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RESISTANCE OF HEXAMETHYLENETETRAMINE TO BIODEGRADATION IN AERATED MUNICIPAL SEWAGE

The effect of various hexamethylenetetramine concentrations (from 0 to 1000 g/m³) on the biochemical treatment of municipal sewage was studied under laboratory conditions. The experimental results show that hexamethylenetetramine (despite a very high resistance to biodegradation) has no adverse influence either on the activated sludge process or on the nitrification of ammonia nitrogen to nitrites.

1. INTRODUCTION

Effluents from industrial processes are mixtures of many different substances and species. While some of these components exhibit a resistance to biodegradation, others do not. It frequently happens that the biodegradability of a given pollutant is not sufficiently known, and it holds for hexamethylenetetramine (referred to as HMTA). The compound of interest occurs, e.g., in wastewaters from the manufacture of spherical supports for catalysts [3] (tab. 1) or in the sorption effluent when formaldehyde is removed from flue gases [10], [11], [13], [14]. In the latter case calcium carbonate suspensions used as chemisorbents in aqueous solutions of ammonium nitrate [13] make formaldehyde combine with ammonia to form HMTA. Consequently, formaldehyde concentration in these solutions becomes very low, whereas HMTA content increases rapidly. Effluents of that kind cannot be discharged either to a recipient stream or to a sewer system [9] until HMTA and organic matter are removed.

Hexamethylenetetramine, $(\text{CH}_2)_6\text{N}_4$, has a ring structure. While nitrogen atoms occur on the vertices of the tetrahedron, carbon atoms are found on the vertices of the octahedron. The structure itself is highly symmetrical.

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Table 1

Composition of industrial wastewater containing HMTA and of the experimental sewage
 Skład ścieków przemysłowych zawierających urotropinę i ścieków miejskich użytych do
 badań

| Component | Unit | Effluent from manufacture of catalyst supports | | Sorption effluent | Municipal sewage |
|--|-------------------------------------|--|---------------------|-------------------|------------------|
| | | 1 | 4 | | |
| turbidity | g/m ³ | 10–25 | 900 | 300 | |
| colour | g/m ³ | yellow | 50–80 | 70 | |
| odour | — | Z5S amines | Z5S formaldehyde | Z3G | |
| pH | pH | 7.88–8.4 | 5.33–5.36 | | 7.72 |
| total alkalinity | g CaCO ₃ /m ³ | 2860–3150 | 6850–7500 | | 255 |
| total acidity | g CaCO ₃ /m ³ | 1350–1500 | 4850–9700 | | — |
| permanganate COD | g O ₂ /m ³ | 109000–132000 | — | | 124 |
| chlorides | g Cl/m ³ | 40300–53000 | — | | 88 |
| organic nitrogen | g N/m ³ | 21910–25760 | 14280–14840 | | 28.4 |
| ammonia nitrogen | g N/m ³ | 14000–49260 | 13220–15260 | | 35 |
| nitrite nitrogen | g N/m ³ | 0 | trace concentration | | 0.3 |
| nitrate nitrogen | g N/m ³ | 0 | 25000–30000 | | 0 |
| dichromate COD | g O ₂ /m ³ | 155820–164670 | 54000–57650 | | — |
| BOD ₅ | g O ₂ /m ³ | 53000–108000 | 2800–7200 | | 290 |
| HMTA | g/m ³ | 65000–80000 | 33200–38000 | | 0 |
| dry residue | g/m ³ | 141040–144290 | 303080–304190 | | 623 |
| residue after roasting | g/m ³ | — | 176090–125420 | | 465 |
| roasting losses | g/m ³ | — | 126990–178770 | | 158 |
| total dissolved matter | g/m ³ | — | 162520–222990 | | 500 |
| mineral dissolved matter | g/m ³ | — | 37790–75680 | | 425 |
| volatile dissolved matter | g/m ³ | — | 124730–147310 | | 75 |
| total suspended solids | g/m ³ | — | 81200–140560 | | 123 |
| mineral suspended solids | g/m ³ | — | 49740–138300 | | 40 |
| volatile suspended solids | g/m ³ | — | 2260–31460 | | 83 |
| solids settleable in Imhoff funnel after | | 5 min | 260–920 | | |
| | | 10 min | 230–830 | | |
| | | 15 min | 210–740 | | |
| | | 30 min | 180–700 | | |
| | | 60 min | 150 | | |
| | | 120 min | 130 | | |
| | | 48 h | — 175 | | |

HMTA is a colourless crystalline substance which sublimates during heating, burns with a light-blue flame, and dissolves in water to yield solutions with a slightly alkaline pH. The dissolution process occurs at a 1 : 1.5 ratio and gives a heat emission of 20.1 J/mol. The water solubility of HMTA decreases with increasing temperature, which is also typical of other tertiary amines.

HMTA is a disinfectant which hydrolyzes in the presence of acids (e.g. sulphuric acid) to form aldehyde and ammonia [12], [15]. Literature reports show that HMTA exerts a moderately toxic effect on the aquatic environment [8]. Thus, *Trutta iridea* fish is unfavourably affected only by very high HMTA concentrations, as that of 5000 g/m³ [2]. Plankton and lower organisms experience the toxic influence of HMTA at concentrations as high as several to ten grams per cubic centimeter. The threshold concentrations for individual species are reported to be as follows [11]: 8 g/dm³ for *Gammarus pulex*, 6.5 g/dm³ for *Epeorus assimilis*, 3.5 g/dm³ for *Vorticella companula*, 12 g/dm³ for *Paramaecium caudatum*, 5 g/dm³ for *Pseudomonas*, 10 g/dm³ for *Scenedesmus*, 5 g/dm³ for *Colpoda*, and 10 g/dm³ for *Daphnia*. It is interesting to note that no undesirable effects were observed in *Daphnia* even after 48 h of HMTA treatment.

The objective of this study was to determine: 1) the resistance of HMTA to chemical oxidation with KMnO₄ and K₂Cr₂O₇ under standard conditions of dichromate COD and permanganate COD determinations, 2) the resistance of HMTA to biochemical degradation under standard conditions of BOD₅ determination by the dilution method, 3) the resistance of HMTA to biochemical degradation in aerated municipal sewage, and 4) the effect of a wide range of HMTA concentrations on the course of the biological treatment process as applied to municipal sewage.

The experiments included preliminary investigations on aqueous solutions of HMTA and respirometric studies involving municipal sewage from the city of Wrocław.

2. PRELIMINARY INVESTIGATIONS

The investigations aimed at determining the relationship between the concentration of HMTA present in the wastewater to be treated and the behaviour of dichromate COD, permanganate COD and BOD₅.

The resistance to chemical oxidation with KMnO₄ or K₂Cr₂O₇ in aqueous solution was studied over a wide range of HMTA concentrations (tabs. 2 and 3). This resistance was found to be low in the presence of either oxidant. Under conditions of dichromate or permanganate COD the amount of oxygen taken up from KMnO₄ or K₂Cr₂O₇ for the oxidation of HMTA approaches 100% of

the theoretical value (tabs. 2 and 3), when HMTA is assumed to oxidize via the route

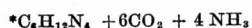


Table 2

HMTA chemical oxidability under conditions of permanganate COD determination

Podatność urotropiny na chemiczne utlenianie w warunkach oznaczania utlenialności

| HMTA content in the sample | From oxidizers (determined) | Oxygen uptake, mg | Percent of theo- retical value according to reaction | |
|-------------------------------|--------------------------------|--|---|-------|
| | | Stoichiometric, according to reaction | (1)* | (2)** |
| mg | | | (1) | (2) |
| 0.05 | 0.06 | 0.0685 | 0.16 | 87.6 |
| 0.10 | 0.13 | 0.137 | 0.32 | 94.9 |
| 0.15 | 0.20 | 0.2055 | 0.48 | 97.3 |
| 0.20 | 0.27 | 0.274 | 0.64 | 98.5 |
| 0.25 | 0.34 | 0.3425 | 0.80 | 99.3 |
| 0.30 | 0.40 | 0.411 | 0.96 | 97.3 |
| 0.35 | 0.47 | 0.4795 | 1.12 | 98.0 |



(1)

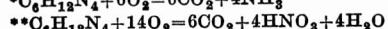
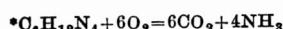
(2)

Table 3

HMTA chemical oxidability under conditions of dichromate COD determination

Podatność urotropiny na chemiczne utlenianie w warunkach oznaczania ChZT

| HMTA content in the sample | From oxidizers (determined) | Oxygen uptake, mg | Percent of theo- retical value according to reaction | |
|-------------------------------|--------------------------------|--|---|-------|
| | | Stoichiometric, according to reaction | (1)* | (2)** |
| mg | | | (1) | (2) |
| 2.0 | 2.7 | 2.74 | 6.4 | 98.5 |
| 2.5 | 3.4 | 3.49 | 8.0 | 99.1 |
| 3.0 | 4.1 | 4.11 | 9.6 | 99.8 |
| 3.5 | 4.8 | 4.80 | 11.2 | 100.0 |
| 4.0 | 5.5 | 5.48 | 12.8 | 100.3 |
| 4.5 | 6.2 | 6.17 | 14.4 | 100.5 |
| 5.0 | 6.8 | 6.85 | 16.0 | 99.3 |
| 6.0 | 8.2 | 8.22 | 19.2 | 99.8 |



(1)

(2)

When it is assumed that the oxidation reaction proceeds according to equation



oxygen uptake will approach 43 % of the theoretical value (tabs. 2 and 3).

The resistance of HMTA to biochemical oxidation under conditions of BOD_5 determination by the dilution method was found to be very high. This is substantiated by the behaviour of BOD which was studied in two solutions with HMTA concentration of 2 g/m³ and 4 g/m³, respectively. Diluted with a mixture of water and municipal sewage, the solutions of interest showed no increase in BOD over a period of 17 days. Thus BOD_5 cannot be adopted as an indicator of water or wastewater contamination with HMTA. For this purpose it is advisable to use organic nitrogen which accounts for 95 to 100 % of the nitrogen content in the HMTA molecule, when the Kjeldahl determination method is employed.

3. RESPIROMETRIC STUDIES

The objective was to determine the resistance of HMTA to biochemical degradation in municipal sewage and to investigate the effect of HMTA concentration on the course of the biological treatment process. Municipal wastewaters are a habitat and a nutrient background of various microorganisms. Respirometric studies of municipal sewage are of great practical importance, as they permit prediction of HMTA behaviour during biological treatment in a municipal sewage treatment plant.

The resistance of HMTA to biodegradation in municipal wastewaters (tab. 1) was studied in a respirometer (fig. 1) adapted to simultaneous measurements of oxygen uptake and carbon dioxide production. The large size of the flasks (about 2 dm³) enables collection of large-volume samples for the analysis of water composition. Oxygen uptake and carbon dioxide production in the respirometer are determined by the manometric method and in a chemical procedure, respectively. The design and operation of the respirometer have been described earlier [4], [5].

The experimental sewage (tab. 1) was poured into 12 respirometric flasks in 1000 cm³ portions. The initial concentrations of HMTA were the following: 0, 50, 100, 250, 500, and 1000 g/m³. Samples with identical initial concentration of HMTA were aerated in two flasks in a simultaneous procedure in order to extend the duration of the run and provide a continued collection of the samples for analysis, when the first of the two flasks had been depleted. In this way, the composition of the aerated water samples was analyzed once a day during

33 successive days (792 h). Experimental temperature (298 K) and number of revolutions of the magnetic stirrer were kept constant throughout the study. The monitoring procedure involved chemical analyses of the wastewater, as well as the measurements of oxygen uptake and carbon dioxide production.

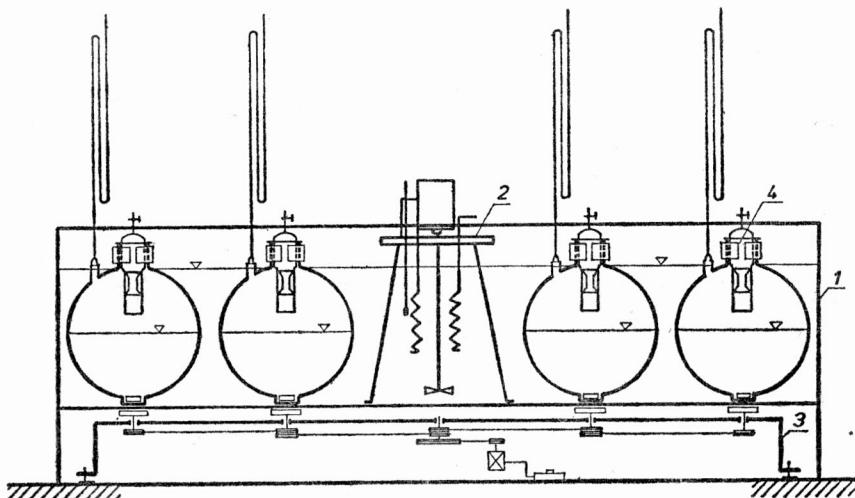


Fig. 1. Respirometer

1 — thermostatic vessel, 2 — thermostat, 3 — magnetic stirrers, 4 — closing cap and suspended vessel receiving KOH

Rys. 1. Respirometr

1 — naczynie termostatyczne, 2 — termostat, 3 — mieszadła magnetyczne, 4 — nakrywka
1 podwieszone naczynko odbierające KOH

In aerated samples there were determined: pH, total alkalinity, permanganate COD, nitrogen (ammonia nitrogen, nitrite nitrogen, nitrate nitrogen) and HMTA concentrations. HMTA concentration in wastewater was determined by colorimetry, using chromotropic acid [7]. The remaining determinations were carried out by standard methods [6].

4. DISCUSSION OF RESULTS

The physicochemical composition of the experimental sewage is given in tab. 1. The addition of various HMTA doses (50, 100, 250, 500 and 1000 g/m³) yielded a proportional increase of alkalinity, organic nitrogen, permanganate COD and a slight increase of pH, but it was without any effect on ammonia nitrogen concentration (tab. 4). As shown by the curves in fig. 2, the aeration process had only a slight influence on the concentration of HMTA in the

wastewater. High initial concentrations decreased insignificantly after almost 300 h of aeration (fig. 2, curves 3-5). When the initial concentrations were low, this effect was observed not earlier than after 600 h (fig. 2, curves 1 and 2).

Table 4

Effect of HMTA concentration on the composition of the experimental sewage
Wpływ stężenia urotropiny na skład ścieków miejskich użytych do badań

| Component | Unit | HMTA concentration, g/m ³ | | | | | |
|------------------|-------------------------------------|--------------------------------------|------|------|------|------|------|
| | | 0 | 50 | 100 | 250 | 500 | 1000 |
| pH | pH | 7.72 | 7.72 | 7.74 | 7.78 | 7.81 | 7.90 |
| total alkalinity | g CaCO ₃ /m ³ | 255 | 270 | 290 | 335 | 420 | 575 |
| permanganate COD | g O ₂ /m ³ | 124 | 200 | 270 | 470 | 810 | 1500 |
| ammonia nitrogen | g N/m ³ | 35 | 35 | 35 | 35 | 35 | 35 |
| organic nitrogen | g N/m ³ | 28.4 | 48.2 | 67.6 | 125 | 218 | 420 |

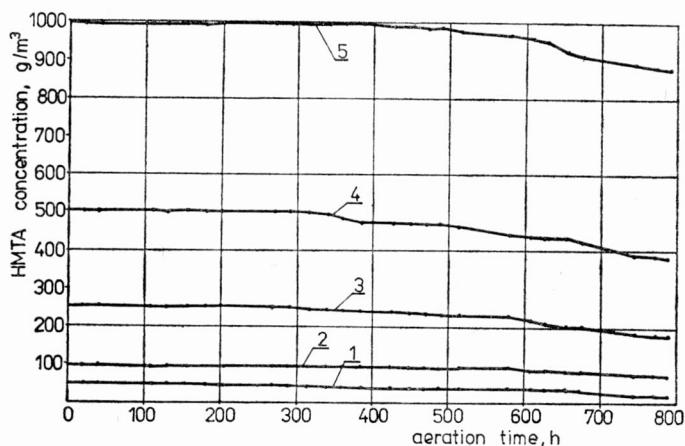


Fig. 2. HMTA concentration versus aeration time
Rys. 2. Zależność stężenia HMTA od czasu napowietrzania

Further extension of the aeration time brought about a slow biochemical degradation of HMTA. This was indicated by the decrease in HMTA concentrations (fig. 2) and permanganate COD (fig. 3) accompanied by an increase of oxygen uptake (fig. 4) and carbon dioxide production (fig. 5). After 792 h of aeration of sewage samples treated with 50 g/m³ doses, HMTA concentration reached a value of about 19 g/m³. In the remaining experimental series the residual HMTA concentrations were higher (fig. 2). Thus, HMTA present in aerated sewage is highly resistant to biochemical degradation. The process should be preceded by an extended adaptation of bacteria.

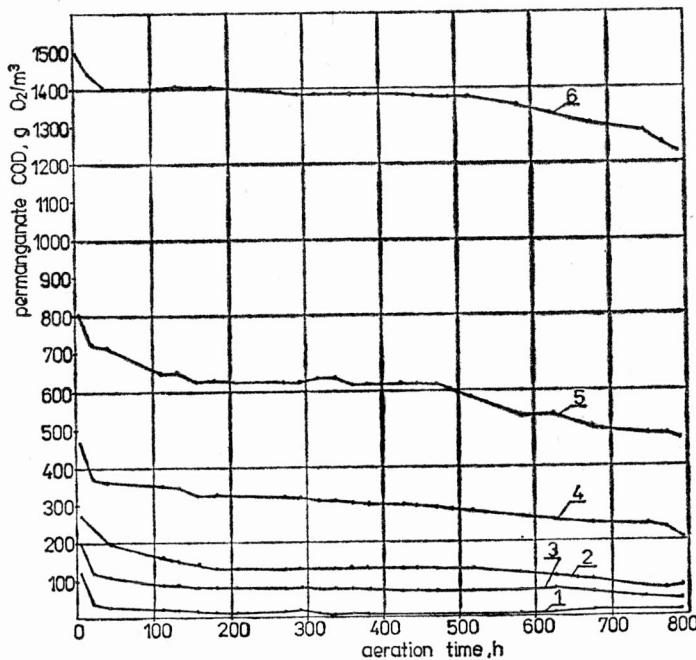


Fig. 3. Permanganate COD verus aeration time

Rys. 3. Zależność utlenialności nadmanganianowej od czasu napowietrzania

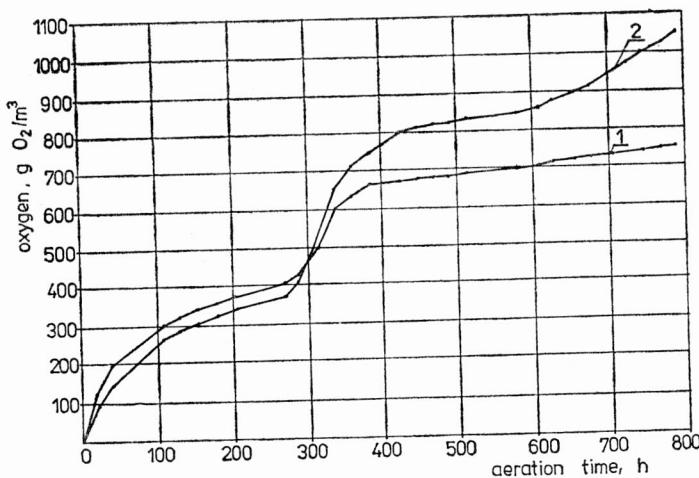


Fig. 4. Oxygen uptake during aeration

1 — sewage with no HMTA, 2 — wastewater with initial HMTA concentration of 100 g/m³

Rys. 4. Pobranie tlenu podeczas napowietrzania

1 — ścieki bez HMTA, 2 — ścieki o początkowym stężeniu HMTA 1000 g/m³

Despite its high resistance to biodegradation, HMTA exerts a moderately toxic effect on aerobic bacteria. This may be concluded from the biodegradation rate of organic substances in the experimental sewage containing various concentrations of HMTA. Thus, the biodegradation rate (measured in terms of oxygen

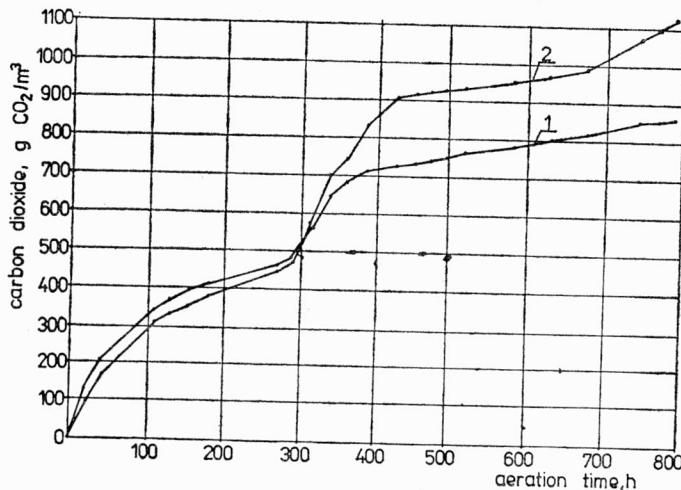


Fig. 5. Carbon dioxide production during aeration

1 - sewage with no HMTA, 2 - wastewater with initial HMTA concentration of 1000 g/m³

Rys. 5. Wydzielanie dwutlenku węgla podczas napowietrzania

1 - ścieki bez HMTA, 2 - ścieki o początkowym stężeniu HMTA 1000 g/m³

uptake (tab. 5) or carbon dioxide production (tab. 6)) for wastewaters with initial HMTA concentration equal to, or less than, 250 g/m³ does not differ from that for organic matter present in municipal sewage with no HMTA content. At the same time, slightly lower quantities of oxygen consumed and carbon dioxide produced were measured for wastewaters with initial HMTA concentrations of 500 and 1000 g/m³ (tabs. 5 and 6).

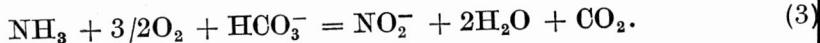
Oxygen uptake and carbon dioxide production curves for no-HMTA wastewater and wastewater with initial HMTA concentration of 1000 g/m³ are plotted in fig. 4. Figures 5 and 6 give the relationship between HMTA concentration and the course of the nitrification processes. As shown by these figures and the data of tab. 7, the presence of HMTA has no inhibitory effect on the nitrification of ammonia nitrogen to nitrite nitrogen (fig. 6) and nitrate nitrogen (tab. 7). Irrespective of the initial HMTA concentration in the wastewater under study, nitrification of ammonia nitrogen to nitrite nitrogen was initiated after 178 h of continuous aeration. Nitrates did not appear in the aerated sewage earlier than after 490 h (tab. 7). While the oxidation of nitrites to nitrates proceeded slowly, the conversion of ammonia to nitrites (NO_2^-) was a rapid process; its duration being of about 269 h. Within this period ammonia nitrogen content decreased significantly. There was also a decrease of alkalinity

Table 5

Oxygen uptake related to initial concentration of HMTA and time of aeration
 Zużycie tlenu w ściekach w zależności od stężenia początkowego urotropiny i czasu napowietrzania

| Duration of exp. h | Initial concentration of HMTA in experimental sewage, g/m ³ | | | | | |
|-----------------------|--|-------|-------|-------|--------|--------|
| | 0 | 50 | 100 | 250 | 500 | 1000 |
| 18.0 | 127.3 | 126.9 | 129.3 | 118.9 | 104.8 | 92.8 |
| 39.0 | 195.2 | 200.1 | 194.9 | 182.5 | 165.3 | 148.7 |
| 111.0 | 301.8 | 304.9 | 313.3 | 304.9 | 290.2 | 267.1 |
| 131.1 | 321.5 | 327.1 | 336.3 | 333.6 | 314.5 | 286.5 |
| 153.5 | 340.3 | 349.0 | 360.9 | 357.9 | 342.6 | 306.0 |
| 178.5 | 359.9 | 367.4 | 378.3 | 378.3 | 362.5 | 328.4 |
| 203.5 | 377.0 | 385.8 | 400.1 | 405.4 | 388.3 | 341.8 |
| 270.5 | 404.1 | 414.2 | 428.4 | 457.5 | 473.4 | 376.7 |
| 292.0 | 429.4 | 438.2 | 466.3 | 543.1 | 577.5 | 416.3 |
| 315.0 | 508.6 | 511.8 | 542.1 | 675.8 | 711.3 | 519.1 |
| 337.0 | 603.0 | 604.9 | 636.3 | 708.7 | 732.4 | 652.3 |
| 358.0 | 638.0 | 643.0 | 673.3 | 739.2 | 754.2 | 718.5 |
| 378.0 | 668.4 | 670.2 | 701.7 | 746.0 | 781.5 | 750.5 |
| 424.0 | 672.4 | 678.7 | 717.0 | 760.0 | 832.2 | 804.9 |
| 447.0 | 677.0 | 683.7 | 722.0 | 765.5 | 838.4 | 812.4 |
| 468.5 | 682.0 | 689.8 | 727.3 | 774.3 | 842.8 | 821.8 |
| 490.5 | 686.4 | 693.6 | 733.0 | 778.5 | 846.7 | 826.6 |
| 514.0 | 690.5 | 698.3 | 737.6 | 781.6 | 852.2 | 832.5 |
| 581.5 | 700.7 | 708.8 | 754.4 | 800.5 | 864.0 | 845.2 |
| 609.5 | 707.7 | 717.6 | 767.5 | 822.9 | 878.2 | 863.2 |
| 627.5 | 715.7 | 731.6 | 777.2 | 835.6 | 891.7 | 880.2 |
| 655.5 | 722.9 | 739.3 | 785.4 | 855.4 | 907.1 | 899.6 |
| 674.0 | 728.2 | 745.9 | 793.7 | 871.0 | 930.1 | 916.1 |
| 745.5 | 746.7 | 766.8 | 827.9 | 981.5 | 992.1 | 1003.8 |
| 772.5 | 751.3 | 773.4 | 840.2 | 928.9 | 1011.1 | 1026.9 |
| 792.0 | 756.5 | 779.2 | 851.6 | 941.4 | 1023.2 | 1052.1 |

(tab. 8). Oxygen uptake (fig. 4) and carbon dioxide production (fig. 5) were found to increase. All these changes are a result of ammonia nitrogen nitrification. The process is described by the following equation



It is the nitrification of ammonia nitrogen that accounts for the nitrite nitrogen level in aerated wastewater. In experimental samples with initial HMTA concentration equal to or higher than 250 g/m³, the concentration of this compound was higher than in the samples with initial HMTA content equal to or less than 100 g/m³, or in zero-HMTA wastewater samples. This

Table 6

Carbon dioxide production related to initial concentration of HMTA and time of aeration
 Ilość wydzielonego ze ścieków dwutlenku węgla w zależności od początkowej zawartości urotropiny i czasu napowietrzania

| Duration of exp. h | Initial concentration of HMTA in experimental sewage, g/m ³ | | | | | |
|-----------------------|--|-------|-------|-------|--------|--------|
| | 0 | 50 | 100 | 250 | 500 | 1000 |
| | Carbon dioxide production, g CO ₂ /m ³ | | | | | |
| 18.0 | 122.8 | 127.2 | 121.6 | 114.2 | 102.3 | 96.7 |
| 39.0 | 201.0 | 206.7 | 196.3 | 183.8 | 173.9 | 165.1 |
| 111.0 | 340.0 | 344.7 | 329.4 | 324.5 | 317.0 | 313.5 |
| 131.1 | 369.5 | 374.2 | 358.0 | 350.8 | 342.7 | 330.2 |
| 153.5 | 391.9 | 398.9 | 380.7 | 371.7 | 364.1 | 353.5 |
| 178.5 | 412.6 | 421.4 | 400.4 | 394.9 | 388.3 | 380.1 |
| 203.5 | — | — | — | — | — | — |
| 270.5 | 461.3 | 489.1 | 471.3 | 468.3 | 459.5 | 447.1 |
| 292.0 | 491.6 | 520.6 | 518.3 | 544.0 | 553.4 | 478.2 |
| 315.0 | 565.1 | 599.1 | 582.3 | 661.2 | 672.9 | 576.8 |
| 337.0 | 649.0 | 681.5 | 670.3 | 694.1 | 704.3 | 700.3 |
| 358.0 | 685.5 | 724.7 | 710.0 | 727.3 | 742.5 | 764.2 |
| 378.0 | 717.9 | 755.4 | 739.4 | 736.6 | 781.9 | 831.0 |
| 424.0 | 725.9 | 764.5 | 749.2 | 746.1 | 842.3 | 906.8 |
| 447.0 | 734.7 | 773.8 | 758.3 | 753.7 | 853.4 | 915.7 |
| 468.5 | 743.5 | 783.0 | 767.5 | 763.6 | 862.2 | 923.6 |
| 490.5 | 752.2 | 790.4 | 775.3 | 771.3 | 869.2 | 928.8 |
| 514.0 | 763.7 | 798.8 | 784.2 | 779.9 | 877.7 | 936.6 |
| 581.5 | 788.9 | 821.5 | 808.7 | 801.1 | 892.0 | 953.1 |
| 609.5 | — | — | — | — | — | — |
| 627.5 | 808.1 | 840.7 | 834.7 | 826.4 | 924.0 | 973.6 |
| 655.5 | — | — | — | — | — | — |
| 674.0 | 817.5 | 851.6 | 853.5 | 855.8 | 967.0 | 997.1 |
| 745.5 | 851.9 | 882.0 | 890.0 | 908.2 | 1044.4 | 1074.9 |
| 772.5 | — | — | — | — | — | — |
| 792.0 | 867.1 | 900.8 | 913.4 | 929.5 | 1083.3 | 1124.7 |

Table 7

Nitrate nitrogen concentration in aerated sewage with various initial concentrations of HMTA

Stężenie azotu azotanowego w napowietrzanych ściekach o różnych początkowych zawartościach urotropiny

| Duration of exp. h | Initial concentration of HMTA, g/m ³ | | | | | |
|-----------------------|--|------|-----|-----|-----|------|
| | 0 | 50 | 100 | 250 | 500 | 1000 |
| | Nitrate nitrogen concentration, g N/m ³ | | | | | |
| 490.5 | 0.14 | 0.15 | 0.2 | 0.2 | 0.2 | 0.2 |
| 514.0 | 0.80 | 0.40 | 0.4 | 0.4 | 0.5 | 0.4 |
| 627.5 | 1.5 | 0.8 | 0.8 | 0.8 | 0.6 | 0.4 |
| 674.0 | 2.0 | 1.5 | 1.0 | 1.0 | 1.0 | 1.0 |
| 745.5 | 2.0 | 1.7 | 1.0 | 1.0 | 1.2 | 1.2 |
| 792.0 | 2.5 | 2.0 | 1.5 | 1.5 | 1.5 | 1.5 |

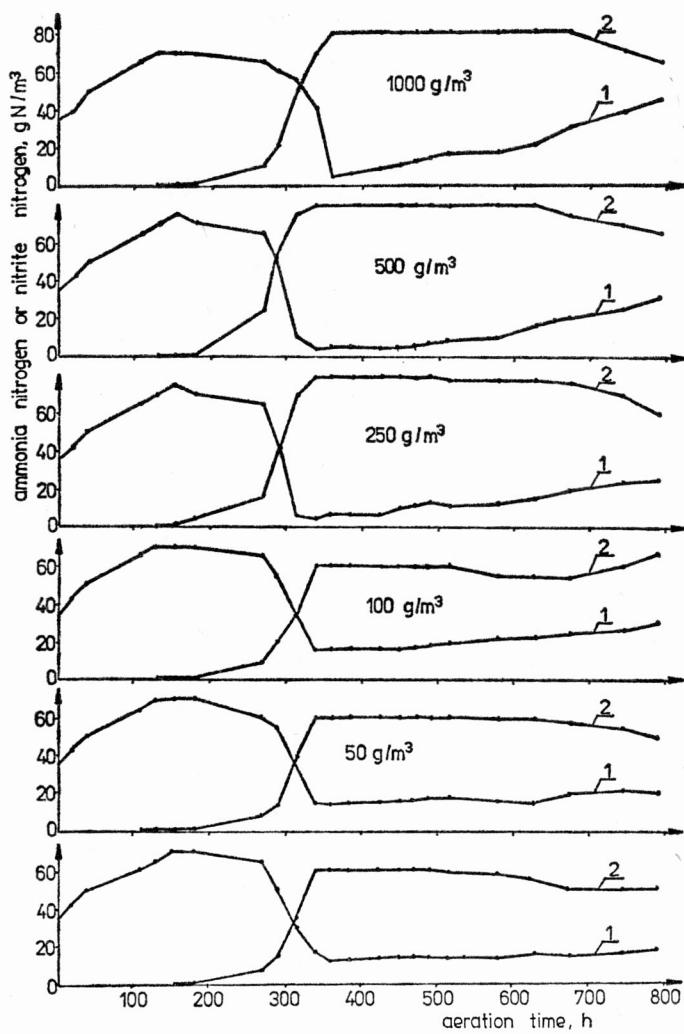


Fig. 6. Behaviour of ammonia nitrogen 1 and nitrite nitrogen 2 in the course of aeration
Rys. 6. Azot amonowy 1 i azot azotynowy 2 podeczas napowietrzania

behaviour is associated with an inhibition of the nitrification process due to the almost complete exhaustion of the buffer volume. The latter is indicated by a very low total alkalinity level (measured after completion of the process (tab. 8)) and, consequently, by a considerable decrease of pH (tab. 9). The high concentrations of ammonia nitrogen, which persisted after the completion of nitrification, also indicate the inhibition of nitrification process in wastewaters with initial HMTA concentration equal to or less than 100 g/m^3 (fig. 6, curve 1). In wastewaters having high HMTA contents the nitrification of ammonia

Table 8

Total alkalinity in aerated sewage with various initial concentrations of HMTA

Zasadowość ogólna w napowietrzanych ściekach o różnych początkowych stężeniach urotropiny

| Duration of exp. h | Initial concentration of HMTA, g/m ³ | | | | |
|-----------------------|---|-----|-----|-----|------|
| | 0 | 50 | 100 | 250 | 1000 |
| | Total alkalinity, g CaCO ₃ /m ³ | | | | |
| 0 | 255 | 270 | 290 | 335 | 420 |
| 358.0 | 20 | 25 | 30 | 55 | 120 |
| 792.0 | 20 | 30 | 40 | 60 | 120 |
| | | | | | 290 |

Table 9

pH of aerated sewage with various initial concentrations of HMTA

Odczyn ścieków napowietrzanych o różnych początkowych stężeniach urotropiny

| Duration of exp. h | Initial concentration of HMTA, g/m ³ | | | | | |
|-----------------------|---|------|------|------|------|------|
| | 0 | 50 | 100 | 250 | 500 | 1000 |
| 0 | 7.72 | 7.72 | 7.74 | 7.78 | 7.81 | 7.90 |
| 358 | 5.73 | 5.92 | 5.97 | 6.84 | 6.90 | 7.07 |
| 792 | 6.08 | 6.32 | 6.34 | 6.74 | 6.91 | 6.56 |

nitrogen proceeds without any inhibition when the total alkalinity level is sufficiently high to kill nitrous acid (HNO₂). Further increase of ammonia nitrogen concentration in the course of the aeration process comes from the biodegradation of HMTA (fig. 6, curve 1). This is indicated on one hand by the increase in oxygen uptake (fig. 4, tab. 5) and carbon dioxide production (fig. 5, tab. 6), and on the other hand by the decrease of HMTA concentration (fig. 2). Hence, HMTA is moderately toxic to the microorganisms that participate in the biodegradation of organic pollutants and in the nitrification of ammonia.

CONCLUSIONS

1. Hexamethylenetetramine, (CH₂)₆N₄, has become increasingly frequent in industrial wastewaters. The presence of this compound accounts for the increase of permanganate COD, dichromate COD and organic nitrogen, and is without any effect on the value of BOD₅.

2. Hexamethylenetetramine present in aerated municipal sewage is highly resistant to biodegradation. The process should be preceded by an extended adaptation of the microorganisms.

3. Very high concentrations of hexamethylenetetramine (1000 g/m^3) in municipal sewage have no unfavourable effect either on the rate of organic matter degradation or on the nitrification of ammonia nitrogen to nitrite nitrogen.

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PODATNOŚĆ UROTROPINY NA BIOCHEMICZNY ROZKŁAD W ŚCIEKACH MIEJSKICH

Przedstawiono wyniki badań nad podatnością urotropiny, czyli sześciometylenocteraminy ($(\text{CH}_2)_6\text{N}_4$), na biochemiczny rozkład w napowietrzanych ściekach miejskich. Doświadczenie wykonano w respirometrach w warunkach laboratoryjnych. Aparatura własnego

pomysłu pozwala mierzyć ilość zużytego tlenu i wydzielonego dwutlenku węgla oraz prowadzić systematyczną kontrolę analityczną składu ścieków. Określono podatność urotropiny na biochemiczny rozkład i jej wpływ na przebieg procesu mineralizacji zanieczyszczeń organicznych w ściekach miejskich. Stwierdzono, że biodegradacja urotropiny w badanych warunkach zachodzi bardzo oporne, a jej stężenie 1000 g/m³ nie wpływa ujemnie ani na szybkość biochemicznego ulteniania związków organicznych zawartych w ściekach, ani na proces nitrifikacji azotu amonowego do azotynowego.

DIE SUSZEPTIBILITÄT VON UROTROPIN ZUM BIOCHEMISCHEN ABBAU IM BELÜFTETEN STÄDTISCHEN MISCHWASSER

Das Verhalten von Urotropin ($(\text{CH}_2)_6\text{H}_4$) während des Belüftungsprozesses wird im Laborverfahren untersucht. Die Untersuchungskonzentration von Urotropin fällt in den Bereich von 0 bis 1000 g/m³. Die Ergebnisse weisen darauf hin, daß diese Substanz keinen ungünstigen Einfluß auf den Verlauf des Belebtschlammverfahrens noch auf die Zersetzung von Ammoniumstickstoff zum Nitritstickstoff ausübt.

ПОДАТЛИВОСТЬ УРОТРОПИНА НА БИОХИМИЧЕСКОЕ РАЗЛОЖЕНИЕ В ГОРОДСКИХ СТОЧНЫХ ВОДАХ

Приведены результаты исследований по податливости уротропина, т. е. гексаметиленететрамина ($(\text{CH}_2)_6\text{H}_4$), на биохимическое разложение в аэрируемых городских сточных водах. Опыты были произведены в респирометрах в лабораторных условиях. Аппаратура собственного замысла позволяет измерять количество израсходованного кислорода и выделенного углекислого газа, а также проводить систематический аналитический контроль за составом сточных вод. Определена податливость уротропина на биохимическое разложение и его влияния на ход процесса минерализации органических загрязнений в городских сточных водах. Отмечено, что биодеградации уротропина в исследуемых условиях происходит с большим трудом, а её концентрация 1000 г/м³ не влияет отрицательно ни на скорость биохимического окисления органических соединений, содержащихся в сточных водах, ни на процесс нитрификации аммиачного азота в нитритный.