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Advanced Oxidation Processes to Reduce Odor Emissions from Municipal Wastewater—Comprehensive Studies and Technological Concepts

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Abstract: Municipal facilities can generate odors caused by substances such as fatty acids, organosulfur compounds, aldehydes, and inorganic gases, especially H_2S. Identifying an effective and cost-efficient solution to the problem is a priority for communities in areas at risk of exposure to odors. The aim of this study was to evaluate the effect of advanced oxidation processes (AOPs) involving Fenton's reagents (Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2) on wastewater profiles and their capacity to reduce putrescibility, H_2S emissions, and odor concentration in the air. The Fe^{2+}/H_2O_2 system proved to be the most efficient in terms of inhibiting the process of redox conditions development, removing organic matter in the wastewater, inhibiting H_2S formation, and reducing odor emissions. H_2S generation in raw wastewater was triggered as early as on day 2 of anaerobic retention, with levels of 5.6 ppm to 64 ppm. After introduction of 0.1 g Fe^{2+}/dm^3 and 2.0 g H_2O_2/dm^3, no H_2S was detected in the gas for 8 days. The odor concentration (OC) of raw wastewater (2980 ± 110 ou_e/m^3) was reduced by $96.3 \pm 1.9\%$ to a level of 100 ± 15 ou_e/m^3. The Fe^{2+}/H_2O_2 system maintained its oxidizing capacity up until day 7, with OC reduction by $96.0 \pm 0.8\%$ to a level of 120 ± 10 ou_e/m^3. On day 10, the OC showed a marked increase to a level 1310 ± 140 ou_e/m^3. The conducted research has proven that Fenton-based AOP systems are a technologically and commercially viable method of deodorization of sewage facilities.

Keywords: municipal wastewater; putrefaction; odor emission; advanced oxidation processes (AOPs); Fenton's reaction; hydrogen sulfide; dynamic olfactometry

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1. Introduction

Municipal facilities can generate odors caused by substances such as fatty acids, organosulfur compounds, aldehydes, and inorganic gases [1]. Most of these odors are generated by anaerobic bacteria by way of organic matter decomposition [2]. The most important product of these processes is hydrogen sulfide (H_2S) [3]. Oxygen reserves in wastewater (whether flowing through sewers or stored in holding tanks) are relatively quickly depleted in the course of organic matter decomposition, thus initiating putrefaction [4]. Anaerobic bacteria use the sulfate ions available in the wastewater for energy, reducing them to sulfide ions. The latter (in the form of H_2S) emanate from the wastewater environment, releasing noxious odors into the environment [5]. The released H_2S can also corrode the concrete of wastewater interceptors and technological components of wastewater storage, transmission, and treatment systems [6]. Another reason why H_2S is removed or prevented from forming is that it poses a serious danger to the health of municipal facility employees and inhabitants of exposed areas [7].

As part of health and environmental programs, the legislatures of highly developed countries (Canada, Japan or USA) have strived to set odor emission limits [8]. Similarly, the regulations of most European Union (EU) countries require that malodorous emissions be monitored and mitigated [9]. Poland has yet to include malodorous substances in applicable emission limits for industrial plants [10]. The issue of odorant emissions is not regulated on an administrative level due to the lack of regulations implementing relevant legal provisions [11]. Nevertheless, the issue is standardized in PN:EN 13725:2007: Air quality. Determination of odor concentration is by dynamic olfactometry, which sets out measurement principles. However, this standard is strictly voluntary under Polish law [12].

The perception of odors as unpleasant and noxious is primarily determined by personal traits, e.g., aroma preferences, temperament, gender, mood, and state of mind [13]. Also important are external factors, which may, in different combinations, either lessen or strengthen the sensation of discomfort generated by the perceived odor. Such factors include the ambient temperature, level of noise, and duration of exposure [14]. As a subjective sense, smell is very difficult to quantify. In effect, it seems that the only analyzer equipped to assess odor nuisance is the human nose [15]. The maximum admissible concentration (MAC) of H_2S is a key consideration for administrators and operators of sewage systems [16]. European Commission Directive 2009/161/EU sets out indicative occupational exposure limit values (IOELV) for H_2S at 10 ppm for the short-term exposure limit (~15 min), and at 5 ppm for eight-hour exposure [17]. Obviously, municipal facility employees are required to have sufficient protective measures [18]. However, accepting heightened H_2S levels for protected networks can be problematic for any third parties who may lack such protection [19].

As such, it is necessary to identify efficient and cost-effective technologies for fast elimination of noxious odors and smells generated by putrefaction in wastewater storage, transport, and treatment systems [20]. Identifying a viable and effective solution to the problem is of great importance to the communities in areas at risk of exposure to odorants, whether periodic or continuous [21]. After all, such exposure impacts quality of life and regional prospects for tourism as well as industrial and general development [22]. The literature data point to the Fenton reaction (Fe^{2+}/H_2O_2), Fenton-like reaction (Fe^{3+}/H_2O_2), and H_2O_2 alone as useful means of organic removal, toxic substance degradation, color removal, and sanitization [23,24]. The effects of AOPs can thus indirectly inhibit the formation and emission of odorants in municipal facilities [25]. There have also been reports on direct and targeted use of such reagents to reduce emissions of H_2S and other foul-smelling substances [26,27].

The importance of the undertaken research issues is mainly based on determination of the mechanisms and applicability of advanced oxidation processes (AOPs) with hydrogen peroxide (H_2O_2) and Fenton's reagent (Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2) in mitigating odor nuisance in sewage facilities. The presented study allows developing and optimizing a solution for the partial or complete removal of H_2S emissions from sewer networks, holding tanks, and sewage treatment plants. Its main aim is to quantify how the presented technology performs in terms of removing odor nuisance, shaping pollutant levels in sewage, and modifying the composition of the emitted gas. Attempts were also undertaken to identify the optimal AOP variant for limiting nuisance smells. Process optimization involved screening the variants for the best Fenton reaction catalyst, chemical reagent dosage, and reaction time, and by this means for the wastewater retention time in the technological system.

2. Materials and Methods

2.1. Initial Assumptions of the Experiment

The course and final effects of Fenton's reaction depend on many variables. The most important ones include the pH value, temperature, reagent doses, type of catalyst, catalyst/oxidant ratio, and the physical factors used, such as UV radiation, ultrasound, magnetic field, and others. The basic and main assumption of the research was to develop a method with significant application values that can be used continuously or periodically in the sewage network systems and in septic tanks. Therefore, the solution had to be economically justified and technologically simple. The basis was the care for the limitation of the applied doses of Fe salts and H_2O_2 as well as the minimization of the necessary technological procedures. Among other things, the commonly used acidification of the wastewater environment and then pH correction were abandoned. The research work began with very low doses of chemical reagents, which were established based on the extensive literature related to wastewater treatment with the use of Fenton's reagent. The aim was to determine the minimum dose of reagents that will allow the organic process of wastewater putrefaction and the production of H_2S for a minimum period of 10 days.

2.2. Study Design

The study was conducted on a laboratory scale in model anaerobic reactors. The experimental set-up was static and divided into five experimental stages (S) designed to determine the impact of chemical reagents on changes in wastewater parameters, its putrescibility, and odor emissions. The stages were distinguished by different types of input reagents, i.e.:

- stage 1 (S1)—Fe^{2+} in the form of $FeSO_4 \cdot 6H_2O$ and hydrogen peroxide (H_2O_2) in the form of 30% perhydrol solution—Fenton reaction;
- stage 2 (S2)—Fe^{2+} in the form of $Fe_2(SO_4)_3$ and hydrogen peroxide (H_2O_2) in the form of 30% perhydrol solution—Fenton-like reaction;
- stage 3 (S3)—hydrogen peroxide (H_2O_2) in the form of 30% perhydrol solution;
- stage 4 (S4)—Fe^{2+} in the form of $FeSO_4 \cdot 6H_2O$;
- stage 5 (S5)—Fe^{2+} in the form of $Fe_2(SO_4)_3$.

Each experimental stage was divided into variants (V) with different chemical reagent inputs. While the same dosage of the AOP catalyst (Fe^{2+}/Fe^{3+}) was maintained across the experiment, the H_2O_2 inputs varied. The reagent doses were calibrated on the basis of existing studies and literature data [28]. The reagent inputs used at this stage of the experiment are given in Table 1.

Table 1. Chemical reagent doses used in the experiment.

VARIANT	**STAGE 1 (S1)**		**STAGE 2 (S2)**		**STAGE 3 (S3)**	**STAGE 4 (S4)**	**STAGE 5 (S5)**
	Fe^{2+} [g/dm^3]	**H_2O_2 [g/dm^3]**	**Fe^{3+} [g/dm^3]**	**H_2O_2 [g/dm^3]**	**H_2O_2 [g/dm^3]**	**Fe^{2+} [g/dm^3]**	**Fe^{3+} [g/dm^3]**
1 (V1)	0.1	0.5	0.1	0.5	0.5	0.1	0.1
1 (V2)	0.1	1.0	0.1	1.0	1.0	-	-
3 (V3)	0.1	2.0	0.1	2.0	2.0	-	-

2.3. Experimental Set-Up

The experiments were conducted in model steel laboratory reactors (with an ac-tive volume of 5.0 dm^3 and total volume of 6.0 dm^3) under anaerobic conditions to promote putrefaction, H2S production, and odorant emission. Thermostatic cabinets kept the temperature at a constant 20 °C. Light penetration into the reactor was lim-ited. Mechanical agitators were used to provide stirring 2 h per day. A diagram of a single reactor is shown in Figure 1.

A total of 5.0 dm^3 of municipal wastewater was fed into the reactor at the beginning of the experimental cycle, with chemical reagents injected afterwards. In S1 and S2. the wastewater was first amended with the target Fe dose, then, after 10 min, with the H_2O_2 at the target Fe:H_2O_2 ratio by weight. To ensure uniform mixing of the reagent, the reactor content was stirred for 2 h per day, then allowed to react in a stagnant reactor. Samples for analysis were taken daily. The monitoring—with the exception of olfactometric measurement—was discontinued when putrefaction was observed in all variants in the given stage.

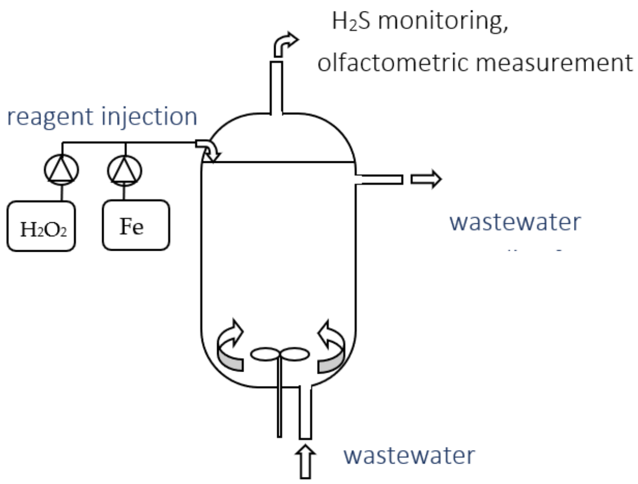

Figure 1. Diagram of the anaerobic reactor used in the experiment.

2.4. Materials

The chemical reagents used for the experiment were provided by Kemipol Sp. z o.o., Police, Poland. Wastewater samples were sourced directly from the sewer network of Olsztyn (Poland) at spots where intense putrefaction produced heightened levels of H_2S gas, leading to nuisance smells. The composition of the municipal wastewater is presented in Table 2.

Table 2. Characteristics of the municipal wastewater used in the experiment.

Parameter	Unit	Value
COD	mgO_2/dm^3	519 ± 91
TOC	mg/dm^3	132 ± 19
BOD_5	mgO_2/dm^3	271 ± 36
TSS	$mg_{d.m.}/dm^3$	380 ± 101
TN	$mgN_{tot.}/dm^3$	68.3 ± 4.2
TP	$mgP_{tot.}/dm^3$	7.1 ± 1.9
Sulfates	$mgSO_4/dm^3$	78 ± 4.9
Sulfides	mgS^{2-}/dm^3	0.123 ± 10
pH	-	7.25 ± 0.25

2.5. Analytical Methods

Once per day, the samples were tested for change in oxidation–reduction potential (ORP) using a Hach Lange HQ 440D multi-parameter meter. Total organic carbon (TOC) was determined in a TOC 1200 analyzer (Thermo Scientific, Waltham, MA, USA). Wastewater putrescibility was determined via methylene blue test PN-76/C-04626. Gas fractions were determined using a gas chromatograph (7890A Agilent, CA, USA) fitted with a thermal conductivity detector. The composition of biogas produced at each reactor was measured every 24 h using a gastight syringe (20 mL injection volume) and a gas chromatograph (GC, 7890A Agilent) equipped with a thermal conductivity detector (TCD). The GC was fitted with the two Hayesep Q columns (80/100 mesh), two molecular sieve columns (60/80 mesh), and Porapak Q column (80/100) operating at a temperature of 70 °C. The temperature of the injection and detector ports were 150 °C and 250 °C, respectively. Helium and argon were used as the carrier gases at a flow of 15 mL/min. COD, total phosphorus ($P_{tot.}$), total nitrogen ($N_{tot.}$), sulfates (SO_4) and sulfides (S^{2-}) were analyzed using cuvette tests for spectrophotometer DR 2800 with a mineralizer (HACH Lange, Düsseldorf, Germany). VSS was determined gravimetrically (part E of EPA Standard Method 2540). BOD_5 was quantified with OxiTop respirometric reactors (WTW GmbH, Weilheim, Germany). The pH was determined using a VWR 1000 L pH meter.

Odor emissions were measured using a T-08 dynamic olfactometer (Ecoma GmbH, Honigsee, Germany). The laboratory is compliant with ISO/IEC 17025:2017 [29], located far away from sources of noise and disruptive light (shielded from direct sunlight), and well-ventilated with odor-free air. Temperature at measurement time was 20 ÷ 23 °C. Samples for analysis were collected using vacuum gas cylinders with built-in fans into a Tedlar bag inside the cylinder. Levels of odorants were determined using the YES/NO method by an odor panel selected in accordance with EN 13725:2003 [30] from 30 persons. For the assessment, the sample was diluted in odor-free air, then presented at different odorant levels to the panel, who quantified the European odor units in one cubic meter (ou_E/m^3). The screening was done one week prior to the experiment. Three measurement sessions were conducted with one day's break in-between. Each panelist conducted 10 individual assessments. The selected panelists had to meet the following criteria: the geometric mean of individual detection threshold for a reference material (n-butanol in nitrogen) had to be within the range of 0.20 ÷ 0.80 µmol/mol; the antilogarithm of the standard deviation, calculated from the base-10 logarithm of the individual detection threshold (in mass concentration units for the reference gas), had to be lower than 2.3.

2.6. Statistical Analysis

Each experiment was repeated three times. Statistical analysis of the results was performed using one-way analysis of variance. Differences were considered significant at $p < 0.05$. Tukey's HSD (honestly significant difference) was used to determine the significance of differences between averaged values for different groups.

3. Results

3.1. Putrefaction

Raw sewage was already putrid by the end of day 1. S1V3 had the longest time-to-putrefaction at 13 days (Figure 2). Lower doses of H_2O_2 accelerated putrefaction, which occurred after 8 and 9 days in S1VT1 and S1V2, respectively. S2 performed significantly worse. At the highest reagent inputs, the oxidation system Fe^{3+}/H_2O_2 (S2V3) suppressed the putrefaction process for 10 days (Figure 2). In S3, H_2O_2 alone managed to halt wastewater putrefaction for a period of 5 days at doses between 0.5 g H_2O_2/dm^3–1.0 g H_2O_2/dm^3 (S3V1–S3V2). The highest doses of the oxidant (S3V3) kept the wastewater in the anaerobic reactor from putrefying for 7 days. The Fe^{2+}-only (S4V1) and Fe^{3+}-only (S5V1) variants showed sub-optimal performance, with wastewater becoming putrid after 3 days' retention time in the system (Figure 2).

3.2. Oxidation–Reduction Potential (ORP)

The ORP of raw sewage dropped to 42.3 ± 3.1 mV after just 1 day under anaerobic conditions. As the experiment went on, the observed levels varied between 123.9 ± 4.2 mV and 192.4 ± 5.7 mV (Figure 3 and Table S1). Introduction of Fe^{2+}/H_2O_2 (S1) significantly reduced the rate of ORP drop-off. At the highest dose of the reagents (S1V3), the value evolved from 280.3 ± 7.4 mV on day 1 to 1.3 ± 0.5 mV on day 9. Longer retention times in the system led to a decrease in ORP below 0 mV. S1V1 and S1V2 maintained positive ORP values for 6 days' retention in the system (Figure 3 and Table S1). Fe^{3+}/H_2O_2 decelerated the ORP decrease in S2 compared to raw wastewater, but not to the extent seen in S1. The best performance was achieved in S2V3, where the decline was held back for 5 days. Amendment with 0.1 g Fe^{3+}/dm^3 and 0.5 g H_2O_2/dm^3 (S2V1) successfully kept ORP above zero for a period of 3 days, whereas doses of 0.1 g Fe^{3+}/dm^3 and 1.0 g H_2O_2/dm^3 (S2V2) did so for 4 days (Figure 3). H_2O_2 alone (S3) failed to match the performance of the Fe/H_2O_2 systems. The oxidant doses used for S3V1 and S3V2 inhibited the redox processes for only 2 days. In contrast, 2.0 g H_2O_2/dm^3 (S3V3) maintained ORP above zero for 4 days. The Fe^{2+}-only (S4V1) and Fe^{3+}-only (S5V1) variants also performed poorly (Figure 3 and Table S1).

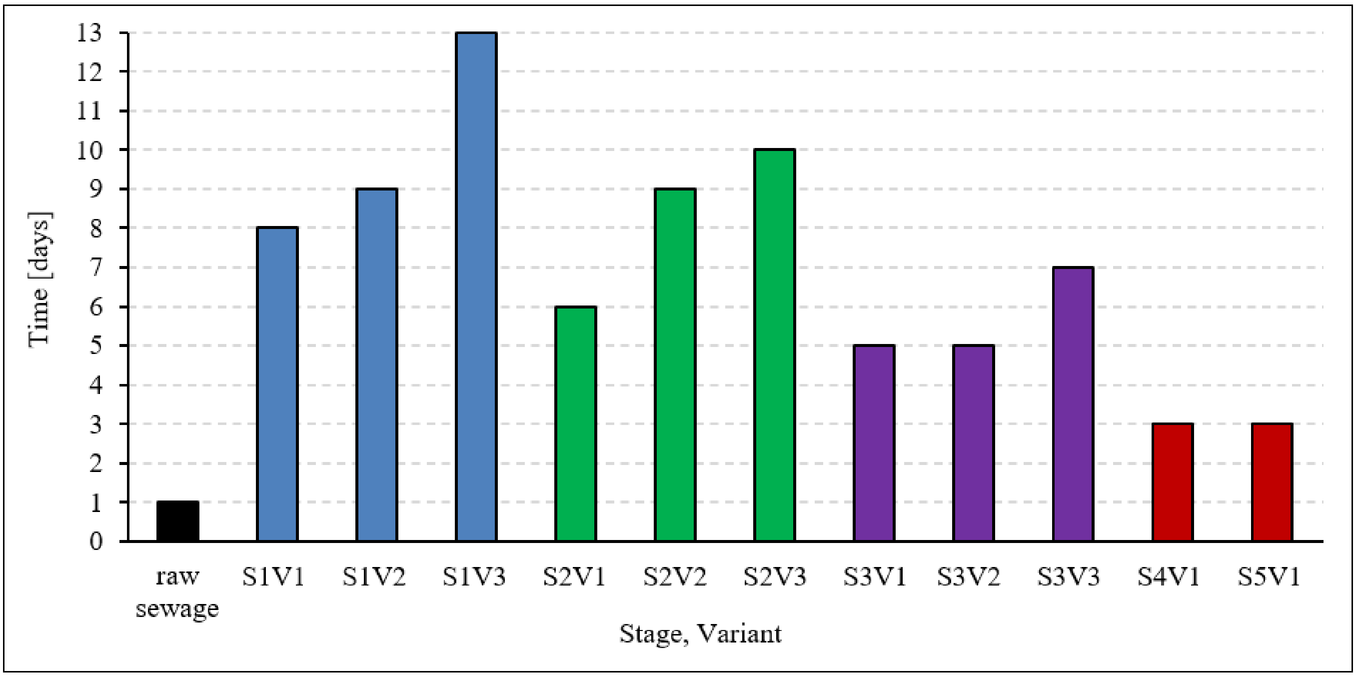

Figure 2. Time-to-putrefaction for wastewater across different variants.

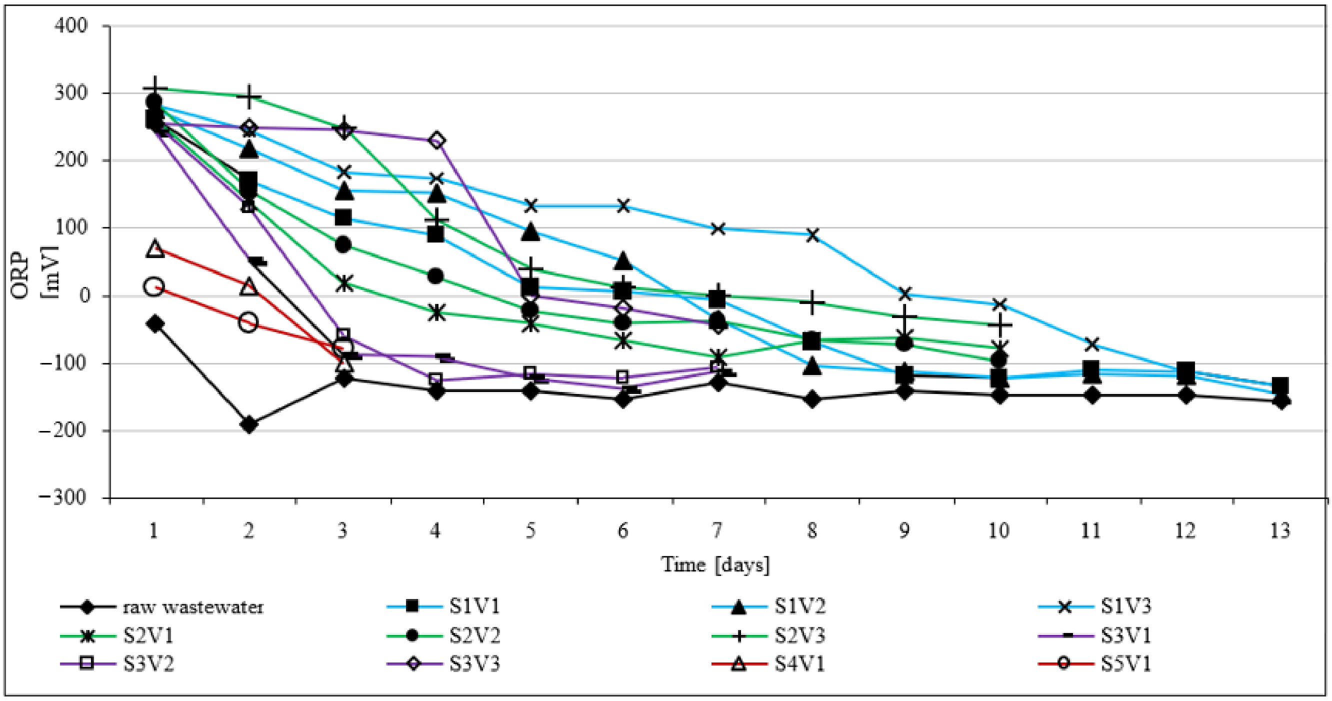

Figure 3. Changes in oxidation–reduction potential across variants.

3.3. TOC

TOC in the raw wastewater averaged between 119.6 ± 8.4 mg/dm^3 and 144.6 ± 12.5 mg/dm^3 (Figure 4 and Table S2). The Fe^{2+}/H_2O_2 oxidizing system (S1) reduced its value to 72.9 ± 3.9 mg/dm^3 in S1V3 to 76.0 ± 4.4 mg/dm^3 in S1V2 after just 24 hours' retention in the system. Variant S2V3 had lower TOCs—between 79.8 ± 5.8 mg/dm^3 and 95.1 ± 8.3 mg/dm^3. Slightly less pronounced removal was noted for S2V1 and S2V2 (Figure 4 and Table S2). Significantly poorer results were obtained when H_2O_2 (S3) or Fe ions (S4, S5) were the sole reagents in the wastewater (Figure 4 and Table S2).

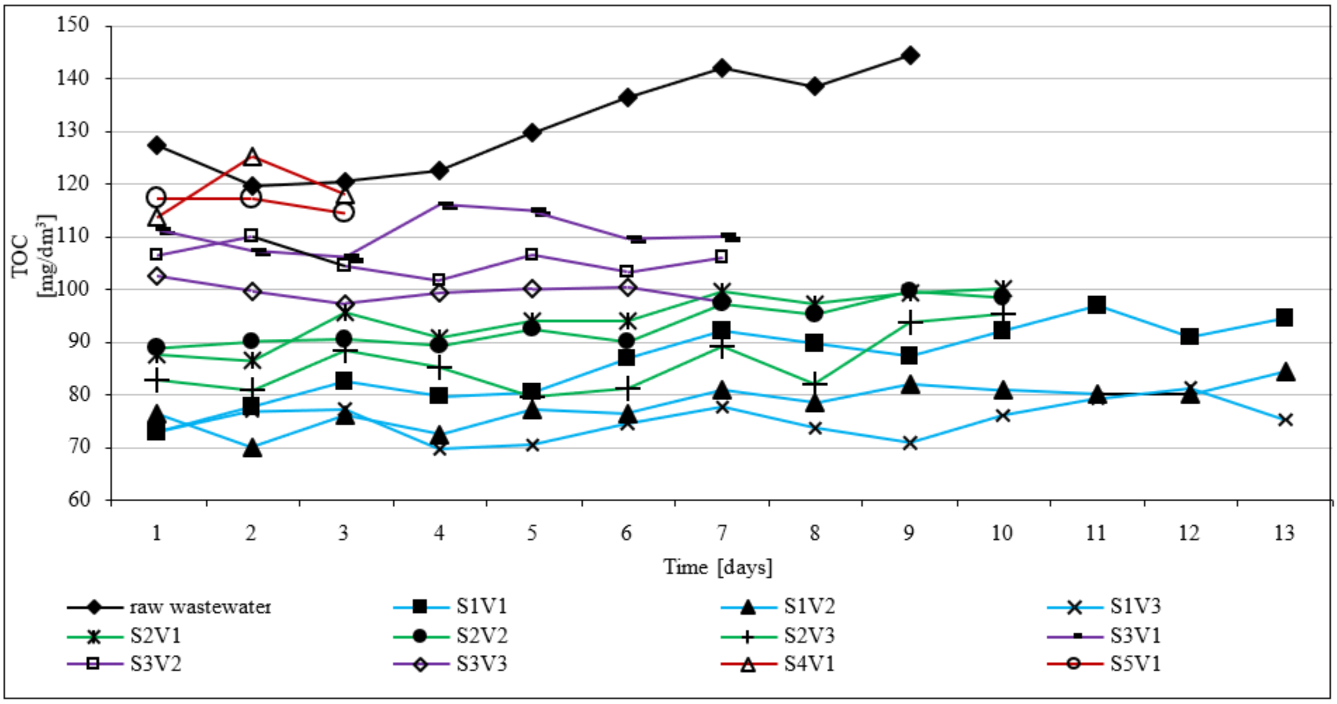

Figure 4. Changes in TOC across variants.

3.4. Changes in pH, Concentrations of Sulfates/Sulfides

The pH of raw wastewater was within the range of 7–7.5. The initial sulfate concentration was 78 ± 4.9 mg/dm^3 and dropped to 28 ± 3.1 mg/dm^3 after thirteen days. The sulfate content of the raw wastewater decreased by 50% by day 9 of the experiment. The concentration of sulfides in the raw wastewater averaged approx. 0.123 ± 10 mg/dm^3 (Table 2).

Across all variants of S1, the pH fell below 7 immediately after introduction of the chemical reagents, then quickly reverted to near-neutral values. Sulfate concentrations in V1–V3 did not significantly change, maintaining levels of 120–130 mg/dm^3. The average values were 0.026 ± 0.09 mg/dm^3, 0.041 ± 0.07 mg/dm^3 and 0.019 ± 0.02 mg/dm^3 in S1V1, S1V2 and S1V3, respectively. In S2 immediately after amendment with reagents, the pH fell below 6, then rebounded slightly to levels of around 7.2 or less. Sulfate concentrations in V1–V3 were approx. 280–300 mg/dm^3. Sulfides averaged 0.013 ± 0.04 mg/dm^3, 0.023 ± 0.11 mg/dm^3 and 0.01 ± 0.01 mg/dm^3 in S2V1, S2V2, and S2V3, respectively.

The pH was near-neutral across all reagent inputs. Concentrations of sulfates were within the range of 20–40 mg/dm^3 in S3V1 and 10 mg/dm^3–42 mg/dm^3 in S3V2 and S3V3. Sulfide levels averaged 0.129 ± 0.21 mg/dm^3, 0.113 ± 0.17 mg/dm^3 and 0.083 ± 0.02 mg/dm^3 in S3V1, S3V2, and S3V3, respectively. In S4V1, the pH dropped to 6.36 ± 0.11 after amendment with Fe salts, then progressively rose to 7.14 ± 0.09. Sulfate and sulfide levels were stable at approx. 100 ± 10 mg/dm^3 and 0.130 ± 0.021 mg/dm^3 (respectively) throughout the experiment. The pH in S5V1 was 6.55–6.91. The concentration of sulfates ranged from 170 mg/dm^3 to 240 mg/dm^3, whereas that of sulfites from 0.040 mg/dm^3 to 0.077 mg/dm^3.

3.5. H_2S Levels

The H_2S in raw wastewater was detected as early as day 2 of anaerobic retention, at levels of 5.6 ppm to 64 ppm. The traditional Fenton reaction proved to be the best at limiting H_2S formation (S1). No H_2S was detected for 8 days in the biogas with the maximum doses of Fe^{2+}/H_2O_2 (S1V3). By comparison, corresponding amounts of Fe^{3+} ions and H_2O_2 in S2V3 inhibited H_2S generation for only 5 days of retention (Figure 5 and Table S3). At the lowest reagent dose, H_2S generation was inhibited for 5 and 3 days (S1VT1 and S2V1, respectively). Once hydrogen sulfide emerged, its levels in the biogas did not exceed 4.0 ppm in either variant. A dose of 0.5 g H_2O_2/dm^3 (S3V1) inactivated H_2S production for a period of 2 days, after which its levels ranged from 5.3 ± 1.1 ppm to 7.3 ± 0.9 ppm (Figure 5 and Table S3). The same inhibition period applied to reactors amended with iron salts only (S4V1, S5V1).

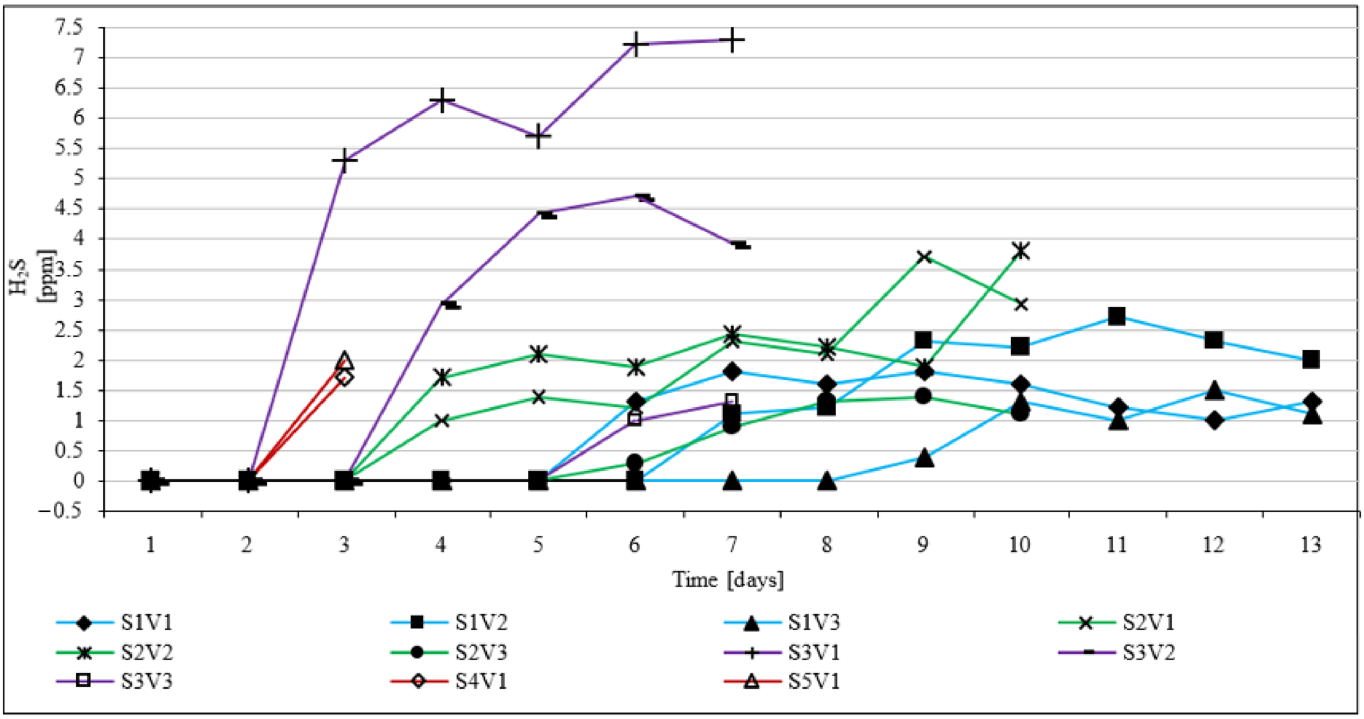

Figure 5. Changes in H_2S in the biogas across variants.

3.6. Concentrations of Other Gases

The composition of the gas generated from raw wastewater was as follows: CH_4—0.0%; CO_2—0.0%; O_2—20.5 ± 1.3%; N_2—79.5 ± 2.1%; H_2S—0.0 ppm; NH_3—0 ppm. Oxygen levels decreased on the second day of the experiment. After H_2S started forming, NH_3 emerged as well at 51 ± 3 ppm. On day 5, NH_3 concentrations started to exceed 500 ppm and remained at around this level until the end (Table S4). In S1V1, NH_3 was first detected on day 6 at 72 ± 2 ppm and did not exceed 93 ± 4 ppm till the end of the experiment. As at day 13, the gas contained 15.8 ± 1.7% oxygen and 48 ± 2 ppm NH_3. In S1V2 and S1V3, NH_3 appeared on day 7 and its concentration was at around 18 ± 3 ppm until day 9. By the end of the experiment, the levels in the two variants had risen to 47 ± 5 ppm and 12 ± 1 ppm, respectively. CO_2 varied between 0.5% and 2.0% across all variants and in raw wastewater (Table S4).

S2V2 exhibited no detectable NH_3 and 20 ± 3% oxygen. In S2V1, NH_3 was present from day 7 (at 90 ± 4 ppm) till day 10 (148 ± 5 ppm), at which point the oxygen fraction was 19.4 ± 1.5%. In S2V3, NH_3 was detected for the first and only time on day 3 at 31 ± 2 ppm (Table S5). Oxygen levels reached 24.3 ± 1.7% after reagent addition, then fell to 22.1 ± 1.6% after ten days. Carbon dioxide levels were between 0.5% and 2.0%.

In S3V1, NH_3 did not exceed the peak value of 170 ± 5 ppm (detected on day 5 of retention). On the second day, the oxygen content was 20.8 ± 1.5%, but fell to 16.0 ± 1.2% by the end of the experiment. CO_2 concentration was 0.1 ± 0.1% on day 2, and 2.4 ± 0.2% on day 7 (Table S6). In S3V2, NH_3 was first noted on day 2 at 18 ± 3 ppm and progressively increased until day 5 (209 ± 6 ppm). By day 7, NH_3 levels dropped to 85 ± 3 ppm. Oxygen concentration on day 2 was 21.3 ± 1.4%, dropping to 18.7 ± 1.1% by the end of the experiment. CO_2 fraction progressively increased throughout the entire retention period and reached 2.3 ± 0.3% on the last day (Table S6). S3V3 had the lowest levels of carbon dioxide—0.2 ± 0.1% on day 2 and 2.1 ± 0.2% at the end. Ammonia appeared on day 2 and its concentration remained at around 30 ± 3 ppm until the end of the variant.

In S4V1, NH_3 appeared on day 2 at 12 ± 1 ppm, rising to 49 ± 2 ppm the next day. CO_2 content did not exceed 0.5 ± 0.1%. Oxygen accounted for 20.0 ± 1.1% of the gas by the end. In S5V1, NH_3 was detected from day 3 onwards at 64 ± 3 ppm. CO_2 was first produced on day 2 at 1.7 ± 0.2%, and its content increased to 2.8 ± 0.3% on day 3. Final oxygen concentration was 19.2 ± 1.3% (Table S7).

3.7. Odor Concentration

Olfactometric testing showed the odor concentration (OC) of raw wastewater to be 2980 ± 110 ou_e/m^3. Raw-wastewater OC increased with time and ranged between 3200 ± 320 ou_e/m^3 and 3550 ± 160 ou_e/m^3 (Figure 6). OC rose by up to 20 ± 2.1% after 4 days of anaerobic retention (Figure 7). The largest decrease in odor emission was found for S1V3, where it was reduced by 96.3 ± 1.2% to a level of 110 ± 60 ou_e/m^3 after just one day. The Fe^{2+}/H_2O_2 system maintained its oxidizing capacity up until day 7, with a 96.0 ± 1.3% OC reduction to a level of 120 ± 10 ou_e/m^3. In the subsequent measurements (day 10 and 13), the OC increased to 1310 ± 140 ou_e/m^3 and 1150 ± 240 ou_e/m^3. Lower inputs of Fe^{2+}/H_2O_2 led to markedly poorer performance. OC rebound was noted as early as day 7 of anaerobic retention, rising to 1420 ± 210 ou_e/m^3 in S1V1 and 1350 ± 90 ou_e/m^3 in S2V2 (Figure 6). Considerably higher OCs were found for the Fe^{3+}/H_2O_2 oxidizing system. In this group of variants, S2V3 showed the highest odor removal at 89.9 ± 1.7%. OC values detected on and before day 7 of anaerobic retention ranged from 300 ± 40 ou_e/m^3 to 590 ± 60 ou_e/m^3. At lower doses of H_2O_2 (S2V1 and S2V2), OC exceeded 1200 ou_e/m^3 after just 4 days, with removal efficiency below 60 ± 2.7%. Fe salt alone was insufficient to achieve high performance. In S4, the OC ranged between 2230 ± 190 ou_e/m^3 and 3260 ± 320 ou_e/m^3, whereas the range for S5 was 2940 ± 230 ou_e/m^3 to 3260 ± 250 ou_e/m^3. Amendment with H_2O_2 alone was not successful in significantly reducing nuisance smells, with the exception of variant S3V3, which produced an 89.6 ± 3.2% reduction (Figure 7). In the same variant, OC was 310 ± 40 ou_e/m^3 on day 4, then started to increase rapidly to a level of 1940 ± 140 ou_e/m^3 (day 10).

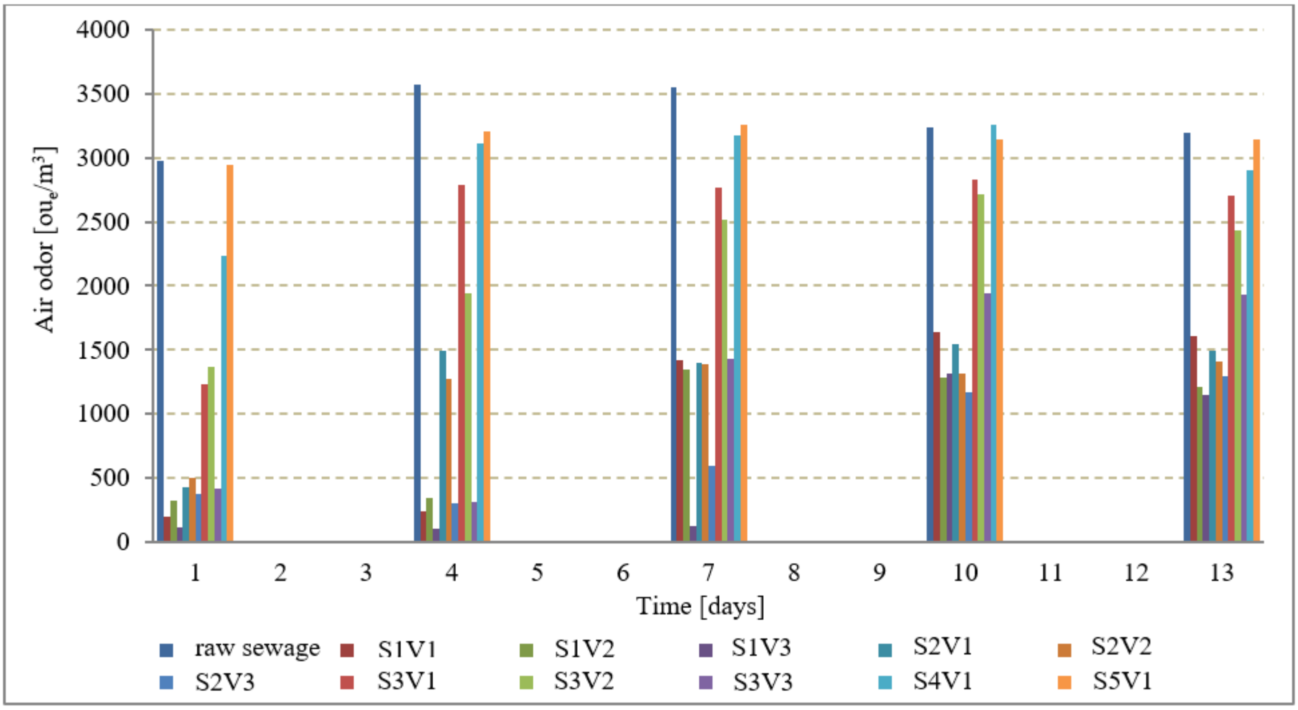

Figure 6. Odor levels in the air across variants.

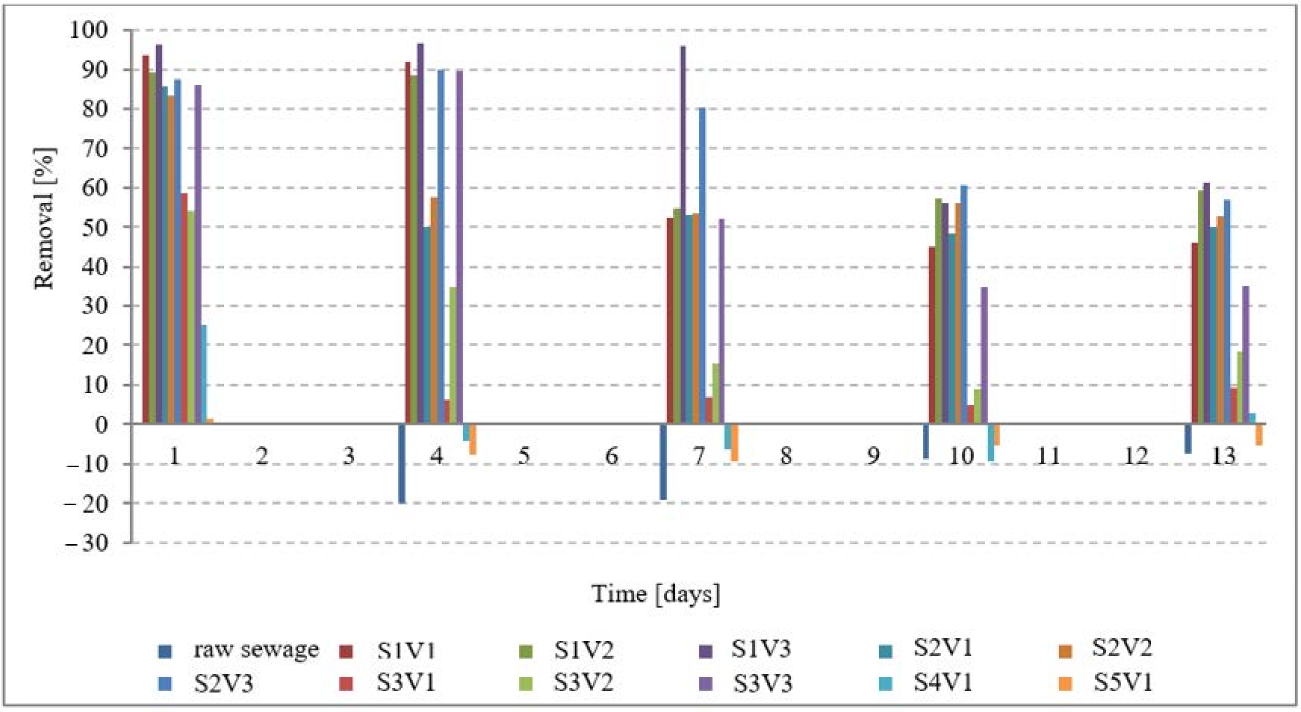

Figure 7. Odor removal across variants.

4. Discussion

Current EU legislature lacks consistent regulations that would comprehensively address odor-nuisance issues [31]. The issue is covered, to some extent, by the BAT (Best Available Techniques), which define the conditions for integrated permits across all EU states, pursuant to Directive 2010/75/EU of the European Parliament and of the Council on industrial emissions (OJ EU 2010, L 334/17). The BAT conclusions point to the need for an odor control plan, including (but not limited to) measures to prevent or limit noxious substance generation [32]. The conclusions require that noxious substances be purged from the air, citing biofilters or two-/three-step air cleaning systems as possible options. This does not, however, preclude other methods, as the notes state that the techniques listed and described in these BAT conclusions are neither prescriptive nor exhaustive [33]. At the moment, there is a dearth of properly documented scientific research aimed at identifying and analyzing deodorization processes and their implementation in water/sewage systems. As the BAT conclusions have already been issued, and further ones have been announced for multiple industries, increased demand should be expected for new deodorization techniques and for upgrades to existing ones.

An experiment conducted in the USA is an example of employing hydrogen peroxide, confirming its suitability for alleviating H_2S-induced noxious odors from sludge [34]. Perhydrol proved to be a very effective and cost-efficient solution. A different study tested how another strong oxidizer in the form of $KMnO_4$ performed in reducing hydrogen sulfide in sludge. Input levels being the same, H_2O_2 removed 87–99% of H_2S, whereas $KMnO_4$ removed only 38–68%. The method was successfully deployed in full scale at a sewage treatment plant in Orlando, Florida [34]. The chemical reactions responsible for removing H_2S with the use of H_2O_2 are directly regulated by the solution's pH [35]:

$$\text{pH} < 8.5\text{: } H_2O_2 + H_2S \rightarrow S + 2H_2O \tag{1}$$

$$\text{pH} > 8.5\text{: } 4H_2O_2 + S^{2-} \rightarrow SO_4{}^{2-} + 2H_2O \tag{2}$$

In the present study, pH remained below 8.5 across all of the experimental variants, which means that H_2S oxidization and odor neutralization proceeded along reaction pathway (4). H_2O_2 alone substantially reduced putrefaction, H_2S production, and odor concentration in the air, but only at the highest dose of the oxidizer—2.0 g H_2O_2/dm^3 wastewater. Even then, this variant performed worse than the AOPs. High levels of H_2O_2 have been shown to reduce H_2S oxidization due to the potential self-consumption of $^{\bullet}OH$, leading to poorer efficiency [36,37]:

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2,\ k = 2.7 \cdot 10^7\ M^{-1}s^{-1} \tag{3}$$

Other researchers have demonstrated that H_2O_2 can be used for effective deodorization. This extends to odorants generated by breweries, such as 2-methylpropanal, 3-methylbutanal, 2-methylbutanal, 3-methyl-1-butanol, n-hexanal, 2-methylbutyl isobutyrate, undecan-2-one, phenylacetaldehyde, myrcene, limonene, linalool, humulene, dimethyl sulfide, and dimethyl trisulfide. It should be noted, however, that the experiment in question used catalytic H_2O_2 degradation with UV irradiation [38]. There has also been field research work to investigate H_2S oxidation with 35% H_2O_2. Dosage was tied to H_2S gas concentration, as well as COD and sulfides in the wastewater. H_2O_2 was found to significantly decrease H_2S emission, with final levels of 4 and 7 ppm (respectively) in the tested sewer networks. Dissolved sulfite levels were between 0.3 mgS/dm^3 and 1.7 mgS/dm^3. COD removal reached approx. 30% [39]. Another pilot-scale study set out to assess AOP (H_2O_2/O_3) performance in taste/odor control and organic carbon removal from aqueous solutions. H_2O_2/O_3 proved effective in removing geosmin and 2-methylisoborneol [40].

The usefulness of AOPs for mitigating odor nuisance in municipal facilities stems from their characteristics and mode of action [41]. The Fenton reaction is particularly well-suited for this purpose, both in its Fe^{2+}/H_2O_2, and Fe^{3+}/H_2O_2 variants. Fenton and Fenton-like reactions can break down odorants into carbon dioxide and other odorless products [42].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \tag{4}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}OOH + H^+ \tag{5}$$

$$OH + {}^{\bullet}OOH + \text{odorants} \rightarrow CO_2 + \text{odorless breakdown products} \tag{6}$$

Hydrogen peroxide and catalysis-derived free hydroxyl radicals ($^{\bullet}OH$) inhibit the formation of hydrogen sulfide. Iron salts, in turn, can fix and render it non-soluble [43]. The reagents do not change the profile of the wastewater, nor increase its toxicity [44]. After the treatment, the wastewater discharged to the treatment plant is not an anaerobic medium. However, it is, at the least, anoxic (free of active putrefaction processes), thus preventing proliferation of sulfur-oxidizing filamentous bacteria (*Beggiatoa*, *Thiohrtix*)—a common problem with activated sludge [45]. Depending on the catalyst, free hydroxyl radicals can form either via a one- or two-step process, as per the following reactions [46,47]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \tag{7}$$

$$Fe^{3+} + H_2O_2 \rightarrow [Fe(HO_2)]^{2+} + H^+ \tag{8}$$

$$[Fe(OH_2)]^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet} \tag{9}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + {}^{\bullet}OH \tag{10}$$

Using Fe^{2+} ions ensures that the Fenton reaction proceeds along a fast, single-step pathway [48]. The Fenton reagent used for S2 was the iron ion Fe^{3+}, derived from $Fe_2(SO_4)_3$. This stage of the study was characterized by reduced performance, which may be attributed to the two-step nature of the Fe^{3+} radical-formation process, which slows down the reaction rates [49]. The process begins with the slow reaction between Fe^{3+} ions and H_2O_2, generating Fe (II) ions and H_2O_2. Once this happens, the typical Fenton reaction can occur between the two products. The Fe^{3+} reaction tends to be significantly slower, though this finding is one upon which researchers are not entirely in agreement [50]. What is certain, however, is that the rate of the Fe^{3+} reaction is bottlenecked by the rate of Fe^{2+} formation.

The oxidizing potential of $^{\bullet}OH$ is very high and can reach 2.80 V. It has been shown that $^{\bullet}OH$ can oxidize H_2S via the following reactions [51,52]:

$$H_2S \rightarrow^{H2O} HS^- + H^+ \tag{11}$$

$$H_2S + {}^{\bullet}OH \rightarrow HS^{\bullet} + H_2O \tag{12}$$

$$HS^- + {}^{\bullet}OH \rightarrow HSOH^{\bullet -} + H^{\bullet} \tag{13}$$

$$HS^{\bullet} + H_2O_2 \rightarrow H_2SO_4 + H_2 \tag{14}$$

$$H_2SO_2{}^{\bullet} + H_2O_2 \rightarrow H_2SO_4 + H_2 \tag{15}$$

$$HSOH^{\bullet -} + H_2O_2 \rightarrow H_2SO_3 + H_2 \tag{16}$$

$$H_2SO_3 + H_2O_2 \rightarrow H_2SO_3 + H_2O \tag{17}$$

$$H_2SO_3 + {}^{\bullet}OH \rightarrow H_2SO_4 + H^{\bullet} \tag{18}$$

Similarly, iron salts are used to fix and remove H_2S as non-soluble, sedimenting sulfides, in a reaction that follows the following formulas [53]:

$$Fe^{3+} + 3H_2S \rightarrow Fe_2S_{3\downarrow} + 6H^+ \tag{19}$$

$$Fe^{2+} + H_2S \rightarrow FeS_{\downarrow} + 2H^+ \tag{20}$$

However, excessive levels of Fe^{2+} as a Fenton reagent can lead to rapid depletion of $^{\bullet}OH$ in the solution, in the course of the following reaction [53]:

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^-, k = 3.0 \cdot 10^8\ M^{-1}s^{-1} \tag{21}$$

ORP is an indicator that characterizes the level of wastewater oxidation [54]. It is also increasingly used to assess the quality of drinking and industrial water, as well as to assess the environmental quality of water bodies [55]. The maintenance of positive ORP values indicates that the environment does not develop anaerobic and reducing conditions [56]. In the case of wastewater with high load of organic compounds, a decrease in ORP below 0 mV causes anaerobic degradation of pollutants, rotting processes, and odorous substance emissions [57]. Therefore, it is an indicator that allows monitoring of the level of oxygenation in wastewater, the knowledge of which and the observed trends of changes allow to predict the beginning of the H_2S production process [58]. The influence of Fenton's reagent on the ORP value is due to the fact that H_2O_2 and free hydroxyl radicals are strong oxidants and electron acceptors from other chemical compounds [59,60]. On the other hand, the effect of maintaining positive ORP values in wastewater is due to the fact that H_2O_2 is decomposed into H_2O and O_2, which directly affects the maintenance of aerobic conditions [61].

The effectiveness of Fenton's reaction in removing odorants is supported by a study on livestock manure [62]. The reduction of volatile fatty acid, indol, and phenol emissions was strongly correlated with reagent input, pH, and the presence of suspended solids. Odorants were completely removed with 40 mM $FeCl_3$ and 400 mM H_2O_2. Elimination of odorants in slurry has resulted in 90–100% removal of foul-smelling emissions beyond the surface [42]. Another study tested Fenton's reagent performance in removing dimethyl disulfide from a model solution, designed to simulate wastewater from poultry feather production. Peak degradation (95%) was achieved at 60 °C for 30 min. The control reaction, with hydrogen peroxide (sans Fe ions), produced only 60% removal [63].

The present study compared the effectiveness of H_2O_2, Fe^{2+}, Fe^{3+}, and advanced oxidation processes (Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2) in suppressing odor-generating processes. It demonstrated that the Fe^{2+}-mediated Fenton variant performed the best in this regard. This held true across all of the wastewater profiles tested during the experiment. Fe^{2+} ions are the most popular and widely-used radical-forming Fenton reagent [64]. The superior performance of Fe^{2+} in terms of inhibiting redox conditions' development, inhibiting hydrogen sulfide formation, and reducing organic levels in wastewater may be attributed to the faster and more efficient formation of free hydroxyl radicals ($OH^{\bullet}$).

5. Process Design

Understanding the mechanisms and assessing the effectiveness of AOPs' application in wastewater deodorization allows us to conclude that this technology is characterized by great application advantages. It is relatively cheap, technologically simple, widely available, and does not require specialized equipment and trained service. Therefore, it is important to develop technological concepts of systems and solutions for the practical use of Fenton's reagent in wastewater transport and storage systems.

The design for this sewage and holding tank AOP deodorization system calls for two components: an injection unit and a monitoring/control/measurement unit. The injection unit includes storage tanks for chemical reactant solutions (Fe salts, hydrogen peroxide) and suitable metering pumps, which can be controlled via signals from the control/measurement equipment or operated manually. Since chemical reagents can be supplied into the sewer system through either pressure-free (drain well, holding tank) or pressurized means (closed sewer pipes), appropriate metering fittings are to be used.

Each station can be equipped with a control system (Figure 8). The capacity and intervals of the metering pumps can be controlled via relays integrated with sensors for detecting H_2S levels, levels of other odorants, wastewater flow rate, organic compound levels, and system temperature. The reagent injection system can be controlled via signals from a single measuring apparatus or via cumulative signals from multiple readings, processed according to pre-set priorities. Of course, the set-up can be expanded to include a system for monitoring parameters which are process-relevant and/or improve management of the installation, e.g., reagent level in storage tanks or metering pump failure. The assembly for measuring selected parameters can be networked to provide system performance information to sewage/holding tank users or administrators.

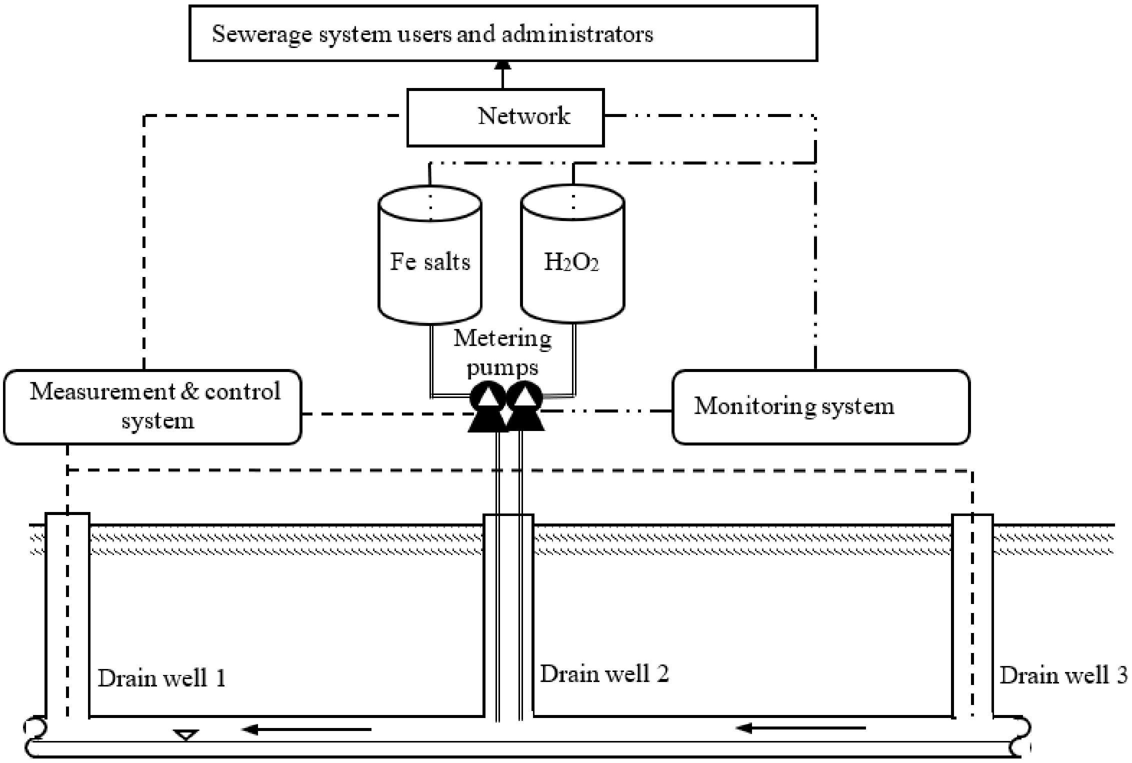

Figure 8. Diagram of the automatic reagent injection system for sewage networks.

In certain cases, if the odors generated are faint and sporadic, the control system can be eschewed in favor of a portable reagent supply station (Figure 9). The Fenton reagent dosage and running time will depend on how much time is needed to eliminate or efficiently reduce the offensive odor. This is controlled manually by a competent and trained operator.

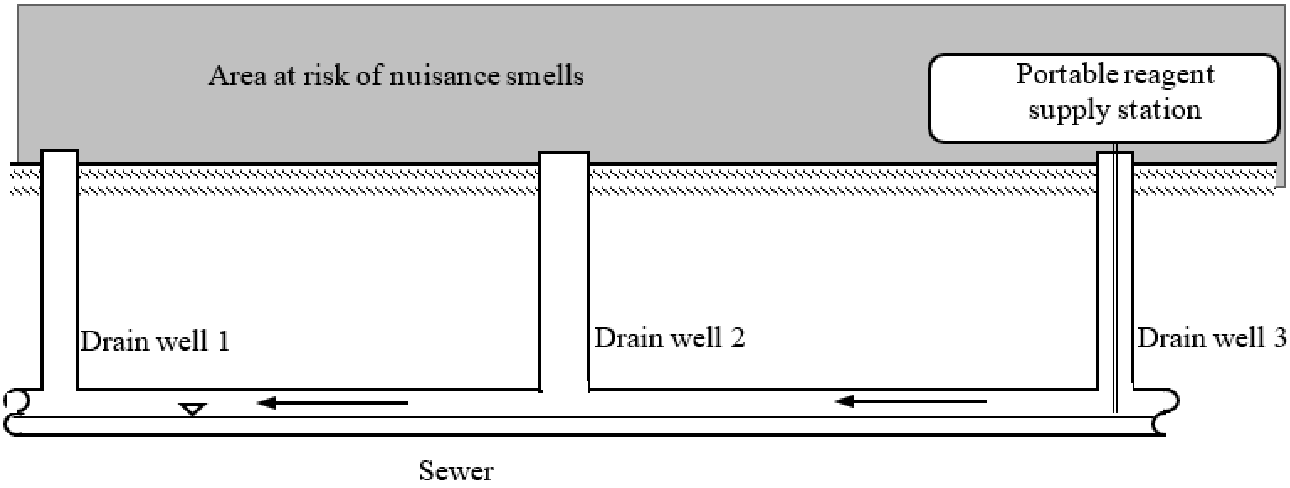

Figure 9. Diagram of the manual reagent injection system for sewage networks, with portable reagent supply station.

A Fenton reagent can likewise be injected into holding tanks (Figure 10). In this case, however, an efficient system must be provided for mixing the collected wastewater with the chemical reagents, e.g., mechanical agitator, ejector, or stirring pump.

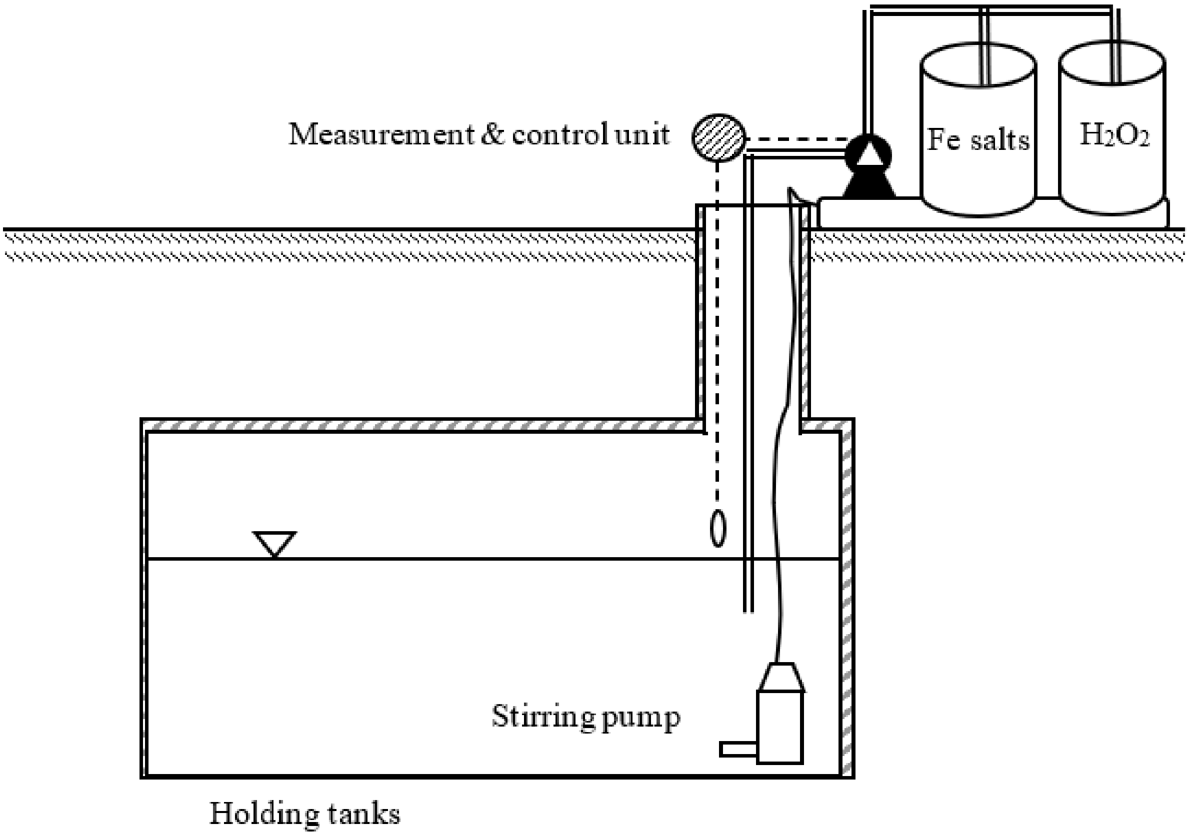

Figure 10. Diagram of the reagent injection system for amending holding tanks.

6. Conclusions

Fenton-based AOP systems are a technologically and commercially viable method of deodorizing sewage facilities. Arguments for the widespread implementation of this technology include universal availability and low cost of chemical reagents, ease-of-use, and high efficiency. The Fe/H_2O_2 system offers a multimodal approach by effectively oxidizing putrescible organics, increasing oxygen in the wastewater (thus reducing ORP), decreasing or eliminating hydrogen sulfide emissions, and inhibiting the activity of anaerobic bacteria that produce foul-smelling metabolites.

The present experiment indicates that the Fe^{2+}/H_2O_2 advanced oxidation process is the optimal choice for inhibiting hydrogen sulfide formation in wastewater. The traditional Fenton reaction proved to be the most efficient in terms of decreasing ORP, removing organic matter in the wastewater, and reducing odorants in the emitted gas. Considerably lower performance was noted for amendment with Fe^{3+} and H_2O_2.

However, regardless of whether radical formation was mediated by Fe^{2+} or Fe^{3+}, the final performance was directly and proportionally correlated with the oxidant (H_2O_2) input. The values of the tested metrics show that amending the wastewater with Fe salt alone has little impact on putrefaction, hydrogen sulfide formation, and odor generation. Similarly, the H_2O_2-only variant also failed to match the performance of the combined Fe/H_2O_2 system.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/atmos13101724/s1, Table S1: Changes in oxidation–reduction potential across variants. Table S2: Changes in TOC across variants. Table S3: Changes in H_2S in the biogas across variants. Table S4: Concentrations of gas constituents (except for H_2S) in S1; Table S5: Concentrations of gas constituents (except for H_2S) in S2; Table S6: Concentrations of gas constituents (except for H_2S) in S3; Table S7: Concentrations of gas constituents (except for H_2S) in S4 and S5.

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