, larger amount of transformed toxic compounds might be generated at pH 5. Thus, considering of the increased toxicity, UV irradiation is not recommended.

The influence of initial Fe²⁺ concentration on the toxicity of treated wastewater was also investigated. The Fe²⁺ was dosed into the wastewater with a molar ratio of H₂O₂:Fe²⁺ in range of 10–30, that corresponds to an initial Fe²⁺ concentration of 1,532–511 mg/L. As shown in Figure 3(c), the wastewater sample of 15:1 and 20:1 show a higher total oxygen consumption than original sample since residence time of 16 h. With 72 h residence time, the total oxygen consumption reached 173.6 (20:1), 176.6 (15:1), 79.2 (10:1) and 84 mL (30:1). It indicates an optimal molar ratio of H₂O₂:Fe²⁺ at 15:1 in Fenton oxidation.

To determine the influence of the hydrogen peroxide dosage on the toxicity of Fenton oxidation treated wastewater, the tests were conducted with a fixed molar ratio of H₂O₂:Fe²⁺ at 15:1 and a varied H₂O₂ dosage of 15–100% NSR. The sample F-15% shows the lowest oxygen consumption rate in Figure 3(d). With residence time of 72 h, the total oxygen consumption reached 20 mL. The toxicity of wastewater was decreased with a higher H₂O₂ dosage. With initial H₂O₂ dosage of 30 and 45%, the oxygen consumption rates reached their highest values of 10.4 and 11.2 mL/h at residence time 21 h. However, the biological available organic compounds were degraded by highly dosed H₂O₂, the highest oxygen consumption rates of sample F-60% and F-100% reached lower of 7.2 and 5.6 mL/h.

As an identical results, the sample of F-30% and F-45% observed total oxygen consumption of 180 and 173 mL at residence time of 72 h. Owing to lower chemical consumption, the favorite H₂O₂ dosage was estimated at 30% NSR. Thus, through the respiration assays, the optimal condition of Fenton oxidation was determined as pH 5, with H₂O₂ dosage of 30% NSR and a molar ratio of H₂O₂:Fe²⁺ at 15:1.

3.4. Biogas production

The biogas production of Fenton sample (F515), original wastewater and anaerobic sludge over a period of 20 days are shown in Figure 4. The original wastewater displayed a noteworthy inhibition on biogas production. Compared with the blank or the treated sample, only roughly one third biogas was produced in first three days. The anaerobic sludge had the lowest absolute
gas production, oppositely a highest biogas production relating to the COD removal. This implies the decay of organisms at nutrient lack condition, the released nutrition from organisms were utilized as feedstock of biogas production.

The sample of Fenton produced 84% more biogas than the sample of original in around 20 days. That confirms to 66% higher gas production relating to COD removal. A higher concentration of biodegradable organic compounds, especially the volatile fatty acids were generated after Fenton reaction (Feki et al. 2020). Through detection by Hach-Lang cuvette LCK365, the organic acid concentration in wastewater was increased from 1.02 to 2.03 g butyric acid equivalents (BAE)/L after Fenton oxidation. After anaerobic treatment for around 20 days, the concentration of organic acid was decreased to 0.28 g BAE/L.

The cuvette of LCK 345 from company Hach Lang was developed in basis of 4-Aminoantipyrine (AAP) method to measure the concentration of small molecular phenolic compounds. It was utilized to track the small phenolic compounds concentration over the wastewater treatment processes. After pretreatment of Fenton oxidation, the concentration of small molecular phenolic compounds was decreased by 70%, from 184 to 55 mg/L. It was further decreased to 24 mg/L after 20 days’ anaerobic treatment. In contrast, 84 mg/L of small molecular phenolic compounds were found in the original wastewater after anaerobic treatment. The organisms got inhibitory effect from phenol with an aqueous concentration of 90 mg/L (Zhao et al. 2015). Therefore, the lower biogas production yield in the sample of original might be owing to a continuous inhibition of small molecular phenolic compounds to organisms.

Figure 5 shows the mass flow of COD over the course of the Fenton oxidation and anaerobic treatment. Through Fenton oxidation, the COD concentration was decreased from 16.4 to 8.7 g/L, equivalents to a 53% COD removal. During anaerobic treatment, the COD concentration was further diluted by the mixed anaerobic sludge. Over the digestion of 20 days, the COD concentration was further decreased from 4.43 to 2.41 g/L. The COD concentration could be further decreased with a longer digestion time. For the future work, the adsorption effects of anaerobic sludge, biomass accumulation and the composition of produced biogas could be investigated.

### 3.5. Cost

The cost of Fenton oxidation was calculated from chemical consumption, sludge disposal, electricity cost and the operation costs. The energy cost of drying or transport were not focused. To be informed by statistics from independent commodity Intelligence Services (ICIS), the market price of technical grade HCl in Germany was assessed at 35–70 €/ton in 2019, thus the price of HCl at 60 €/ton was used in this work (Barker 2019). The sale price of H₂O₂ varied in range of 700–1,200 $/ton, in this work it was fixed at 800 €/ton (Ciriminna et al. 2016). The price of ferrous sulfate heptahydrate was estimated at 115 $/ton (97 €/ton) (Fac. MR 2018).

The NaOH was utilized to neutralize the pH value of treated wastewater to around 7. The price of NaOH was indicated with 300–500 €/ton (400 €/ton in this work) (Barker 2018). The sludge disposal costs vary strongly based on geographical region and the it’s composition. In the region of Lahn Dill in Germany, the disposal price of the industrial sludge, which...
may have a high iron content was set at 220 €/ton (Lahn-Dill 2018). In this work, the disposal price of sludge was estimated at 220 €/ton. The electric consumption of the Fenton process was largely independent of the operational parameters. The energy consumption of UV irradiation was defined as additional electricity in Table 9, the price of electricity for industrial utilization was set at 0.11 €/kwh (Hein et al. 2021).

The operation costs of Fenton oxidation with different setting conditions are shown in Figure 6. The absolute costs of Fenton oxidation are between 7.3 and 33.5 euro per ton wastewater, while the specific COD elimination costs varied between 2.2 and 18.8 €/kg COD$_{el}$. With an initial pH of 5 or 5, the main cost were the hydrogen peroxide with a share of 56–59%, the lye was used for the neutralization (18%) and the sludge disposal observed a share of 13–16%. The sample of pH 8.9 showed...
the least absolute cost (no chemical costs for the adjustment of the pH value before and after the process), however owing to an inefficient reaction, it performed the high relative cost of 12.2 €/kg CODeli.

The electricity cost of 2 hours’ UV irradiation was at around 8.3 €/ton wastewater. Although the electricity cost shared around 40–46% of total costs in UV-Fenton oxidation, the organic compounds were not obviously better degraded. The Table 9 | Parameter costs of Fenton oxidation or UV-Fenton oxidation in lab-scale

| Sample | pH 3 | pH 5 | pH 8.9 |
|--------|------|------|--------|
| Acid [€/ton] | 0.87 | 0.75 | 0.75 |
| H₂O₂ [€/ton] | 7.46 | 7.46 | 7.46 |
| FeSO₄·7H₂O [€/ton] | 0.5 | 0.5 | 0.5 |
| Neutralization [€/ton] | 2.3 | 2.2 | 1.83 |
| Sludge [€/ton] | 2.1 | 1.7 | 2.0 |
| Additional Electricity [€/ton] | – | – | 8.3 |
| Total [€/ton] | 13.3 | 12.6 | 20.8 |
| COD removal [%] | 55% | 59% | 74% |
| Relative cost [€/kg COD] | 2.4 | 2.4 | 3.5 |

The Figure 6 | Total cost and cost of COD reduction after Fenton reaction or UV-H₂O₂ oxidation with variate conditions. (a) pH = 3, 5, 8.9, Fe²⁺ = 18.3 mM, H₂O₂ = 275 mM; (b) UV = 15 W, pH = 5 and 8.9, Fe²⁺ = 18.3 mM, H₂O₂ = 275 mM; (c) pH = 5, H₂O₂ = 275 mM, Molar ratio of H₂O₂:Fe²⁺ = 10–30; (d) pH = 5, Molar ratio of H₂O₂:Fe²⁺ = 15, H₂O₂ = 137.5–917 mM (NSR value of 15–100%).
cost of COD degradation reached 3.46 and 18.83 €/kg COD\textsubscript{eli} in tests with an initial pH of 5 and 8.9. Considering of the high energy cost, the UV-Fenton oxidation is not recommended in treatment of the condensate from gasification process.

The influence of the initial Fe\textsuperscript{2+} on the costs was also investigated. As shown in Figure 6(c), the three highest costs of these tests were H\textsubscript{2}O\textsubscript{2} consumption (55–64%), neutralization (15–18%) and sludge disposal (13–27%). Owing to a higher Fe\textsuperscript{2+} dosage, the costs of neutralization, sludge disposal in the test with a molar ratio of H\textsubscript{2}O\textsubscript{2} : Fe\textsuperscript{2+} of 10 : 1, was slightly higher than others. However, owing to a higher COD removal efficiency, the relative cost of COD elimination were similar in range of 2.26–2.19 €/kg COD\textsubscript{eli}.

Figure 6(d) shows the cost of Fenton oxidation with H\textsubscript{2}O\textsubscript{2} dosage of 15–100% NSR at molar ratio of H\textsubscript{2}O\textsubscript{2}:Fe\textsuperscript{2+} of 15:1. The largest share of expenses in these tests is the H\textsubscript{2}O\textsubscript{2}. With rising H\textsubscript{2}O\textsubscript{2} dosages from 15% to 100% NSR, the cost share of H\textsubscript{2}O\textsubscript{2} increases from 51% to 74%. The COD removal was increased correspondingly from 20% to 51%. That conforms to the increasing of relative cost of COD elimination from 2.2 to 4.2 €/kg COD\textsubscript{eli}. Moreover, the costs of sludge disposal were increased correspondingly from 1.4 to 4.0 €/ton. The lowest cost of COD degradation was 2.2 €/kg at H\textsubscript{2}O\textsubscript{2} dosage of 30% NSR.

4. CONCLUSIONS

The detoxifying effect of Fenton oxidation on a biomass gasification condensate was assessed using respiration inhibition assays. Through the thorough analysis of the samples after Fenton oxidation, the most cost-efficient operational parameters were determined with a total operational cost of 2.2 €/kg COD\textsubscript{eli}. The test with an initial pH 5, 30% NSR dosage of hydrogen peroxide and a molar ratio of H\textsubscript{2}O\textsubscript{2}:Fe\textsuperscript{2+} of 15:1 produced the most efficient pretreatment results. Compared with the original wastewater, the total oxygen consumption of Fenton oxidation treated sample was increased by 316% in a three days’ respiration inhibition assay. The biogas production yield relating to COD removal was increased by 81% from 0.97 to 1.61 L\textsubscript{biogas}/g COD\textsubscript{eli}. Compared with conventional Fenton reaction, which aimed at the complete COD removal, the dosage of H\textsubscript{2}O\textsubscript{2} and Fe\textsuperscript{2+} was decreased by 30 and 93% in this work. Moreover, to sustainably reuse the Fenton sludge in future, the sludge production yield and iron content in produced precipitates were found to be between 6.2–18.1 kg/ton wastewater and 0.4–16.8%.

However, two major issues of Fenton oxidation should be overcome: the low removal efficiency of ammonium and high residual iron concentration in the effluent. The electro-Fenton oxidation approaches to overcome these challenges. It requires lower consumption of oxidant and Fe\textsuperscript{2+}, leading to lower residual iron concentration in effluent, higher removal rates of nitrogen and lower sludge yields.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Babu, D. S., Srivastava, V., Nidheesh, P. V. & Kumar, M. S. 2019 Detoxification of water and wastewater by advanced oxidation processes. Science of The Total Environment 696, 133961. Available from: https://linkinghub.elsevier.com/retrieve/pii/S004565352030391X (accessed 3 February 2022).

Barker, C. 2018 Chemical Profile: Europe Caustic Soda. Available from: https://www.icis.com/explore/resources/news/2018/11/01/10276478/chemical-profile-europe-caustic-soda/

Barker, C. 2019 German, Belgian HCl Contract Prices Rise for 2019. Available from: https://www.icis.com/explore/resources/news/2019/01/25/10311220/german-belgian-hcl-contract-prices-rise-for-2019 (accessed 20 September 2021).

Brillas, E. 2020 A review on the photoelectro-Fenton process as efficient electrochemical advanced oxidation for wastewater remediation. treatment with UV light, sunlight, and coupling with conventional and other photo-assisted advanced technologies. Chemosphere 250, 126198. Available from: https://linkinghub.elsevier.com/retrieve/pii/S004565352030391X (accessed 3 February 2022).

Cetinkaya, S. G., Morcali, M. H., Akarsu, S., Ziba, C. A. & Dolaz, M. 2018 Comparison of classic Fenton with ultrasound Fenton processes on industrial textile wastewater. Sustainable Environment Research 28 (4), 165–170. Available from: https://linkinghub.elsevier.com/retrieve/pii/S2468203917303138 (accessed 3 February 2022).

Ciriminna, R., Albanese, L., Meneguzzo, F. & Pagliaro, M. 2016 Hydrogen peroxide: a key chemical for today’s sustainable development. ChemSusChem 9 (24), 3374–3381. Available from: https://onlinelibrary.wiley.com/doi/10.1002/cssc.201600895 (accessed 20 September 2021).
Cravotta, C. A. 2008 Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 2: geochemical controls on constituent concentrations. Applied Geochemistry 23 (2), 203–226. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0883292707002788 (accessed 28 January 2022).

Fact.MR 2018 Ferrous Sulfate Market Forecast, Trend Analysis & Competition Tracking – Global Market Insights 2018 to 2028. Available from: https://www.factmr.com/report/1954/ferrous-sulfate-market (accessed 20 September 2021).

Farzad, S., Mandegari, M. A. & Gorgens, J. F. 2016 A critical review on biomass gasification, co-gasification, and their environmental assessments. Biofuel Research Journal 3 (4), 483–495. Available from: http://www.biofueljournal.com/article_32132.html (accessed 19 November 2021).

Feki, E., Battimelli, A., Sayadi, S., Dhouib, A. & Khroufi, S. 2020 High-rate anaerobic digestion of waste activated sludge by integration of electro-fenton process. Molecules 25 (3), 626. Available from: https://www.mdpi.com/1420-3049/25/3/626 (accessed 30 January 2022).

Gamaralalage, D., Sawai, O. & Nunoura, T. 2019 Degradation behavior of palm oil mill effluent in Fenton oxidation. Journal of Hazardous Materials 364, 791–799. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0304389418305405 (accessed 29 January 2022).

Gan, Q., Hou, H., Liang, S., Qiu, J., Tao, S., Yang, L., Yu, W., Xiao, K., Liu, B., Hu, J., Wang, Y. & Yang, J. 2020 Sludge-derived biochar with multivalent iron as an efficient Fenton catalyst for degradation of 4-Chlorophenol. Science of The Total Environment 725, 138299. Available from: https://linkinghub.elsevier.com/retrieve/pii/S004896972031812X (accessed 31 January 2022).

Gao, L., Cao, Y., Wang, L. & Li, S. 2022 A review on sustainable reuse applications of Fenton sludge during wastewater treatment. Frontiers of Environmental Science & Engineering 16 (6), 77. Available from: https://link.springer.com/10.1007/s11783-021-1511-6 (accessed 28 January 2022).

Grimm, D. & Wösten, H. A. B. 2018 Mushroom cultivation in the circular economy. Applied Microbiology and Biotechnology 102 (18), 7795–7803. Available from: http://link.springer.com/article/10.1007%2Fs00253-018-9226-8 (accessed 10 August 2021).

Guo, Y., Xue, Q., Zhang, H., Wang, N., Chang, S., Fang, Y., Wang, H., Yuan, F., Pang, H. & Chen, H. 2018 Highly efficient treatment of real benzene dye intermediate wastewater by simple limestone and lime neutralization-coagulation with improved Fenton oxidation. Environmental Science and Pollution Research 25 (31), 31125–31135. Available from: http://link.springer.com/10.1007/s11356-018-3101-0 (Accessed 28 January 2022).

Huang, J., Zhang, J., Liu, J., Chen, J., Xie, W., Kuo, J., Lu, X., Chang, K., Wen, S., Sun, G., Cai, H., Buyukada, M. & Evrendilek, F. 2018 Combustion behaviors of spent mushroom substrate using TG-MS and TG-FTIR: thermal conversion, kinetic, thermodynamic and emission analyses. Bioresource Technology 266, 389–397. Available from: https://linkinghub.elsevier.com/retrieve/pii/S096085241830885X (accessed 10 August 2021).

Hu, X., Wang, X., Ban, Y. & Ren, B. 2011 A comparative study of UV–Fenton, UV–H₂O₂ and Fenton reaction treatment of landfill leachate. Environmental Technology 32 (9), 945–951. Available from: http://www.tandfonline.com/doi/abs/10.1080/09593330.2010.521953 (accessed 27 September 2021).

Huang, J., Liu, J., Chen, J., Xie, W., Kuo, J., Lu, X., Chang, K., Wen, S., Sun, G., Cai, H., Buyukada, M. & Evrendilek, F. 2018 Combustion behaviors of spent mushroom substrate using TG-MS and TG-FTIR: thermal conversion, kinetic, thermodynamic and emission analyses. Bioresource Technology 266, 389–397. Available from: https://linkinghub.elsevier.com/retrieve/pii/S096085241830885X (accessed 10 August 2021).

Ji, Q., Tabassum, S., Hena, S., Silva, C. G., Yu, G. & Zhang, Z. 2016 A review on the coal gasification wastewater treatment technologies: past, present and future outlook. Journal of Environmental Science and Technology 16 (2), 801–186. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0165237018310003 (accessed 11 August 2021).

Ji, Q., Tabassum, S., Hena, S., Silva, C. G., Yu, G. & Zhang, Z. 2016 A review on the coal gasification wastewater treatment technologies: past, present and future outlook. Journal of Cleaner Production 126, 38–55. Available from: https://linkinghub.elsevier.com/retrieve/pii/S095965261630066X (accessed 11 August 2021).

Ji, Q., Tabassum, S., Hena, S., Silva, C. G., Yu, G. & Zhang, Z. 2016 A review on the coal gasification wastewater treatment technologies: past, present and future outlook. Journal of Cleaner Production 126, 38–55. Available from: https://linkinghub.elsevier.com/retrieve/pii/S095965261630066X (accessed 11 August 2021).

Kaur, P., Sangal, V. K. & Kushwaha, J. P. 2019 Parametric study of electro-Fenton treatment for real textile wastewater, disposal study and its cost analysis. International Journal of Environmental Science and Technology 16 (2), 801–810. Available from: http://link.springer.com/10.1007/s13762-018-1696-9 (accessed 3 February 2022).

Lahn-Dill 2018 A. Preisliste (Direktanlieferung AWZ Aßlar). Abfallwirtschaft Lahn-Dill. Available from: https://www.awld.de/de/Gebuehren-Preise/Preisliste/ (accessed 20 September 2021).

Liu, M., Xu, G. & Li, G. 2011 Gasification as a new thermal processes of sewage sludge utilization. In 2011 International Conference on Multimedia Technology, Hangzhou, China. IEEE, pp. 4454–4457. Available from: http://ieeexplore.ieee.org/document/6003362/ (accessed 19 November 2021).

Menon, P., Anantha Singh, T. S., Pani, N. & Nidheesh, P. V. 2021 Electro-Fenton assisted sonication for removal of ammoniacal nitrogen and organic matter from dye intermediate industrial wastewater. Chemosphere 269, 128739. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0045653520329374 (accessed 5 February 2022).

Mishra, L., Paul, K. K. & Jena, S. (2021) Coke wastewater treatment methods: mini review. Journal of the Indian Chemical Society 98(10), 100133. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0019452221001333 (accessed 22 November 2021).

Muzylka, R., Chrubasik, M., Stelmach, S. & Sajdak, M. 2015 Preliminary studies on the treatment of wastewater from biomass gasification. Waste Management 44, 135–146. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0956053X15300209 (accessed 11 August 2021).
Nidheesh, P. V., Couras, C., Karim, A. V. & Nadais, H. 2021 A review of integrated advanced oxidation processes and biological processes for organic pollutant removal. Chemical Engineering Communications, 1–43. Available from: https://www.tandfonline.com/doi/full/10.1080/00986445.2020.1864626 (accessed 27 January 2022).

OECD/OCDE 2010 Test no. 209: activated sludge, respiration inhibition test (carbon and ammoniumoxidation). OECD Guidel. Test. Chem. Sect. 2 Ef. Biot. Syst https://doi.org/10.1787/9789264070080-en.

Phillips, S. 2003 Impact of iron salts on activated sludge and interaction with nitrite or nitrate. Bioresource Technology 88 (3), 229–239. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0960852402003140 (accessed 27 September 2021).

Pignatello, J. J., Oliveros, E. & MacKay, A. 2006 Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. Critical Reviews in Environmental Science and Technology 36 (1), 1–84. Available from: http://www.tandfonline.com/doi/abs/10.1080/10643380500326564 (accessed 10 July 2020).

Ribeiro, J. P. & Nunes, M. I. 2021 Recent trends and developments in Fenton processes for industrial wastewater treatment – a critical review. Environmental Research 197, 110957. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0013935121002516 (accessed 27 September 2021).

Sansaniwal, S. K., Pal, K., Rosen, M. A. & Tyagi, S. K. 2017 Recent advances in the development of biomass gasification technology: a comprehensive review. Renewable and Sustainable Energy Reviews 72, 363–384. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1364032117300394 (accessed 19 November 2021).

Sharma, A., Ahmad, J. & Flora, S. J. S. 2018 Application of advanced oxidation processes and toxicity assessment of transformation products. Environmental Research 167, 223–233. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0013935118305748 (accessed 13 August 2021).

Su, X., Li, X., Ma, L. & Fan, J. 2019 Formation and transformation of schwertmannite in the classic Fenton process. Journal of Environmental Sciences 82, 145–154. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1001074218336702 (accessed 29 January 2022).

Tong, S., Shen, J., Jiang, X., Li, J., Sun, X., Xu, Z. & Chen, D. 2021 Recycle of Fenton sludge through one-step synthesis of animeted magnetic hydrochar for Pb2+ removal from wastewater. Journal of Hazardous Materials 406, 124581. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0304389420325711 (accessed 31 January 2022).

Tripathi, L., Dubey, A. K., Gangil, S. & Singh, P. L. 2013 Waste water treatment of biomass based power plant. International Conference on Global Scenario in Environment and Energy 5 (2), 761–764.

Umor, N. A., Ismail, S., Abdullah, S., Huzaifah, M. H. R., Huzir, N. M., Mahmood, N. A. N. & Zahrin, A. Y. 2021 Zero waste management of spent mushroom compost. Journal of Material Cycles and Waste Management 25 (5), 1726–1736. Available from: https://link.springer.com/10.1007/s10163-021-01250-3 (accessed 10 August 2021).

Usman, M., Ren, S., Ji, M., O-Thong, S., Qian, Y., Luo, G. & Zhang, S. 2020 Characterization and biogas production potentials of aqueous phase produced from hydrothermal carbonization of biomass – major components and their binary mixtures. Chemical Engineering Journal 388, 124201. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1385894720301923 (accessed 27 January 2022).

Wang, M., Zhao, Z. & Zhang, Y. 2019 Disposal of Fenton sludge with anaerobic digestion and the roles of humic acids involved in Fenton sludge. Water Research 165, 114900. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0043135419306748 (accessed 31 January 2022).

Wang, Y., Wang, H., Jin, H., Zhou, X. & Chen, H. 2022 Application of Fenton sludge coupled hydrolysis acidification in pretreatment of wastewater containing PVA: performance and mechanisms. Journal of Environmental Management 304, 114305. Available from: https://www.sciencedirect.com/science/article/pii/S0043135419306767 (accessed 31 January 2022).

Widjaya, E. R., Chen, G., Bowtell, L. & Hills, C. 2018 Gasification of non-woody biomass: a literature review. Renewable and Sustainable Energy Reviews 89, 184–193. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1364032118301138 (accessed 19 November 2021).

Williams, B. C., McMullan, J. T. & McCahey, S. 2021 An initial assessment of spent mushroom compost as a potential energy feedstock. Bioresource Technology 4.

Wu, C., Chen, W., Gu, Z. & Li, Q. 2021 A review of the characteristics of Fenton and ozonation systems in landfill leachate treatment. Science of The Total Environment 762, 143131. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0048969720366614 (accessed 31 January 2022).

Zhang, Y. & Zhou, M. 2019 A critical review of the application of chelating agents to enable Fenton and Fenton-like reactions at high pH values. Journal of Hazardous Materials 362, 436–450. https://linkinghub.elsevier.com/retrieve/pii/S0304389418308306 (accessed 27 January 2022).

Zhang, H., Liu, J., Ou, C., Faheem, Shen, J., Yu, H., Jiao, Z., Han, W., Sun, X., Li, J. & Wang, L. 2017 Reuse of Fenton sludge as an iron source for NiFe2O4 synthesis and its application in the Fenton-based process. Journal of Environmental Sciences 53, 1–8. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1001074216301619 (accessed 31 January 2022).

Zhang, J., Liu, J., Evrendilek, F., Zhang, X. & Buyukada, M. 2019a TG-FTIR and Py-GC/MS analyses of pyrolysis behaviors and products of cattle manure in CO2 and N2 atmospheres: kinetic, thermodynamic, and machine-learning models. Energy Conversion and Management 195, 346–359. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0196890419305679 (accessed 11 August 2021).

Zhang, M., Dong, H., Zhao, L., Wang, D. & Meng, D. 2019b A review on Fenton process for organic wastewater treatment based on optimization perspective. Science of The Total Environment 670, 110–121. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0048969719311684 (accessed 3 February 2022).
Zhao, Q., Han, H., Fang, F., Zhuang, H., Wang, D. & Li, K. 2015 Strategies for recovering inhibition caused by phenolic compounds in a short-cut nitrogen removal reactor treating coal gasification wastewater. *Journal of Water Reuse and Desalination* 5 (4), 569–578. Available from: https://iwaponline.com/jwrd/article/5/4/569/30276/Strategies-for-recovering-inhibition-caused-by (accessed 22 November 2021).

Zhu, H., Han, Y., Xu, C., Han, H. & Ma, W. 2018 Overview of the state of the art of processes and technical bottlenecks for coal gasification wastewater treatment. *Science of The Total Environment* 637–638, 1108–1126. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0048969718316899 (accessed 12 August 2021).

First received 6 December 2021; accepted in revised form 12 February 2022. Available online 25 February 2022