

EFFECT OF THE APPLICATION OF ADVANCED OXIDATION TECHNOLOGY ON THE EFFECTIVENESS OF ANAEROBIC TREATMENT OF WASTEWATERS WITH A HIGH CONCENTRATION OF FORMALDEHYDE

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Abstract: The objective of this study was to determine the effect of advanced oxidation process with the use of Fenton's reaction on the effectiveness of anaerobic treatment of wastewaters originating from the wood industry that were characterized by a high concentration of formaldehyde. Experiments were established to analyze changes in COD content and in the concentration of formaldehyde in treated wastewaters, additional analyses were carried out to assay quantitative and qualitative changes in the biogas produced. The first stage of the experiment involved analyses of the effectiveness of the tested wastewaters treatment only in the process of methane fermentation. At the second stage of the experiment, the biological process was preceded by chemical pre-treatment of wastewaters with Fenton's reagent. The conducted study proved that the investigated variants of chemical pre-treatment of wastewaters had a significant effect on increasing the total biogas production. In contrast, no significant effect of the applied technology was demonstrated on changes in the concentration of the analyzed contaminants in the treated wastewaters.

INTRODUCTION

Wastewaters originating from the wood industry are characterized by high contents of organic compounds, toxic substances, dyes, surface-active compounds and other structurally-complex additives [10]. Wastewaters of this type frequently contain significant quantities of formaldehyde which is applied in technological processes, mainly for the strengthening and preservation of products [7]. Concentrations of contaminants present in wood wastewaters affect directly the fact that they are difficult to treat in aerobic and anaerobic biological systems [12].

Hence, a need emerges to search for technological solutions that would enable achieving high final effects of the treatment process. In many cases, where difficulties

or restrictions appear in the application of biological methods, multi-stage solutions are being introduced that are based on the exploitation of physical, chemical and biochemical phenomena [9].

An alternative to the currently used methods may be cutting-edge technologies based on the coupled application of chemical and biological methods [13]. A high effectiveness of this type of technological systems was described in many reference works [1, 6]. One of the methods of chemical pre-treatment of wastewaters is the application of Fenton's reaction. A high rate of wastewaters degradation as well as universality and high effectiveness make the methods of advanced oxidation increasingly considered these days as promising technologies of wastewaters treatments and sewage sludges processing [2, 15]. One of the methods of advanced oxidation is the so-called Fenton's reaction proceeding with the use of H_2O_2 and iron ions as a catalyst of the process. The mechanism of reaction leads to catalytic degradation of H_2O_2 in the presence of Fe^{2+} , which results in the generation of reactive hydroxyl radicals OH^\cdot with a very high oxidizing potential reaching 2.8 V [13]. The characteristics of Fenton's reaction and investigations conducted so far indicate that this method may be applied as a competitive technology supporting processes of hardly-degradable contaminants present in wastewaters.

The objective of this study was to determine the effect of advanced oxidation process with the use of Fenton's reaction on the effectiveness of anaerobic treatment of wastewaters originating from the wood industry that were characterized by a high concentration of formaldehyde. Experiments were established to analyze changes in COD content and in the concentration of formaldehyde in treated wastewaters, additional analyses were carried out to assay quantitative and qualitative changes in the biogas produced.

Table 1. Contents of contaminants in wastewaters used in the experiments

Parameter	Unit	Mean value	Min. value	Max. value	Standard deviation
COD	mg O_2/L	145,900	130,120	206,300	28,472.4
BOD ₅	mg O_2/L	75,300	62,200	79,500	12,647.1
Formaldehyde	mg/L	22,000	35,000	45,000	9,533.6

METHODS

The study presented in this article was conducted on a laboratory scale. Experiments were carried out with wood wastewaters originating from an industrial plant producing chipboards. The detailed characteristics of the wastewaters used in the experiment is presented in Table 1.

Anaerobic sludge applied as the inoculum in model fermentation tanks originated from closed fermentation tanks located in a municipal wastewater treatment plant Lyna in Olsztyn (Poland). The tanks are used for the stabilization of stirred crude sludge and operate with the following technological parameters:

- loading: 2.0 kg o.d.m./m³ · d,
- hydraulic retention time: 20 days,
- process temperature: 35°C.

The main parameters characterizing the sewage sludge applied in the experiment are presented in Table 2.

Table 2. Parameters of anaerobic sludge used in the experiments

Parameter	Unit	Min. value	Max. value	Mean value	Standard deviation
pH	–	7.89	8.08	7.98	0.10
Hydration	[%]	97.40	98.10	97.75	0.49
Dry matter	[%]	1.90	2.60	2.25	0.31
Volatile substances	[% d.m.]	47.32	51.04	49.18	2.63
Ash	[% d.m.]	48.96	52.68	50.82	1.86
CST	[s]	466	479	472.5	9.2
Eluate COD	[mgO ₂ /dm ³]	736	752.8	744.4	11.9
Eluate TOC	[mg/dm ³]	413.95	681.45	547.7	189.15

The experiments were conducted in two separate technological systems corresponding to a laboratory scale. At the first stage, the effectiveness of the anaerobic process of wastewaters treatment was determined in terms of the removal of organic substances characterized by the COD parameter and formaldehyde, as well as in terms of the quantity and quality of biogas produced. The second stage involved analyses of the effect of advanced oxidation with the use of Fenton's reactions on the final outcomes of the methane fermentation. Both stages of the experiment were divided into six series depending on sewage sludge loading with a feedstock of organic compounds expressed by the COD value. So low loadings resulted from the bactericidal properties of formaldehyde.

- series I – 0.0 kg COD/m³ · d
- series II – 0.025 kg COD/m³ · d
- series III – 0.05 kg COD/m³ · d
- series IV – 0.15 kg COD/m³ · d
- series V – 0.3 kg COD/m³ · d
- series VI – 0.6 kg COD/m³ · d

Model fermentation tanks were incubated for 20 days at a temperature of 37°C. The anaerobic process was conducted in model fermentation tanks by the WTW company (Wissenschaftlich-Technische Werkstätten GmbH), constituted by reaction tanks 0.5 dm³ in volume fastened tightly with measuring and registering devices. The applied research method enables determining the activity of anaerobic sludge, susceptibility of the applied organic substrates to biodegradation as well as the quantity and composition of gaseous metabolites. The devices were registering and analyzing changes in partial pressure in a measuring tank triggered by the production of biogas in anaerobic processes run by microorganisms. In each of the experimental variants, 100 cm³ of anaerobic sludge was introduced to reaction tanks, and then the adopted quantities of organic substrate were dosed in.

The complete measuring kit composed of a reaction tank and a measuring-registering device was placed in a thermostatic cabinet with hysteresis not exceeding ± 0.5°C. The

value of pressure in the reaction tank was registered every 15 min. Two days before the end of the measurements, 30% sodium base (NaOH) was introduced to a special container placed inside the reaction tank. It enabled the precipitation of carbon dioxide (CO₂) from the gaseous phase. A drop in pressure inside the reaction tank corresponded to the quantity of carbon dioxide, whereas the value of the remaining pressure was due to methane content. Contents of the tanks were agitated with the use of magnetic stirrers. Calculations performed in respirometric analyses are based on the equation of perfect gas:

$$n = \frac{p \times V}{R \times T} \quad (1)$$

where:

- n – moles of gas [mol]
- p – pressure of gas [Pa]
- V – volume of gas [m³]
- R – universal gas constant [8.314 J/mol · K]
- T – temperature [K].

Carbon content in the gaseous phase was computed with the following equation:

$$n_{CO_2} + n_{CH_4} = \frac{p_1 \times V_g}{R \times T} \times 10^{-4} \quad (2)$$

where:

- $n_{CO_2} + n_{CH_4}$ – moles of carbon dioxide and methane produced [mol]
- p_1 – difference in gas pressure in a measuring vessel at the beginning and at the end of experiment, caused by oxygen consumption and absorption of CO₂ produced [hPa]
- V – volume of gaseous phase in measuring tank [ml]
- R – gas constant [8.314 J/mol · K]
- T – temperature of incubation [K]
- 10⁻⁴ – conversion factor of Pa into hPa and of m³ into cm³

Carbon dioxide content in the gaseous phase was calculated with the following formula:

$$n_{CO_2} = \left(\frac{p_1 \times V_g - p_2 \times (V_g - V_{KOH})}{R \times T} \right) \times 10^{-4} \quad (3)$$

where:

- n_{CO_2} – moles of carbon dioxide produced [mol]
- p_2 – difference in gas pressure in a respective measuring vessel at the end of experiment minus pressure in the blind sample after KOH solution addition [hPa]
- V_{KOH} – volume of KOH solution [mL].

Methane content in the gaseous phase was computed from the formula:

$$n_{CH_4} = n_{CO_2+CH_4} - n_{CO_2} \quad (4)$$

At the second stage of the experiment, before feeding wastewaters to model fermentation tanks they had been pre-treated with the use of the Fenton's reaction. A source of iron(II) ions was $FeSO_4 \cdot 6H_2O$ solution, whereas hydrogen peroxide (H_2O_2) was introduced to the wastewaters in the form of a 30% perhydrol solution. The Fenton's reagent was applied at the following doses: 3.0 g/dm³ of hydrogen peroxide and 0.3 g/dm³ of Fe^{2+} , that were adjusted based on the literature data and a previous research of the authors [3].

The process of advanced oxidation was conducted using model laboratory tanks with the active volume of 1.0 dm³ equipped in magnetic stirrers. The tested wastewaters were fed to the tank in a dose of 0.5 dm³ at the beginning of the experimental cycle. Next, the chemical reagents were dosed in the following order: firstly the adopted doses of iron ions, and after 10 minutes hydrogen peroxide in a constant ratio of iron to hydrogen peroxide reaching 1:10 (w/w). For uniform distribution of Fenton's reagent the wastewaters with the reagents were mixed with the efficiency of 500 rpm for 15 min, and then with the efficiency of 100 rpm for 180 min using magnetic stirrers.

The total retention time in advanced oxidation tanks reached 195 min. Before having been fed to model fermentation tanks, the wastewaters were subjected to basic physicochemical analyses. In the course of the experiment, changes in COD were analyzed with the dichromate method and these in formaldehyde with the HACH 8110 method. Additional assays were carried out for the quantity and quality of biogas produced.

RESULTS

The initial concentration of contaminants in crude wastewaters is presented in Table 1. At both stages of the experiment, comparable technological outcomes were achieved in terms of the analyzed contaminants in the applied loading range of 0.025 kg COD/m³ · d to 0.15 kg COD/m³ · d (Table 3). The quality of the treated wastewaters was found to depend directly on the loading of model fermentation tanks with a feedstock of organic compounds. The concentrations of contaminants at the efflux were increasing proportionally to the increasing loading of tanks with COD feedstock. The best results were achieved at the experimental model loading in the range of 0.025 kg COD/m³ · d to 0.15 kg COD/m³ · d, where the final concentration of formaldehyde reached from 0.13 to 0.26 mg/L and that of COD from 1076 mg O₂/L to 1818 mg O₂/L at stage I. In the course of the study, it was stated that the application of advanced oxidation technology had a positive effect on the effectiveness of reducing concentrations of the analyzed contaminants at the highest applied loading with organic compounds feedstock, i.e. from 0.3 kg COD/m³ · d to 0.6 kg COD/m³ · d (Table 3).

In the course of the experiment, the advanced oxidation was observed to exert a significant effect on the final biogas production (Figure 1). It was proved that the pre-treatment of wastewaters with the Fenton's reaction enabled reaching a higher

Table 3. Comparison of removal effectiveness of organic contaminants, expressed by COD, and formaldehyde at both stages of the experiment

Loading with COD feedstock [kg COD/m ³ · d]	Stage I		Stage II	
	COD	Formaldehyde	COD	Formaldehyde
	mg O ₂ /L	mg/L	mg O ₂ /L	mg/L
0.0	762.1	–	762.1	–
0.025	1076.3	0.13	1380.4	0.14
0.05	1584.9	0.22	1662.8	0.31
0.15	1818.6	0.26	1930.4	0.33
0.30	3608.5	13.1	3249.6	11.8
0.60	4752.5	37.8	4219.2	31.4

production of biogas, irrespective of fermentation tanks loading with the tested feedstock of organic compounds. In the case of the loading reaching 0.025 kg COD/m³ · d, the quantity of biogas produced corresponded to 371.0 m³/kg of COD fed at the stage preceded by the chemical pre-treatment and to 215.1 m³/kg of COD fed during direct fermentation of the analyzed wastewaters. With the loading of 0.6 kg COD/m³ · d, the quantity of biogas produced was comparable in both experimental stages. The highest production of biogas was achieved in the series with the loading of 0.05 kg COD/m³ · d. It reached 577.3 m³/kg COD at the stage of direct fermentation and 704.0 m³/kg COD at the stage with chemical pre-treatment using Fenton's reagent (Figure 1).

The study proved that the inclusion of the stage of chemical pre-treatment to the technological systems had a direct effect on deterioration of the qualitative composition of biogas (Figure 3). This dependency was especially tangible when the tanks were fed with small feedstocks of organic compounds. At the value of this technological parameter reaching 0.025 kg COD/m³ · d, the percentage content of methane in biogas accounted for 70.2% at stage I and for 34.4% at stage II. The organic compounds feedstock of 0.6 kg COD/m³ · d enabled reaching 32.3% of methane in biogas at stage I, whereas wastewaters fermentation after their chemical pre-treatment yielded 25.0% methane production. Analyses showed that the qualitative composition of biogas was directly influenced by the applied loading with organic compounds. The increasing value of this technological parameter resulted in diminishing methane production (Figure 2).

Taking into account the quantity of produced biogas and its quantitative composition, it was stated that the total quantity of produced methane was comparable at both experimental stages, irrespective of fermentation tanks loading with a feedstock of organic compounds (Figure 1). Significant differences occurred in the case of 0.05 kg COD/m³ · d loading, where methane content reached 380 m³/kg COD at the stage of biological treatment and 239 m³/kg COD at the stage with Fenton's reagent application. Respective values achieved at the other loadings were very similar to each other (Figure 1).

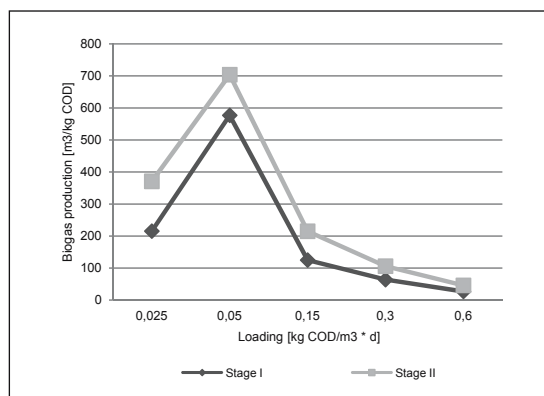


Fig. 1. Biogas production

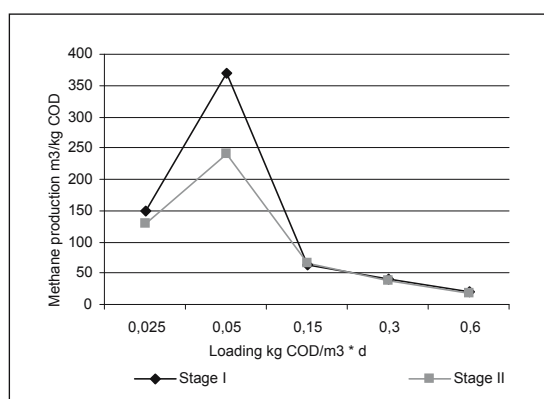


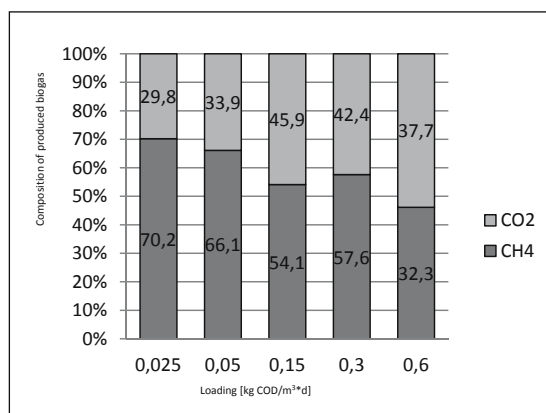
Fig. 2. Methane production

DISCUSSION

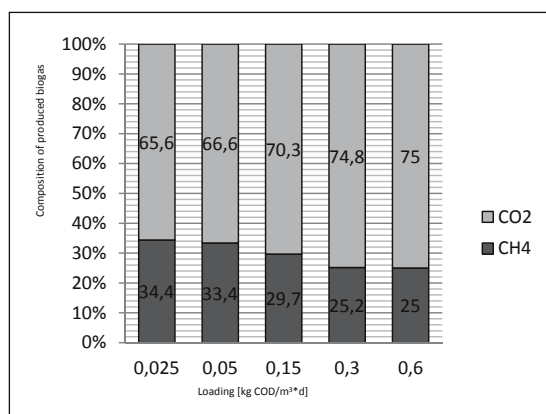
The two-stage process of wastewaters treatment based on the use of advanced oxidation and biological methods has been applied in many technological systems. Positive outcomes have been achieved once integrating the chemical process with bioreactors operating both under aerobic and anaerobic conditions.

Rodrigues *et al.* (2009) conducted some research on textile wastewaters by coupling the process of chemical oxidation of wastewaters with the Fenton's reagent and biodegradation run in an SBR type reactor. They managed to achieve very good results, and in the case of organic contaminants to reach similar process effectiveness as in our study, i.e. effectiveness of organic matter removal at the level of 90.2% COD and 96.1% BOD₅ [13].

Alike experiments were carried out by Fongsatitkul and co-workers, who were treating wastewaters from the textile industry with the use of three different technological



STAGE I



STAGE II

Fig. 3. Qualitative composition of biogas

systems. The first involved only the biological process, the second was combining chemical oxidation with Fenton's reagent and biological treatment in an SBR type reactor, whereas the third assumed the reversal of the second variant. Results achieved by those authors demonstrated that the most effective appeared to be the second variant which enabled reaching 80% effectiveness of removal of organic compounds expressed by the COD value. In the other two variants, the effectiveness of the removal process did not exceed 30% [5].

Wang *et al.* postulated the application of this technology for the treatment of wastewaters containing high quantities of surface-active compounds and sulfates. The chemical pre-treatment of wastewaters with the use of Fenton's reagent improved the effectiveness of organic compounds removal and increased wastewaters susceptibility to biodegradation. Coupling these methods enabled reaching 94% removal of organic compounds [14].

Moussavi *et al.* also suggested the efficient coupling of chemical and biological processes for the treatment of toxic wastewaters which, like in the reported study, were contaminated with formaldehyde. At the first stage of the study, they applied catalytic oxidation with $O_3/MgO/H_2O_2$ for 120 minutes, which yielded 79% formaldehyde removal and 65.5% organic compounds removal. At the second stage of the experiment, those authors applied biological treatment in an SBR type reactor operating in a 24 h cycle, which eventually led to the complete removal of formaldehyde from wastewaters and to efficient 98% removal of organic compounds expressed by COD [12].

In turn, Erden G. *et al.* proved that the application of pre-treatment with Fenton's reagent before the process of methane fermentation had a positive effect on methane production. Once applying preliminary chemical oxidation and the fermentation process using both meso- and thermophilic conditions, those authors managed to achieve 1.3 time more methane than in the case of the biological method applied alone. Wastewaters applied in their study originated from a municipal wastewater treatment plant, whereas the ratio of chemical reagents at the stage of chemical oxidation reached 0.067 g Fe(II) per gram of H_2O_2 and 60 g H_2O_2/kg d.m. [4]. These results are, however, different from findings described in this article, which indicate the negative impact of wastewaters pre-treatment with the use of Fenton's reagent on the final results of the fermentation process.

Khoufi S. *et al.* were investigating the effects of applying Fenton's reagent during methane fermentation of wastewaters originating from fats production. The application of Fenton's reagent enabled removing 65.8% of polyphenolic compounds and diminishing wastewaters toxicity from 100% to 66.9%, which improved the effectiveness of anaerobic fermentation at the successive stage of the experiment. In addition, the coupled application of the processes allowed for decreasing high contents of COD, suspended matter and lipids [8].

Other authors, i.e. Martinez N., S., S. and co-workers, used chemical oxidation for the treatment of highly-contaminated sewage where COD reached 362,000 mg/L. The optimal conditions applied in the study included: 3g H_2O_2 and 0.3 g Fe(II). In the first 10 minutes of the reaction, they managed to achieve 90% of the total COD removal, which finally accounted for 56.4%. This study proved that chemical oxidation was an efficient pre-treatment method of this type of wastewaters, where the application of biological methods is impossible. This may constitute a very interesting solution with the industrial application of Fenton's reagent, for it enables a significant COD reduction in a very short time [11].

CONCLUSIONS

At both stages of the experiment, comparable technological effects were achieved in respect of COD values and formaldehyde concentrations in the treated wastewaters in a loading range of 0.025 kg COD/ $m^3 \cdot d$ to 0.15 kg COD/ $m^3 \cdot d$. The quality of the treated wastewaters was found to directly depend on the applied loading of fermentation tanks with a feedstock of organic compounds. The values of the parameters examined at the efflux were increasing proportionally to the increasing loading of the fermentation tanks with COD feedstock. The application of the advanced oxidation exerted a positive effect on the effectiveness of contaminants reduction at the highest tanks

loading with organic compounds feedstock, i.e. in the range of $0.3 \text{ kg COD/m}^3 \cdot \text{d}$ to $0.6 \text{ kg COD/m}^3 \cdot \text{d}$.

The experiment demonstrated a significant effect of advanced oxidation on the final outcomes of biogas production. It was proved that pre-treatment of wastewaters with the use of Fenton's reaction enabled higher production of biogas, irrespective of fermentation tanks loading with a feedstock of organic compounds. In addition, the study proved that the inclusion of the stage of chemical pre-treatment to the technological system affected directly the deterioration of the qualitative composition of biogas. This dependency was especially tangible when the tanks were fed with small feedstocks of organic compounds. The experiments showed that the qualitative composition of biogas was directly affected by the applied loading with organic compounds. The increasing values of this technological parameters resulted in diminished production of methane.

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ZASTOSOWANIE ZAAWANSOWANEJ TECHNOLOGII UTLENIANIA NA SKUTECZNOŚĆ BEZTLENOWEGO ROZKŁADU ŚCIEKÓW O WYSOKIM STĘŻENIU FORMALDEHYDU

Celem prowadzonych badań było określenie wpływu procesu pogłębionego utleniania z zastosowaniem reakcji Fentona na efektywność beztlenowego oczyszczania ścieków pochodzących z przemysłu drzewnego, które charakteryzowały się wysoką koncentracją formaldehydu. W eksperymentach analizowano zmiany wartości ChZT oraz koncentracji formaldehydu w ściekach oczyszczonych, badano również zmiany ilości i składu jakościowego powstającego biogazu. W pierwszym etapie doświadczenia analizowano efektywność oczyszczania testowanych ścieków jedynie w procesie fermentacji metanowej. W drugiej części eksperymentu proces biologiczny poprzedzono wstępnym oczyszczaniem chemicznym z zastosowaniem odczynnika Fentona. Przeprowadzone badania udowodniły, iż testowane warianty wstępnej chemicznej obróbki ścieków wpłynęły istotnie na zwiększenie całkowitej ilości produkowanego biogazu. Nie stwierdzono natomiast znaczącego wpływu zastosowanej technologii na zmiany koncentracji analizowanych wskaźników zanieczyszczeń w ściekach oczyszczonych.