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# FORMALDEHYDE BIODEGRADATION BY ACTIVATED SLUDGE UNDER AEROBIC CONDITIONS

The objective of this study was to examine formaldehyde biodegradation by activated sludge under aerobic conditions. Moreover, the influence of formaldehyde on the removal process of other pollutants (COD, ammonium, ortophosphates, nitrates) from municipal wastewater is presented. The formaldehyde source was chemical agent of Aqua Kem type used in portable toilets, with formaldehyde concentration of 266 g/dm$^3$. The technological systems used enable highly effective formaldehyde removal. After 24 hrs of treatment the effectiveness of formaldehyde removal was over 90%, irrespective of biomass concentration, initial formaldehyde concentration and activated sludge loading. The most effective variant of the experiment was at formaldehyde concentration in raw wastewater amounting to 1000 mg/dm$^3$. In this case, biomass concentration in the reactor was about 3000 mg d.m. /dm$^3$. After 12 hrs of the operation time the effectiveness of formaldehyde removal was 99.9%.

## 1. INTRODUCTION

Formaldehyde is the common name of formic aldehyde ($CH_2O$), the simplest aliphatic aldehyde. Under normal conditions, this compound is a colourless gas of a characteristic pungent smell. It can be mixed unlimitedly with water, alcohols, ethers, hydrocarbons and turpentine [1]–[3].

The origin of formaldehyde in the environment is both natural as well as anthropogenic (man-made). Nowadays, the synthesis of this compound in natural environment makes up marginal parts of the total amount of formaldehyde. Some quantities can be generated during photochemical reaction, atmospheric discharge, fires and plant vegetation [1]. Man's economic and industrial activities are the basic cause of excessive formaldehyde emission to natural ecosystems [1], [4]–[6]. A 40% solution (formalin) that is obtained by catalytic oxidation of methanol, the most common formaldehyde form [7].

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Formic aldehyde is a common chemical compound widely used in the chemical industry, medicine, metallurgy, rubber industry, paper-making industry, textile industry, wood processing, dyestuff industry, cosmetic industry and in technology of plastics production [2], [8]–[10].

Widespread use of formaldehyde and its toxic and carcinogenic properties compel regular control of its content in the environment [1], [7], [11]. The monitoring of water, soil and atmospheric ecosystems and designing of technological systems for effective formaldehyde removal seem to be necessary. Formic aldehyde penetrates through the living organisms and can cause general body poisoning [1], [3], [10]. A long-lasting contact with formaldehyde causes diseases of the central nervous system, the touch, feeling disturbances, pain and high temperature. In an organism, formic aldehyde can be oxidized to formic acid that fixes the enzymes containing iron, which results in disturbances of cell respiration [1], [7], [12], [13]. It is known that in the environment this compound intensifies the toxicity of other pollutants such as carbon oxide (CO) or sulphur dioxide ($SO_2$).

Recently, chemical toilets commonly used on yachts became another source of formaldehyde. Formic aldehyde is one of the refill components of such portable toilets, the task of which is fast and effective water removal and faecal matter dissolving. For this reason chemical reagents must be characterised by strong dewatering properties, preventing accumulation of gases. Moreover, they should add to faecal biodegradation before the final utilisation and make it possible to keep toilets clean. In technological assumptions, it is accepted that these biologically and chemically aggressive mixtures should be neutralized by faecal matter. However, it often happens that this substance, present in portable toilets, is not completely used and deactivated. Sometimes large amounts of formaldehyde get through to municipal waste treatment plants operated with activated sludge.

The main goal of this study was to determine the possibility of biodegradation of formaldehyde that comes from agents used in chemical toilets. Moreover, the impact of this chemical substance on the removal of other pollutants from municipal wastewater was investigated.

## 2. MATERIALS AND METHODS

The experiments were carried out on the laboratory scale, at ambient temperature of 20 °C. In the research, SBR type model reactors of the total volume of 1.5 $dm^3$ and operating volume of 1.0 $dm^3$ were used. Each of the reactors was equipped with fine-bubble diffusers (figure 1). During aeration the oxygen concentration was kept at a level of 3.0 mg $O_2/dm^3$. Laboratory SBR reactors operated in a modified 24-hour cycle mode. The operating cycle consisted of four phases: feeding, aeration (reaction), sedimentation and decantation. The time of each of the operating phases corresponds to that of a classic cycle in SBR bioreactor.

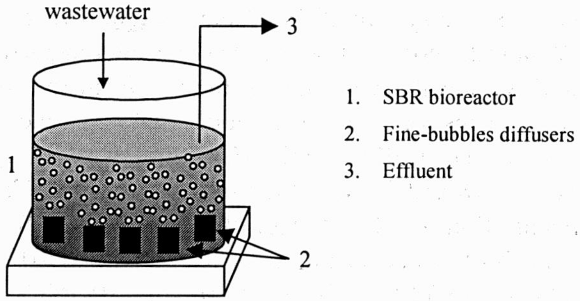


Fig. 1. Scheme of the research installation

Activated sludge used in the experiment was taken from SBR reactor that was supplied with synthetic diary wastes (made of powdered milk and water). The reactor with activated sludge culture served both didactic and experimental purposes.

The research was carried out in three stages at different initial concentration of formaldehyde in treated raw wastewater, variable activated sludge concentration in the reactors and thereby different activated sludge loading.

Table 1

Technological parameters of wastewater treatment during the experiment

| Stage | Series | Working volume of reactors | Biomass concentration | Formaldehyde concentration |
|---|---|---|---|---|
| I | I | 1 dm$^3$ | 1500 mg d. m./dm$^3$ | 1000 mg/dm$^3$ |
| | II | | 2250 mg d. m./dm$^3$ | |
| | III | | 3000 mg d. m./dm$^3$ | |
| II | I | 1 dm$^3$ | 250 mg d. m./dm$^3$ | |
| | II | | 500 mg d. m./dm$^3$ | 1000 mg/dm$^3$ |
| | III | | 750 mg d. m./dm$^3$ | |
| | IV | | 1000 mg d. m./dm$^3$ | |
| III | I | 1 dm$^3$ | 750 mg d. m./dm$^3$ | 2000 mg/dm$^3$ |
| | II | | 1500 mg d. m./dm$^3$ | |
| | III | | 2250 mg d. m./dm$^3$ | |
| | IV | | 3000 mg d. m./dm$^3$ | |

In the first and second stages, changes of the wastewater compounds during biodegradation were analysed at formaldehyde concentration of 1000 mg/dm$^3$. In the third stage, the effectiveness of wastewater treatment was determined for the initial formaldehyde content of 2000 mg/dm$^3$. Activated sludge concentration in model reactors varied with experimental series, ranging from 250 mg d. m./dm$^3$ to 3000 mg d. m./dm$^3$. The content of activated sludge in the particular stages and series of the experiment is shown in table 1.

The source of formaldehyde was chemical agent Aqua Kem applied in portable toilets, with formaldehyde concentration of 266 g/dm$^3$. Directly before treatment a predetermined amount of Aqua Kem was introduced onces to municipal wastes. In the research, wastewater was taken from a sewage system of the Campus of the University of Warmia and Mazury in Olsztyn. Wastewater composition was that typical of municipal wastes.

Samples of treated wastewater were taken directly from the reactors and before parameter analysis the wastes were filtrated. Formaldehyde concentration in treated wastes was analysed colorimetrically by MBTH method using HACH DR/2010 spectrophotometer after 8, 12, 18 and 24 hrs of the experiment [14]. The wastes were assayed for the concentration of COD according to Polish Standard [PN-74/C-04578/03], ammonium (N–$NH_4$) according to [PN-73/C-04576/01], nitrates (N–$NO_3$) according to [PN-73/C-04576/08] and orthophosphates (P–$PO_4$) according to [PN-89/C-04537/03]. COD, ammonium nitrogen, nitrates and orthophosphates were determined once after 24 hrs. Additionally, oxygen concentration in SBR reactors was measured using dissolved oxygen pocket meter OXI 330i/SET WTW.

## 3. RESULTS

In the first stage of the research, each of the laboratory reactors with activated sludge was supplied with municipal wastewater containing 1000 mg $CH_2O/dm^3$. Depending on the series in this part of the experiment, biomass concentration was in the range of 1500–3000 mg d.m./$dm^3$ (table 1). High effectiveness of formaldehyde re-

Table 2

Changes of formaldehyde concentration and percentage removal during treatment process in different series of the experiment (Concentr. – concentration, Eff. – treatment effectiveness)

| | | Reaction time [h] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 0 | 8 | | 12 | | 18 | | 24 | |
| Stage | Series | Concentr. [mg/dm$^3$] | Concentr. [mg/dm$^3$] | Eff. [%] | Concentr. [mg/dm$^3$] | Eff. [%] | Concentr. [mg/dm$^3$] | Eff. [%] | Concentr. [mg/dm$^3$] | Eff. [%] |
| I | I | 1000 | 17.25 | 98.2 | 7.17 | 99.3 | 4.36 | 99.3 | 0.40 | 99.9 |
| | II | 1000 | 6.85 | 99.3 | 4.55 | 99.5 | 0.36 | 99.9 | 0.28 | 99.9 |
| | III | 1000 | 4.53 | 99.5 | 0.96 | 99.9 | 0.14 | 99.9 | 0.14 | 99.9 |
| II | I | 1000 | 122.02 | 87.8 | 119.43 | 88.1 | 104.78 | 89.6 | 62.02 | 93.8 |
| | II | 1000 | 121.11 | 87.9 | 109.08 | 89.1 | 90.52 | 91.0 | 41.12 | 95.9 |
| | III | 1000 | 83.47 | 91.7 | 70.00 | 93.0 | 53.12 | 94.7 | 9.18 | 99.1 |
| | IV | 1000 | 63.75 | 93.6 | 40.30 | 95.9 | 22.17 | 97.8 | 8.85 | 99.1 |
| III | I | 2000 | 184.00 | 92.1 | 157.50 | 90.8 | 101.05 | 94.9 | 44.50 | 97.7 |
| | II | 2000 | 101.50 | 95.8 | 83.50 | 94.90 | 31.55 | 98.8 | 23.60 | 98.4 |
| | III | 2000 | 81.00 | 96.5 | 69.00 | 95.9 | 32.90 | 98.3 | 12.05 | 99.4 |
| | IV | 2000 | 44.55 | 97.9 | 41.00 | 97.7 | 18.20 | 99.0 | 6.85 | 99.6 |

moval was observed for each of the technological variants. After 8 hrs of the operation this efficiency ranged from 98.2% to 99.5% depending on activated sludge concentration in the reactors. After 24 hrs of treatment the effluent contained from 0.14 mg $CH_2O/dm^3$ to 0.40 mg $CH_2O/dm^3$ (table 2, figure 2).

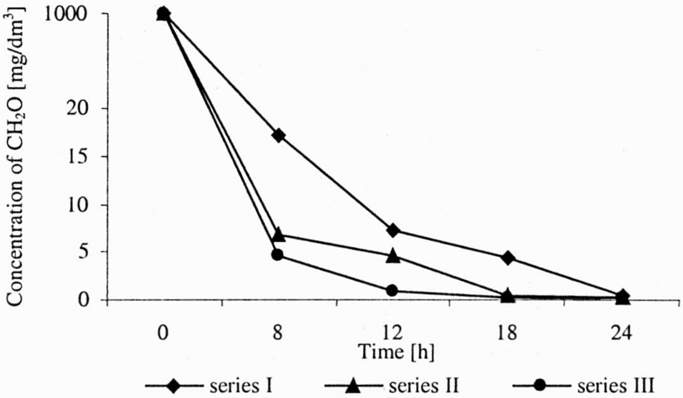


Fig. 2. Changes of formaldehyde concentration in the first stage of the experiment versus time of effluent treatment and biomass concentration (initial formaldehyde concentration: 1000 mg $CH_2O/dm^3$, biomass concentration: series I – 1500 mg d. m./$dm^3$, series II – 2250 mg d. m./$dm^3$, series III – 3000 mg d. m./$dm^3$)

The concentration of organic compounds in raw wastewater, expressed as COD, was approximately 100 mg $O_2/dm^3$, however, after the addition of Aqua Kem agent it increased to 188.7 mg $O_2/dm^3$ (table 3). The effectiveness of organic compounds removal mostly depended on the experimental series. The highest COD concentration in the effluent was for the reactor with activated sludge concentration of 1500 mg d.m./$dm^3$. In this case, organics content was 90.0 mg $O_2/dm^3$. In other variants of this stage, the efficiency of organic compounds removal was higher, amounting approximately to 71% (table 3).

Nitrogen transformation in the first stage of the research correlated with the technological variants. After the addition of Aqua Kem agent the concentration of ammonium nitrogen in wastes was 3.42 mg $N–NH_4/dm^3$. The effectiveness of ammonium removal increased proportionally to biomass concentration in the reactors (table 3). The most effective was the third variant at activated sludge concentration of 3000 mg d.m./$dm^3$. The efficiency of ammonium removal was about 69%. In this case, nitrification was most effective, which is confirmed by nitrate concentration after 24 hrs of wastewater treatment. The initial nitrate content was 0.03 mg $N–NO_3/dm^3$ and there was an increase in the concentration of this compound to 0.44 mg $N–NO_3/dm^3$ in series III (table 3).

Table 3

Changes of the concentration and the percentage removal of the parameters of wastes after 24 hours of treatment process in different series of the experiment (w – raw wastes, wf – raw wastes containing formaldehyde, tw – treated wastes, Eff. – treatment effectiveness)

| Stage | Series | COD | | | | $N–NH_4$ | | | | $N–NO_3$ | | | | $P–PO_4$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Concentration [mg $O_2/dm^3$] | | | Eff. [%] | Concentration [mg /$dm^3$] | | | Eff. [%] | Concentration [mg/$dm^3$] | | | Eff. [%] | Concentration [mg/$dm^3$] | | | Eff. [%] |
| | | w | wf | tw | | w | wf | tw | | w | wf | tw | | w | wf | tw | |
| I | I | 101.0 | 188.7 | 90.0 | 52.3 | 1.43 | 3.42 | 3.09 | 9.6 | 0.02 | 0.03 | 0.15 | – | 32.85 | 31.27 | 13.67 | 56.3 |
| | II | 101.0 | 188.7 | 55.0 | 70.8 | 1.43 | 3.42 | 2.06 | 39.7 | 0.02 | 0.03 | 0.37 | – | 32.85 | 31.27 | 4.05 | 87.0 |
| | III | 101.0 | 188.7 | 54.5 | 71.1 | 1.43 | 3.42 | 1.07 | 68.7 | 0.02 | 0.03 | 0.44 | – | 32.85 | 31.27 | 2.10 | 93.3 |
| II | I | 190.0 | 384.0 | 212.0 | 44.8 | 1.35 | 6.25 | 2.84 | 54.5 | 0.0 | 0.03 | 0.14 | – | 24.4 | 27.9 | 27.0 | 3.2 |
| | II | 190.0 | 384.0 | 198.0 | 48.5 | 1.35 | 6.25 | 2.40 | 61.6 | 0.0 | 0.03 | 0.10 | – | 24.4 | 27.9 | 26.0 | 6.8 |
| | III | 190.0 | 384.0 | 144.0 | 62.5 | 1.35 | 6.25 | 1.28 | 79.5 | 0.0 | 0.03 | 0.10 | – | 24.4 | 27.9 | 17.5 | 37.3 |
| | IV | 190.0 | 384.0 | 112.0 | 70.8 | 1.35 | 6.25 | 0.74 | 88.2 | 0.0 | 0.03 | 0.09 | – | 24.4 | 27.9 | 15.7 | 43.7 |
| III | I | 122.0 | 352.0 | 168.0 | 52.3 | 0.6 | 6.68 | 5.82 | 12.8 | 1.32 | 0.93 | 0.32 | 65.6 | 16.05 | 35.1 | 25.0 | 28.7 |
| | II | 122.0 | 352.0 | 162.0 | 54.0 | 0.6 | 6.68 | 4.65 | 30.4 | 1.32 | 0.93 | 0.35 | 62.4 | 16.05 | 35.1 | 16.5 | 53.0 |
| | III | 122.0 | 352.0 | 131.0 | 62.8 | 0.6 | 6.68 | 4.19 | 37.3 | 1.32 | 0.93 | 0.37 | 60.2 | 16.05 | 35.1 | 13.5 | 61.5 |
| | IV | 122.0 | 352.0 | 97.0 | 72.5 | 0.6 | 6.68 | 4.05 | 39.4 | 1.32 | 0.93 | 0.44 | 52.7 | 16.05 | 35.1 | 10.15 | 71.1 |

The agent containing formaldehyde that was supplied to the technological system did not cause an increase in orthophosphate concentration and even a smaller amount of this compound was detected. The initial orthophosphate concentration was 31.27 mg P–$PO_4$/dm$^3$. In series I, II and III, the reduction effectiveness was 56%, 87% and 93%, respectively (table 3).

For the sake of high efficiency of the removal of pollutants, especially formaldehyde biodegradation in the first stage of the experiment, in the next series of the second stage the concentration of activated sludge in the reactors was reduced. In this stage, bacterial biomass concentration ranged from 250 mg d.m./dm$^3$ to 1000 mg d.m./dm$^3$ at the initial formaldehyde concentration of 1000 mg/dm$^3$ (table 1). In this part of the experiment, $CH_2O$ biodegradation was slower than in the first stage but after 8 hrs of treatment in the reactor most formaldehyde removal was over 85% for all technological variants. With an increase in treatment time there was a decrease in formaldehyde concentration (table 2). Finally, the effluent contained 62.02 mg $CH_2O$/dm$^3$ for the lowest activated sludge concentration of 250 mg d.m./dm$^3$. In all the other cases, the effectiveness of formaldehyde removal was higher and the results are presented in figure 3.

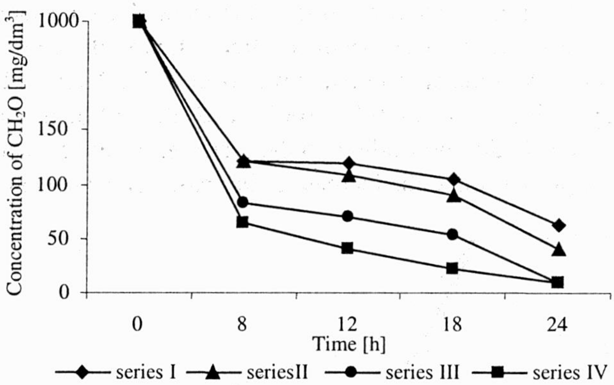


Fig. 3. Changes of formaldehyde concentration in the second stage of the experiment versus time of effluent treatment and biomass concentration (initial formaldehyde concentration: 1000 mg $CH_2O$/dm$^3$, biomass concentration: series I – 250 mg d. m./dm$^3$, series II – 500 mg d. m./dm$^3$, series III – 750 mg d. m./dm$^3$, series IV – 1000 mg d. m./dm$^3$)

COD concentration in municipal wastewater that was used in the second stage of the experiment was 190 mg $O_2$/dm$^3$ and after adding Aqua Kem agent it increased to 384 mg $O_2$/dm$^3$. The results indicated that after 24 hrs of treatment the organic content was in the range of 112.0 mg $O_2$/dm$^3$–212 mg $O_2$/dm$^3$ depending on the technological variant (table 3).

After supplying the agent containing formaldehyde, ammonium nitrogen concentration was 6.25 mg N–$NH_4$/$dm^3$ and the highest removal effectiveness was observed in the reactor with the highest biomass concentration (table 3). The residual ammonium concentration in treated wastewater was 0.74 mg N–$NH_4$/$dm^3$. The efficiency of ammonium removal in the particular series of this stage of the experiment ranged from 54% to 88%. Similar nitrate concentration in the effluent from all reactors was in the range of 0.9 mg N–$NO_3$/$dm^3$–0.14 mg N–$NO_3$/$dm^3$, the initial content being 0.03 mg N–$NO_3$/$dm^3$ (table 3).

In this stage of the research, the effectiveness of orthophosphate removal was relatively low. Due to the low activated sludge concentration the content of these compounds decreased in series I and II by 3.2% and 6.8%, respectively (table 3). Simultaneously with an increase in biomass concentration there was an increase in removal efficiency of orthophosphate but it was lower than in the first stage of the experiment. After 24 hrs of the residence time in the technological system there was 15.7 mg P–$PO_4$/$dm^3$, with the initial concentration of 24.4 mg P–$PO_4$/$dm^3$ (table 3).

In the third stage of the research, wastewater contained 2000 mg $CH_2O$/$dm^3$. The concentration of activated sludge differed, ranging from 750 mg d.m./$dm^3$ to 3000 mg d.m./$dm^3$ (table 1). Higher formaldehyde loading did not influence the higher removal effectiveness of this organic substance. A decrease in formic aldehyde concentration was observed with the extension of retention time in the technological system (table 2, figure 4). A highly effective reduction was obtained after 8 hours of treatment process. In all bioreactors, formaldehyde removal efficiency was over 90%. After 24 hrs the removal of this compound again increased to 97%–100% and the effluent contained 44.5 mg $CH_2O$/$dm^3$–6.85 mg $CH_2O$/$dm^3$ depending on the series of the experiment. Removal effectiveness increased in proportion to the increase in biomass concentration (table 2, figure 4).

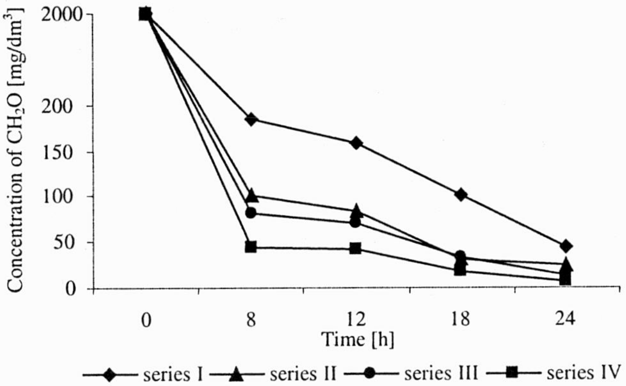


Fig. 4. Changes of formaldehyde concentration in the third stage of the experiment versus time of effluent treatment and biomass concentration (initial formaldehyde concentration: 2000 mg $CH_2O$/$dm^3$, biomass concentration: series I – 750 mg d. m./$dm^3$, series II – 1500 mg d. m./$dm^3$, series III – 2250 mg d. m./$dm^3$, series IV – 3000 mg d. m./$dm^3$)

Chemical oxygen demand (COD) in treated wastes, in the third part of the study, was 352.0 mg $O_2/dm^3$. The efficiency of COD removal correlated with activated sludge concentration in the reactors. The percentage removal of these compounds ranged from 52% to 73% (table 3). High formaldehyde concentration in treated wastes caused a decrease in nitrification effectiveness. At the initial ammonium nitrogen concentration of 6.68 mg $N–NH_4/dm^3$ the effluent contained at least 4.05 mg $N–NH_4/dm^3$. There was a decrease in nitrate concentration with relation to the content in raw wastes. In the effluent, there was from 0.32 mg $N–NO_3/dm^3$ to 0.44 mg $N–NO_3/dm^3$ (table 3). The agent containing formaldehyde used in the experiment caused an increase in orthophosphate concentration to the value of 35.1 mg $P–PO_4/dm^3$. During treatment there was a reduction of this form of phosphorus in series I, II, III and IV correspondingly by 28.7%, 53%, 61.5% and 71.1% (table 3).

## 4. DISCUSSION

The aim of the study was to determine the possibility of formaldehyde biodegradation by activated sludge under aerobic conditions. Aqua Kem disinfecting and dewatering agent containing formic aldehyde is used in chemical toilets. In the present research, the authors tried to determine the influence of formaldehyde concentration and activated sludge loading by this compound on the effectiveness of formic aldehyde removal as well as organic carbon compounds and orthophosphates removal and nitrification efficiency.

Under aerobic conditions during biological treatment of wastewater containing formaldehyde the removal of this compound is possible due to two different mechanisms. The first way of formic aldehyde deactivation is the connection with the proteins of activated sludge microorganisms. The other way of eliminating this substance from wastewater is biochemical oxidation to direct product – formic acid, and next to carbon dioxide and water [1], [3], [11].

The experiments proved the possibility of effective formaldehyde removing from wastewater by activated sludge under aerobic conditions. Based on the results obtained it can be concluded that formaldehyde biodegradation increased with an increase in activated sludge concentration in the reactors and with a decrease in microflora pollutant loading. Treated wastes contained formaldehyde of the concentration of 1000 $mg/dm^3$ and 2000 $mg/dm^3$. Taking into account the fact that formic aldehyde is a compound of high toxicity, having destructive influence on the cells of living microorganisms, it was used in quite large amounts.

It has been reported in the literature that formaldehyde reacts with DNA, RNA chains and protein structures causing their destruction, which directly leads to the death of microorganisms' cells or inhibits their activity [1], [3], [9]. The US Environmental Protection Agency (USEPA) included this chemical compound in the group of substances that increase the risk of tumour disease [9].

The most common way of formaldehyde biodegradation is the use of fermentative, anaerobic systems with activated sludge [7], [13], [15], [16]. It has been shown that anaerobic technology can reduce exploitation costs connected with the intensive aeration. Moreover, fermentation gas can be recovered to make up the energy source [9]. Widespread use of these technological systems is not always possible. Fermentation reactors are not useful and cause much trouble when treating wastewater with high formic aldehyde concentration [17]–[20].

The examination of the treatment process of wastewater coming from wood processing or synthetic wastes containing glucose proved that formaldehyde removal effectiveness depended mostly on this compound concentration, type of wastewater and the retention time in the technological system [9]. High formaldehyde removal effectiveness was obtained when the concentration of this substance in wastes from wood industry did not exceed 200 mg/dm$^3$ and 400 mg/dm$^3$ in synthetic wastes with the addition of glucose. The best treatment results were obtained after 6–8 days of the wastewater retention in the system. Such technological conditions enable achieving over 90% effectiveness of formaldehyde removal. It was shown that with an increase of formic aldehyde concentration in wastes there was an inhibition of COD removal and methanogenesis. In series with synthetic wastewater prepared on the basis of glucose, 50% inhibition of gasification was observed at formaldehyde concentration over 300 mg/dm$^3$. The tests with wood-glue wastewater indicated that the toxic concentration was lower and the inhibition of methanogenesis was observed at formic aldehyde content about 150 mg/dm$^3$ [9].

The examples of studies confirm the fact that anoxic biodegradation of pollutants containing formaldehyde is highly effective under precisely determined technological conditions. It seems that treatment technologies of wastewater including formic aldehyde involving fermentative bioreactors can be a well-founded solution when formaldehyde concentration is below 500 mg/dm$^3$.

In the research concerning the reduction of pollutants supplied to wastewater with Aqua Kem agent, the concentration of these substances was several times higher and depending on the experimental stage it was 1000 mg/dm$^3$ or 2000 mg/dm$^3$. It can be assumed that so high formaldehyde concentration in raw wastewater would cause a decrease in wastewater treatment effectiveness in anaerobic bioreactors and inhibit the gasification. Furthermore, the treatment process of wastewater containing formaldehyde was really effective under aerobic conditions. Under optimal technological conditions the reduction of this chemical compound was over 90% already after 8 hrs. of the treatment in the system. According to the literature data such a high formaldehyde removal efficiency in anaerobic systems can be obtained at considerably longer retention time.

According to many authors formaldehyde is a moderately acute toxic compound and has a negative influence on microflora of anaerobic activated sludge. HUSER et al. [16] observed severe inhibition of acetates and, what follows, inhibition of methane production for formaldehyde dose over 300 mg/dm$^3$. Besides, it has been reported that formic aldehyde inhibits gasification at lower concentrations in the range of 10–100 mg/dm$^3$. This was observed for dairy wastewater treatment in anaerobic bioreactors [7].

The removal of formaldehyde originating from Aqua Kem agent was due to aerobic technology with activated sludge. Of course, the energy-consuming wastewater treatment is connected with high oxygen concentration (3.0 mg $O_2$/dm$^3$) in aerobic tank and this fact causes an increase in exploitation costs of such appliances. On the other hand, effective treatment of wastewater with high formaldehyde concentration would be possible. Moreover, such a technological system that is used in our experiments has a simple construction and is easy to operate. In a direct way it limits service and operating costs as well as damage to the system.

Some experiments were carried out concerning the effective removal of formaldehyde and other organic compounds and nutrients [2], [15]. A synthetic and a real wastewater from glue industry was tested. Besides high formaldehyde concentration, the wastes contained considerable amounts of urea. The aim of such investigation was to propose effective methods for simultaneous COD and formaldehyde removal, hydrolysis of organic nitrogen fraction in the form of urea to ammonium, nitrification and denitrification to atmospheric nitrogen [15]. The system designed included a multifid upflow filter, operating under anoxic and anaerobic conditions for formaldehyde biodegradation, urea hydrolysis and denitrification and a biofilm airlift suspension reactor for nitrification. The stability of the system when formaldehyde overloads take place and the influence of formaldehyde on urea hydrolysis and denitrification were determined. The results showed that formaldehyde (with concentration up to 1000 mg/dm$^3$) was metabolised and used as a carbon source and electron donor for denitrification. Denitrification or formaldehyde removal was apparently not affected by urea loading rate in the system [15].

In aerobic reactors for treatment of municipal wastewater containing chemical agent (including formaldehyde), only nitrification was observed. In this case, ammonium nitrogen oxidation to nitrates correlated with the formaldehyde concentration and activated sludge loading. With an increase in biomass loading there was a decrease in effective nitrification and nitrate concentration in treated wastewater. The lower nitrification effectiveness was observed in the third stage of the experiment when formaldehyde concentration in raw wastewater was on the level of 2000 mg/dm$^3$. In this case, there was a total inhibition of nitrification and nitrate concentration in raw wastes was higher than that in treated wastes after 24 hrs of retention in the reactor. In order to achieve complete nitrogen removal from the system, additional anoxic denitrifying tank should be designed. Another way of nitrogen removal would consist in providing temporary anaerobic conditions or in limiting oxygen supply to the nitrifying reactor.

There are results concerning an increase in nitrification rate in the case of formaldehyde supplied to the system. Formaldehyde quantity amounting to 55 mg/dm$^3$ supplied to the technological system with biological filters caused an increase in concentration of nitrate oxidized forms. Of course, this formaldehyde concentration was several times lower in proportion to formaldehyde concentration accepted in the presented experiment [21].

The systems for formaldehyde biodegradation by activated sludge under aerobic conditions were tested fewer times than the technologies with fermentative reactors. The literature data report that in aerobic systems high treatment effectiveness can be achieved for wastewater from synthetic resin production that contains formic aldehyde of concentration of 128 mg/dm$^3$. Moreover, the effective treatment of such wastes is possible after long activated sludge adaptation and after 18 hrs of aeration. Formaldehyde removal efficiency ranged from 93% to 99% [8]. Long adaptation time of activated sludge used in the systems to wastewater from synthetic resin production is needed not only for the sake of high formaldehyde concentration but also for the wastewater composition. This is confirmed by the results of our experiments with municipal wastewater including high formic aldehyde concentration. In this case, formaldehyde removal effectiveness was 99% and the reduction was achieved in a relatively short time and without activated sludge adaptation.

Similar effectiveness of the treatment process of wastewater from glue industry was observed. A 99% efficiency of formaldehyde removal was obtained in aerobic reactor with activated sludge, with the initial concentration ranging from 220 mg/dm$^3$ to 4000 mg/dm$^3$. The experiment was carried out effectively during 92 days and after that additional anoxic tank was used in order to promote ammonification and denitrification [2].

Technological progress and increasing industrialization cause that wastewater contains high amounts of toxic and hazardous substances [6]. This group of compounds include undoubtedly formaldehyde and even its low concentration in the environment can harmfully affect living organisms [1], [3], [10]. It is frequent that such substances influence physicochemical processes of water treatment and limit the rate of self-purification. There is a real need to design more effective technologies and systems that would contribute to higher removal effectiveness of hazardous chemical substances.

## 5. CONCLUSIONS

1. The treatment process of wastewater containing formic aldehyde by activated sludge under aerobic conditions is highly effective. After 24 hrs of treatment the effectiveness of formaldehyde removal was over 90% irrespective of biomass concentration and activated sludge loading.

2. The reduction of formaldehyde concentration decreased simultaneously with a decrease in biomass concentration in the reactors and with an increase in formic aldehyde content in raw wastewater.

3. Chemical oxygen demand (COD) was decreased by 44%–72.5%, ammonium nitrogen and orthophosphate concentration decreased by 9%–88.2% and 3%–93.3%, respectively, depending on the technological systems used.

4. An increase in activated sludge loading influenced negatively the removal efficiency of ammonium (N–$NH_4$) and orthophosphates (P–$PO_4$).

5. The effectiveness of ammonium removal increased correspondingly with an increase in biomass concentration in SBR reactors. The highest efficiency of 88.2% was obtained in the system at biomass concentration of 1000 mg d.m./$dm^3$ and at the initial ammonium concentration of 6.25 mg/$dm^3$ (stage II, series IV).

6. The lowest orthophosphate removal efficiency of 3.2% was achieved at the initial orthophosphate concentration of 27.9 mg P–$PO_4$/$dm^3$ and biomass concentration of 250 mg d.m./$dm^3$. The most effective technological variant (93.3% removal) was at biomass concentration of 3000 mg d.m./$dm^3$, at the initial orthophosphate concentration of 31.27 mg P–$PO_4$/$dm^3$ and at formaldehyde concentration of 1000 mg $CH_2O$/$dm^3$.

7. The lowest COD removal effectiveness of 44.8% was obtained at biomass concentration of 250 mg d.m./$dm^3$, at the initial COD concentration of 384 mg $O_2$/$dm^3$. The most effective technological variant was at biomass concentration of 3000 mg d.m./$dm^3$. In these cases, depending on the stage of the experiment, COD removal efficiency ranged from 71.1% to 72.5%.

8. With an increase in formaldehyde concentration in raw wastewater there was a decrease in nitrification efficiency.

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## BIODEGRADACJA FORMALDEHYDU METODĄ OSADU CZYNNEGO W WARUNKACH TLENOWYCH

Celem badań było stwierdzenie, czy można poddać biodegradacji formaldehyd pochodzący ze środków stosowanych w toaletach chemicznych oraz określenie, w jakim stopniu ten związek wpływa na proces usuwania innych zanieczyszczeń zawartych w ściekach bytowo-gospodarczych. Eksperyment wykonano w skali laboratoryjnej, używając modelowych reaktorów typu SBR o objętości całkowitej 1,5 $dm^3$ i objętości czynnej 1,0 $dm^3$. Osad czynny pochodził z reaktora typu SBR, którego cykl pracy odpowiadał klasycznemu układowi faz mieszania i napowietrzania. Źródłem formaldehydu był środek chemiczny typu Aqua Kem zawierający 266 g/$dm^3$ formaldehydu i wykorzystywany w eksploatacji toalet przenośnych. W zależności od wariantu koncentracja biomasy wahała się od 250 mg s. m./$dm^3$ do 3000 mg s. m./$dm^3$, stężenie formaldehydu zaś od 1000 mg/$dm^3$ do 2000 mg/$dm^3$. Zastosowane układy technologiczne pozwoliły wydajnie usuwać formaldehyd z oczyszczanych ścieków. Po 24 h oczyszczania uzyskano ponad 90-procentową skuteczność oczyszczania we wszystkich wariantach technologicznych, niezależnie od koncentracji biomasy w reaktorach, początkowego stężenia formaldehydu w ściekach i obciążenia osadu czynnego ładunkiem zanieczyszczeń. Najskuteczniejszy okazał się wariant, w którym stężenie formaldehydu w ściekach surowych wynosiło 1000 mg/$dm^3$, a koncentracja biomasy w reaktorze była utrzymywana na poziomie 3000 mg s. m./$dm^3$. Ten układ technologiczny zapewnił 99.9% usunięcie formaldehydu już po 12 h oczyszczania. Ograniczono również wartość ChZT w przedziale 44%–72%, azotu amonowego w przedziale 9%–88% i ortofosforanów w przedziale 3%–93%. Skuteczność oczyszczania spadała wraz ze wzrostem obciążenia osadu czynnego ładunkiem zanieczyszczeń. Stwierdzono również, że wraz ze wzrostem koncentracji formaldehydu w ściekach surowych spadała sprawność procesu nitryfikacji.