BOGUSŁAWA GOMÓŁKA, EDWARD GOMÓŁKA*

THE EFFECT OF FINAL PRODUCTS OF PYRIDINE BIODEGRADATION ON CHEMICAL CHARACTERISTICS OF AERATED MUNICIPAL WASTEWATER

The paper discusses a part of investigations on the biodegrability of pyridine in aerated municipal wastewater, and on chemical changes occurring in this wastewater due to the secondary chemical reactions following the biodegradation process.

1. CHARACTERISTICS OF PYRIDINE AND WASTEWATER

Pyridine, C_5H_5N, has a heterocyclic structure and belongs to alkaloids. It is colourless or yellowish transparent liquid with a tart, pervasive smell, its reaction is weakly alkaline; specific gravity amounts to 0.983 kG/dm^3, melting and boiling temperatures being 315 K and 388.5 K, respectively [17]. Pyridine is in every proportion mixable with water, ethanol, ether, and benzene. It appears in a coal tar together with different methylpyridines and quinolines, whose mixtures are known as pyridine bases. The latter constitute 2% of a total coal tar [14].

Pyridine is a highly toxic compound, due to its easy penetration through the skin and its irritative action towards the mucous membrane and conjunctive during the aspiration of its vapours. The olfactory sensitivity threshold ranges from 0.0004 to 0.005 mg/dm^3 C_5H_5N, the threshold of irritating action of vapours varies within 0.0016–0.006 mg/dm^3, and admissible concentration of vapours in air amounts to 0.05 mg/dm^3 of pyridine [4, 11].

Pyridine is a widely applied in pharmaceutic and chemical industries as a raw material in synthesis of many organic compounds, drugs and dyes. It is also used as a solvent in leather and rubber industries and in production of printcloth. It may be used in denatu-

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* Institute of Environment Protection Engineering, Wrocław Technical University, Wrocław, Poland.

ration of ethanol and as an insecticide [4, 12]. As a result of such a broad application, pyridine is also present in wastewaters of many branches of industry [1] (coke, gas, chemical, pharmaceutical, rubber and leather industries).

Being a strongly toxic compound its presence in wastewater exerts a harmful effect on secondary wastewater treatment plant as well as on stream biota, and deteriorates organoleptic properties of the water, although the corresponding literature data are rather scarce. The admissible concentrations of pyridine in the stream water is 0.2 mg/dm³ [19]. At the concentration of 5 mg/dm³ pyridine inhibits the nitrification process and causes pathological changes.

A specific smell of the pyridine is detectable in the stream water at the concentration over 2.5 mg/dm³.

A number of authors were concerned with biological treatment of wastewaters containing pyridine. According to KALABINA and ROGOVSKAYA [10] and admissible concentration of this compound in wastewater is 50–200 mg/dm³. ZDYBIEWSKA and KWIATKOWSKA conducted the investigations on the effect of pyridine (doses from 10 to 300 mg/dm³) on the process of biological treatment of phenol wastewater. As a result of this process the pyridine removals from 93% to 98% were reported [19]. According to JUNOVSKAYA [18] the concentration of pyridine equal to 1000 mg/dm³ impairs the treatment of phenol wastewater with activated sludge, by inhibiting the growth of the latter. MALANEY [13] has stated that the decomposition of pyridine takes place after 16 h of adaptation. Data from Soviet Union suggest the concentration of 400 mg/dm³ of pyridine as the admissible for the biological treatment of wastewater.

The investigations conducted so far allowed to state that pyridine is not easily biodegradated and requires a previous adaptation of the activated sludge.

The purpose of this paper was to determine the biodegrability of pyridine in municipal wastewater, and to establish the effect of the products of pyridine decomposition on the change in composition of the effluent.

The investigations were performed using municipal wastewater from Wrocław, characterized by the following physico-chemical composition: turbidity 110 mg/dm³, colour — 45 mg/dm³, fecal smell, permanaganate value — 86 mg/dm³ O_2, COD — 374 mg/dm³ O_2, BOD_5 — 210 mg/dm³ O_2, chlorides — 74 mg/dm³ Cl, sulphates — 93 mg/dm³ SO_4^{-2}, organic nitrogen — 17.2, ammonium nitrogen — 23.5, nitrite nitrogen — 0.01 mg/dm³ N. Nitrate nitrogen was entirely absent. Total and mineral solids amounted to 540 mg/dm³ and 323, respectively, total hardness — 5.29 mg/dm³.

2. PROCEDURES AND ANALYTICAL CONTROL

The respirometer (fig. 1) used in the investigations was characterized by a large volume of the flasks. This enabled a simultaneous measurement of the oxygen consumed and carbon dioxide produced as well as sampling of relatively large volumes of wastewater
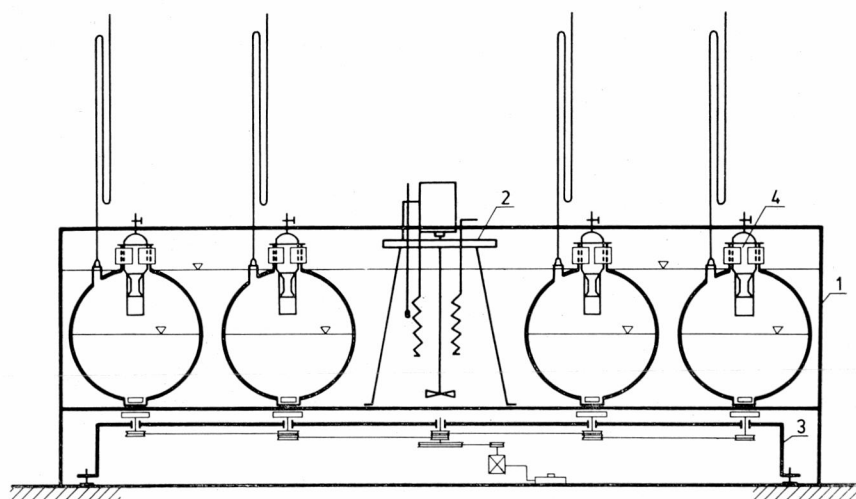
Fig. 1. Scheme of the respirometer
Rys. 1. Schemat respirometru

from respirometric flask for physico-chemical and bacteriological analysis of the mixed liquor. A detailed description of the respirometer is given in reference [6].

The following procedure has been applied:

For the fresh municipal wastewater taken from pumping station (after separation of the settleable solids) the following quantities of pyridine were added: 0, 100, 200, 300, 400, 500, 600 and 700 mg/dm³. The samples of the uniform mixtures were taken for physico-chemical analysis in order to establish the initial composition of raw wastewaters.

The addition of pyridine caused distinct changes in the smell of the raw wastewaters and in their value (from 7.3 to 8.4), alkalinity (from 5.2 to 13.1 mval/dm³), acidity (from 0.6 to 0 mval/dm³), COD (from 374 to 435 mg O_2/dm³) and organic nitrogen content (from 17.2 to 140 mg N/dm³). The respiratory flasks were filled with 1 dm³ of the wastewaters containing pyridine and aerated at 293 K during 20 days.

As a process control, oxygen consumption and carbon dioxide production measurements were conducted as well as systematic chemical mixed liquor analysis in daily intervals was performed including determinations of permanganate consumption and concentrations of pyridine and nitrogen compounds. Both before and after the experiments the full analysis of wastewater was made, its results are given in table 1.

Physical-chemical analysis of the wastewater was made according to the Polish standard methods [6, 7, 9, 15, 16], whereas the content of pyridine in wastes was determined by colorimetric method based on the reaction of pyridine with bromocyane, which results in formation of an orange-coloured compound — alphaanilinephenyldihydropyridine [8, 14].

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Physico-chemical composition of wastewater after the experiments have been completed

Parameter	Unit	0	100	200	300	400	500	600	700
Turbidity*	mg/dm³	Transparent							
Colour	mg/dm³	40	40	40	40	40	40	40	40
Odour	—	Z3R	Z3R	Z3R	Z3R	Z3R	Z3R	Z3R	Z3R
pH		7.6	7.8	8.3	8.3	8.3	8.4	8.4	8.4
Basicity	meg/dm³	3.5	3.9	9.0	10.4	11.6	12.7	14.0	15
Acidity	meg/dm³	0.3	0.2	0	0	0	0	0	0
Permanganate consumption**	mg/dm³O₂	9.6	18.2	9.4	8.9	8.7	9.8	12.2	11.8
COD**	,,	26.7	30.0	25.4	24.6	27.3	29.2	28.0	29.8
BOD₅** (1 : 2)	,,	4.2	4.8	6.2	5.8	5.8	6.0	7.2	6.6
Chlorides	mg/dm³Cl	74	75	—	—	—	—	—	75
Sulphates	mg/dm³SO₄	96	94	—	—	—	—	—	97
Organic nitrogen**	mg/dm³N	1.3	1.4	1.1	1.0	1.3	1.5	1.7	1.8
Ammonium nitrogen	,,	0.06	0.3	53.3	72.2	89.1	105	123	137
Nitrite nitrogen	,,	0.07	7.0	0	0	0	0	0	0
Nitrate nitrogen	,,	24	8.8	0	0	0	0	0	0
Total solids	mg/dm³	352	344	274	270	240	264	252	261
Mineral solids	,,	306	296	236	217	210	217	211	213
Volatile solids	,,	46	48	38	53	30	47	41	48
Settleable solids***	cm³/dm³	3.2	3.6	4.3	6.0	7.3	9.8	11.4	14.3
Total suspended solids	mg/dm³	26.7	101.9	136.1	177.3	198	247	269.7	316
Mineral suspended solids	,,	7.2	62.2	79.4	99.2	107	111	120	123
Volatile suspended solids	,,	19.5	39.7	56.7	78.1	91	136	149.7	193
Total hardness	meq/dm³	4.49	4.0	3.3	3.1	3.0	2.9	2.9	2.9

* After 2h of sedimentation in Immhoff cone.
** Determination made from sample filtrated through filter paper.
*** After 2 hrs in Immhoff's cone.

3. DISCUSSION OF RESULTS

Preliminary investigations were started from the determining of the succeptibility of pyridine to chemical oxidation applying the standard procedure of the permanganate consumption [7, 9], COD [7, 16] and degradable organics [2, 5]. The tests were conducted using elutions of pyridine in the distilled water which were treated by the strong oxidants ($KMnO_4$, $K_2Cr_2O_7$). From the analyses it follows that pyridine is not easily oxidized in standard conditions of permanganate comsumption test (about 3% of the theoretical oxygen demand) as well as in COD test using $K_2Cr_2O_7$ (below 3%), and in the degradable organics test (only 0.4% of TOD) [5]. In the last test binormal $K_2Cr_2O_7$ solution was applied in a strongly acid environment of the mixture of phosphoric and sulphuric acids. The external heating was not used. The results from BOD test by the dilution method [1] have also proved that pyridine is bioresistant under conditions of the test.

The basic investigations of the pyridine biodegrab lity by respirometric method have been conducted parallelly in 8 flasks using two apparatus, presented in fig. 1. This made it possible to determine the effect of different concentrations of pyridine on mineralization of organic compounds in wastewater of the same initial composition. Initial concentrations of pyridine in the mixture with municipal wastewater ranged from 0 to 700 mg/dm^3.

The kinetics of the biodegradation of pyridine in the respirometer in municipal waste-water environment is presented in fig. 2. It can be seen that a slight decrease in pyridine
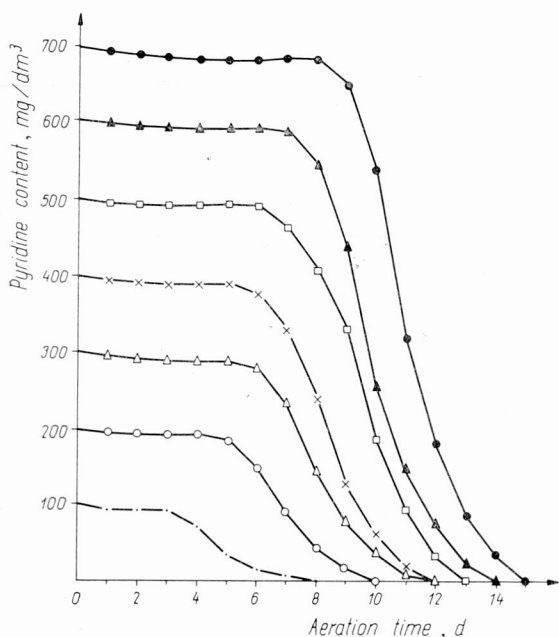
Fig. 2. Pyridine concentrations vs. time of wastewater aeration

Rys. 2. Zależność zawartości pirydyny od czasu napowietrzania ścieków
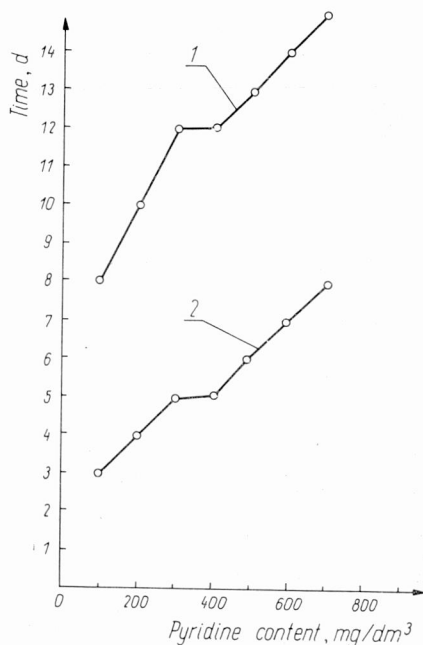
Fig. 3. Lag time and total pyridine degradation vs. its concentration in wastewater

1 — decay of pyridine in wastewater, 2 — the beginning of pyridine degradation

Rys. 3. Zależność czasu zastoju i całkowitego rozkładu pirydyny od jej stężenia w ściekach

1 — zanik pirydyny w ściekach, 2 — początek procesu rozkładu pirydyny

concentration takes place in the first day of aeration, then its concentration remains constant for the next several days. Hence, it should be supposed that this initial pyridine removal is caused by physicochemical processes (adsorption on colloidal particles). From fig. 2 it follows that stagnation period in the biodegradation process of pyridine, due to the bacterial adaptation to the compound, is the longer the higher is its initial concentration in the wastewater. Lag time versus the initial dose of pyridine is shown in fig. 3 (curve *1*). After lag period concentration of pyridine rapidly decreases until its total decay (fig. 2).

Time at which a total decay of pyridine in the wastewater takes place, depends on the initial concentration of pyridine. Excluding lag time it can be assumed that the aerobic degradation of pyridine within the range of the examined concentrations lasts for 5–7 days with a slight time increasing tendency with the increasing initial dose (fig. 4). The rate of pyridine degradation varies in time, at first raising until it reaches the maximal value, thereupon
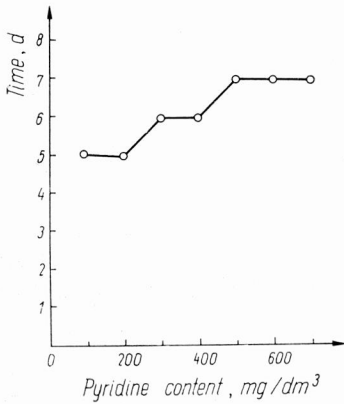
Fig. 4. Time of pyridine degradation vs. its initial concentration in wastewater

Rys. 4. Zależność czasu rozkładu pirydyny od jej dawki początkowej w ściekach
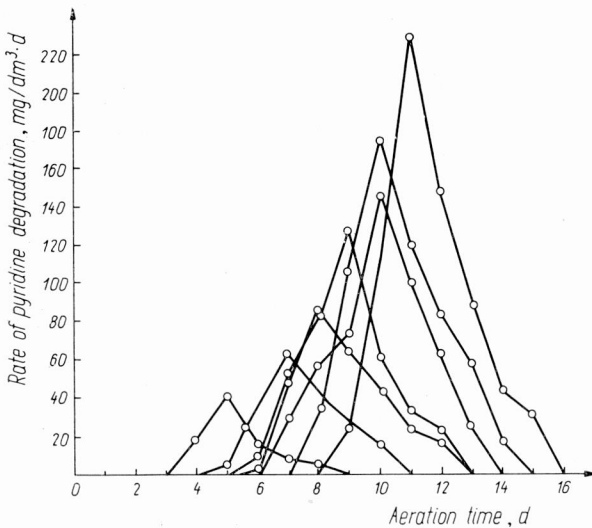
Fig. 5. Rate of pyridine degradation vs. time of wastewater aeration

Rys. 5. Przebieg rozkładu pirydyny w zależności od czasu napowietrzania ścieków
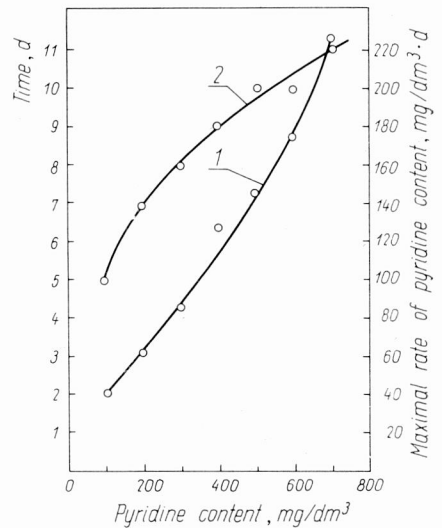
Fig. 6. Rate of pyridine degradation vs. its initial concentration in wastewater

1 — maximal rate of pyridine in wastewater,
2 — time at which the maximal rate is reached

Rys. 6. Zależność czasu i szybkości rozkładu pirydyny od jej stężenia początkowego w ściekach

1 — maksymalna szybkość ubytku pirydyny w ściekach, 2 — czas w którym następuje maksymalny ubytek pirydyny w ściekach

decreasing (fig. 5). For different initial contents of pyridine the maximal values of the degradation rate are shifted in time (fig. 6, curve 2), due to different lag periods. Fig. 6 presents also the dependence of the maximal pyridine degradation rate on its initial concentration in wastewater (curve 1). According to the definition, the degradation rate

$$V = \frac{dZ}{dt} = k'Z$$

where

V — rate of the substrate (pyridine) decrease, mg/dm³ d,
Z — substrate concentration, mg/dm³,
t — time, d,
$k' = kX_V$, d⁻¹
k — rate constant, dm³ d⁻¹ MLVSS,
X_V — concentration of biomass, mg MLVSS/dm³.
Thus the rate constant is given by the formula

$$k' = \frac{V}{Z}, \text{ mg MLVSS/dm}^3 \cdot \text{d}.$$

It is possible to calculate the average rates of pyridine degradation in wastewater for the given initial concentration. These rates increase from 12.5 to 46.7 mg/dm³·d, with the increasing concentration of pyridine, while the values of the rate coefficient
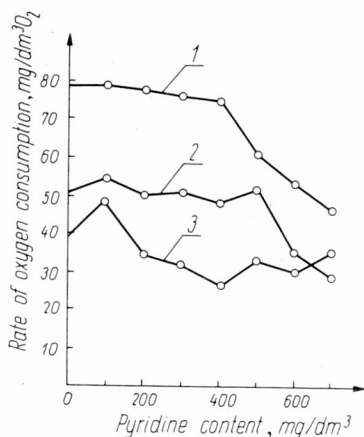

Fig. 7. Rate of oxygen consumption
vs. initial concentration of pyridine
in wastewater

1 — in first day of aeration, 2 — in second day
of aeration, 3 — in third day of aeration

Rys. 7. Szybkość zużycia tlenu w zależności od dawki początkowej pirydyny
w ściekach

1 — w pierwszym dniu napowietrzania, 2 —
w drugim dniu napowietrzania, 3 — w trzecim
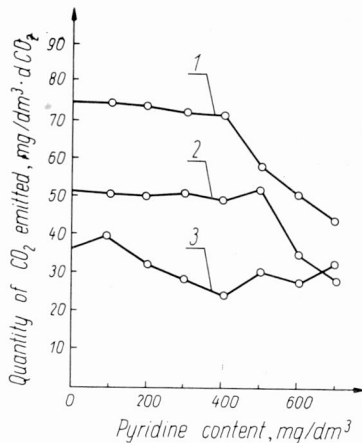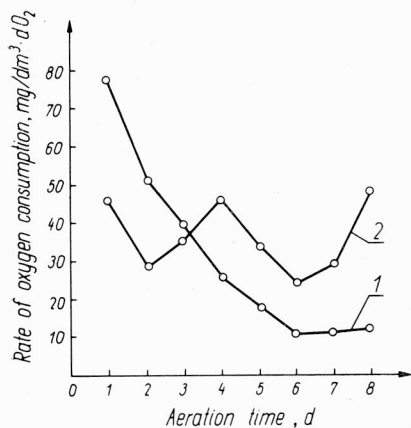dniu napowietrzania

Fig. 8. Rate of carbon dioxide production vs. initial concentration of pyridine
in wastewater

1 — in first day of aeration, 2 — in second day
of aeration, 3 — in third day of aeration

Rys. 8. Szybkość wydzielania CO_2
w zależności od dawki początkowej
pirydyny w ściekach

1 — w pierwszym dniu napowietrzania, 2 —
w drugim dniu napowietrzania, 3 — w trzecim
dniu napowietrzania

Fig. 9. Rate of oxygen consumption vs.
aeration time

1 — municipal wastewater, 2 — municipal waste-
water with pyridine (700 mg/dm³)

Rys. 9. Szybkość zużycia tlenu w zależności
od czasu napowietrzania

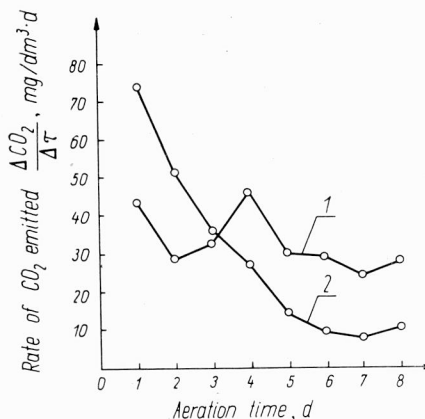1 — ścieki miejskie, 2 — ścieki miejskie o zawartości
pirydyny 700 mg/dm³

Fig. 10. Rate of carbon dioxide production
vs. aeration time

1 — wastewater with pyridine (700 mg/dm³), 2 —
municipal wastewater,

Rys. 10. Szybkość wydzielania dwutlenku
węgla w zależności od czasu napowietrzania

1 — ścieki o zawartości 700 mg/dm³ pirydyny, 2 —
ścieki miejskie
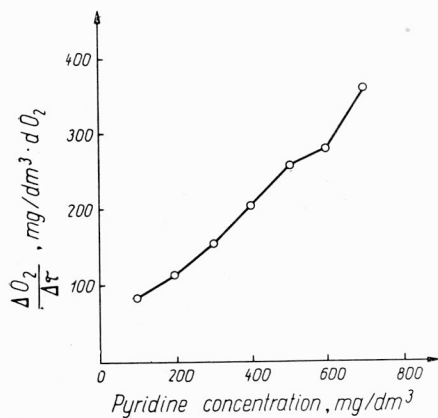

Fig. 11. Maximal oxygen consumption during
pyridine degradation vs. its initial concen-
tration in wastewater

Rys. 11. Maksymalna szybkość zużycia tlenu
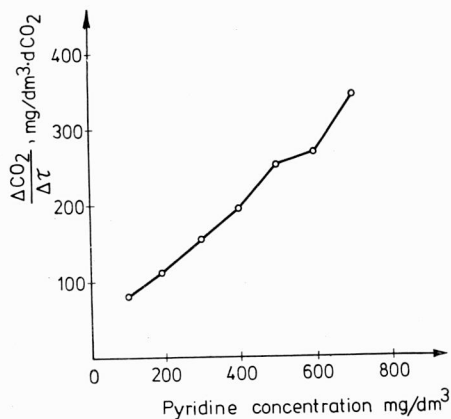w czasie rozkładu pirydyny w zależności od jej
dawki początkowej w ściekach

Fig. 12. Maximal production of carbon
dioxide during degradation of pyridine vs. its
initial concentration in wastewater

Rys. 12. Maksymalna szybkość wydzielania
dwutlenku węgla w czasie rozkładu pirydyny
w zależności od jej dawki początkowej
w ściekach

decrease from 0.125 to 0.067 d^{-1} due to the inhibitory effect of high concentrations of pyridine during the adaptation period of microorganisms to the degradation of the compound.

The initial concentration of pyridine in the raw wastewater, higher than 400 mg/dm^3 inhibits biodegradation of the wastewater organics, which is manifested in the first and second days of aeration by slow oxygen consumption (curves *1* and *2*, fig. 7) and of carbon dioxide production (fig. 8, curves *1*, *2*). From the shape of the curves *3* (figs 7 and 8) some increase both in the consumption of oxygen and production of CO_2 during third day of the aeration can be noticed, which would indicate the abated inhibitory effect of pyridine, the advanced bacterial adaptation to these concentrations of pyridine, and the raising intensity of the decomposition of the wastewater organics. Inhibitory effect of pyridine in wastewater is also illustrated by the diagrams of oxygen consumption (fig. 9) and carbon dioxide production (fig. 10) for the municipal wastewater without pyridine and with a dose of 700 mg/dm^3. In the first case both parameters have decreasing tendency in course of aeration, while in the second case the curve of oxygen consumption has a more complex shape: during first two days process rate decreases showing a considerable deviation from the rate of oxygen consumption, in municipal wastes — which is related to a toxic effect of pyridine, then — for the two next days — it increases. This is associated with the degradation of the wastewater organics which are more biodegradable than pyridine and which have not been biodegraded at the first stage. With the decreasing amounts of these compounds the rate of O_2 consumption decreases, and as soon as the bacteria are adapted to the degradation of pyridine (after 8 days) the parameter increases again.

Similar shape has the curve of carbon dioxide production for pyridine-containing wastewater (dose of 700 mg/dm^3, fig. 19, curve *1*). The dependence of maximal daily rates of oxygen consumption on the initial concentration of pyridine in the aerated wastewater is shown in fig. 11, while the respective relationships for CO_2 are shown in fig. 12.

The quantities of the oxygen consumption and carbon dioxide production are shown graphically in figs. 13 and 14. The inhibitory effect of high concentrations of pyridine on biochemical processes in the initial stage of organics mineralization as well as the pyridine decomposition itself is manifested in the quantities of oxygen consumed and carbon dioxide produced.

The quantities of consumed oxygen versus initial contents of pyridine and various times of wastewater aeration are shown in fig. 15. In the first day of aeration one observes a slight consumption of oxygen decreasing with the increasing doses of pyridine (curve *1*), and the raising quantities of O_2, proportional to the pyridine concentration in wastewater until its complete degradation (curve *2*). Since the oxidation processes in wastewater are continued, the curve *3* in fig. 15 illustrating the quantity of the oxygen consumed after 20 days of aeration is situated above the curve *2*. After the decay of pyridine the biodegradation process is continued, involving more resistant compounds, and autooxidation of cellular material (in endogenic respiration process) takes place. This is illustrated by the
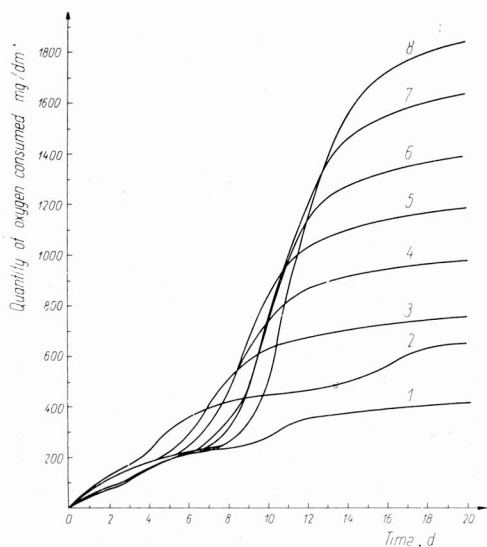
Fig. 13. Time-dependence of oxygen consumption
1 — municipal wastewater, wastewater with initial concentrations: *2* — 100 mg/dm³, *3* — 200 mg/dm³, *4* — 300 mg/dm³, *5* — 400 mg/dm³, *6* — 500 mg/dm³, *7* — 600 mg/dm³, *8* — 700 mg/dm³

Rys. 13. Zależność zużycia tlenu od czasu
1 — ścieki miejskie, *2* — ścieki o początkowej zawartości pirydyny: 100 mg/dm³, *3* — 200 mg/dm³, *4* — 300 mg/dm³, *5* — 400 mg/dm³, *6* — 500 mg/dm³, *7* — 600 mg/dm³, *8* — 700 mg/dm³
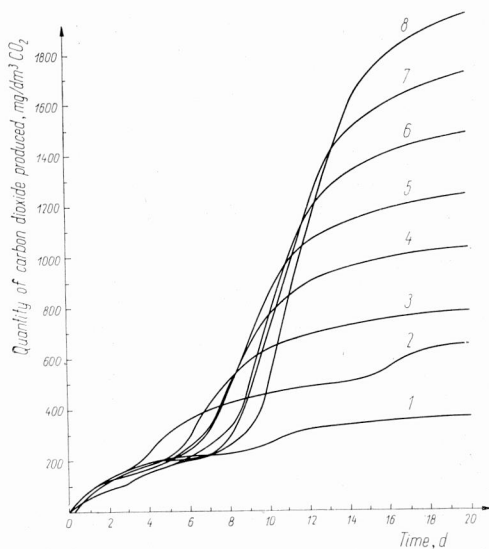
Fig. 14. Time-dependence of the produced carbon dioxide
1 — municipal wastewater, wastewater with initial concentration of pyridine: *2* — 100 mg/dm³, *3* — 200 mg/dm³, *4* — 300 mg/dm³, *5* — 400 mg/dm³, *6* — 500 mg/dm³, *7* — 600 mg/dm³, *8* — 700 mg/dm³

Rys. 14. Zależność ilości wydzielonego dwutlenku węgla od czasu
1 — ścieki miejskie, *2* — ścieki o początkowej zawartości pirydyny 100 mg/dm³, *3* — 200 mg/dm³, *4* — 300 mg/dm³, *5* — 400 mg/dm³, *6* — 500 mg/dm³, *7* — 600 mg/dm³, *8* — 700 mg/dm³

graph presented in fig. 16 which shows that after a complete degradation of pyridine oxygen consumption and carbon dioxide production still occur (fig. 17).

Biodegradation of pyridine is also followed by the increase in the concentration of ammonium nitrogen (fig. 18). In the municipal wastewater without pyridine and in those containing 100 mg/dm³ of C_5H_5N the concentration of ammonium decreases in course of aeration. This is due to nitrification which in municipal wastewater starts after 6 days of aeration (fig. 19), and in the wastewater with 100 mg/dm³ of pyridine, after 12 days (fig. 20). Nitrification of ammonium is also manifested in the inflection points of the curves *1* and *2* as well as in the quantities of the oxygen consumed (fig. 13) and carbon dioxide produced (fig. 14, curves *1* and *2*). Since in municipal wastewater with pyridine, nitrification process occurs solely in the sample containing as low as 100 mg/dm³ of pyridine, the shape of curves of oxygen consumption and curves for carbon dioxide production (curve *2*) differs significantly from the higher pyridine doses, shown in figs. 13 and 14 for they have two inflection points. The first is the consequence of pyridine biodegradation, while the second is related to the nitrification of ammonium. If the increase in oxygen consumption
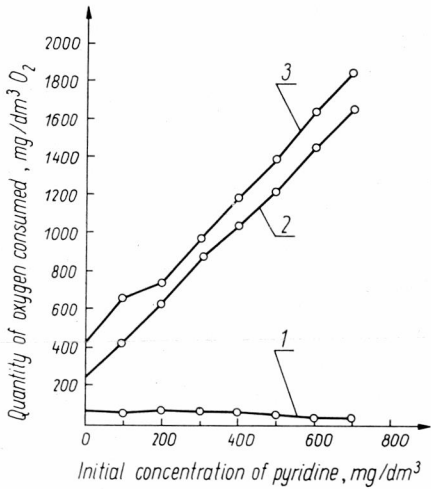
Fig. 15. Oxygen consumption vs. initial concentrations of pyridine in wastewater
1 — after first day, *2* — up to pyridine decay, *3* — after 20 days of aeration

Rys. 15. Zależność ilości zużytego tlenu od początkowych stężeń pirydyny w ściekach
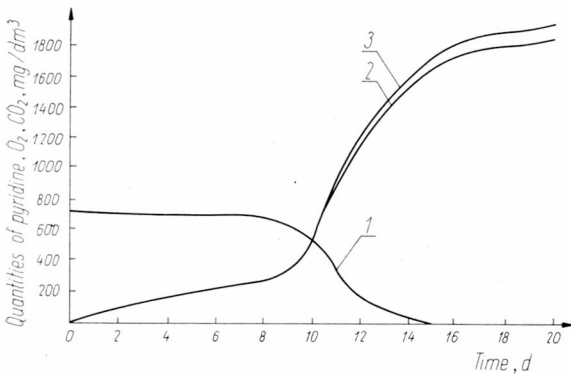*1* — po pierwszej dobie, *2* — do chwili zaniku pirydyny, *3* — po 20 dobach napowietrzania

Fig. 16. Concentrations of pyridine, amounts of oxygen consumed and carbon dioxide produced vs. aeration time of wastewater with 700 mg/dm³ of pyridine
1 — concentration of pyridine, *2* — amounts of oxygen consumed, *3* — amounts of carbon dioxide produced

Rys. 16. Zawartość pirydyny, ilość zużytego tlenu i wydzielonego dwutlenku węgla od czasu napowietrzania ścieków zawierających 700 mg/dm³ pirydyny
1 — zawartość pirydyny, *2* — ilość zużytego tlenu, *3* — ilości wydzielonego dwutlenku węgla
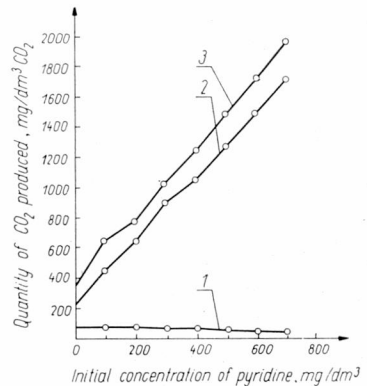

Fig. 17. Amounts of carbon dioxide produced vs. initial concentrations of pyridine in wastewater
1 — after first day, *2* — up to the decay of pyridine, *3* — after 20 days of aeration

Rys. 17. Ilości wydzielonego dwutlenku węgla w zależności od początkowych stężeń pirydyny w ściekach
1 — po pierwszej dobie, *2* — do chwili zaniku pirydyny, *3* — po 20 dobach napowietrzania ścieków

due to nitrification process is obvious, then the intensified production of carbon dioxide during ammonium nitrification is due to formation of nitrous acid which releases the equivalent quantity of CO_2 from the salts of carbonic acid, according to the reaction

$$HNO_2 + HCO_3^- = NO_2^- + H_2O + CO_2.$$
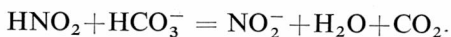
Since the nitrification process takes place after biodegradation of pyridine then the quantities of oxygen consumed and carbon dioxide produced in municipal wastewater without pyridine and in those with 100 mg/dm³ of pyridine are different (curve 3, figs. 13 and 15).
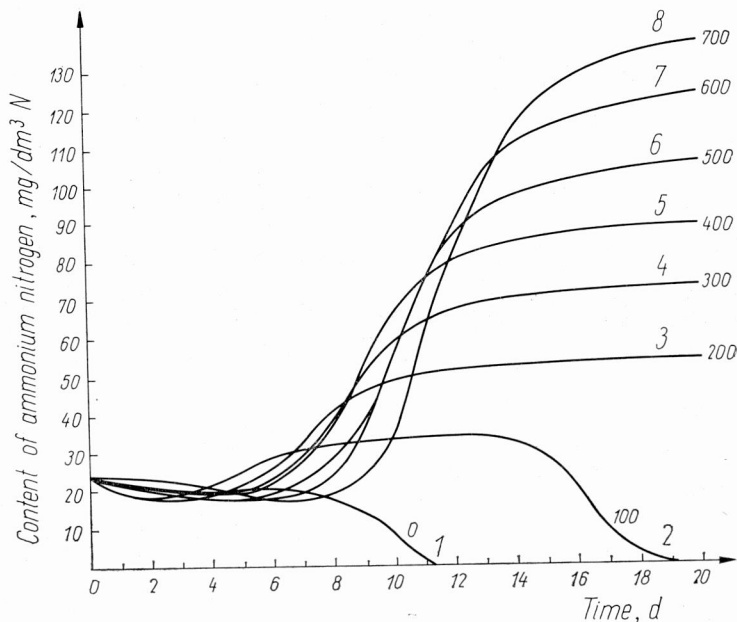

Fig. 18. Concentration of ammonium nitrogen vs. aeration time

1 — for municipal wastewater, for wastewater with initial concentrations of pyridine: 2 — 100 mg/dm³, 3 — 200 mg/dm³, 4 — 300 mg/dm³, 5 — 400 mg/dm³, 6 — 500 mg/dm³, 7 — 600 mg/dm³, 8 — 700 mg/dm³

Rys. 18. Zależność zawartości azotu amonowego od czasu napowietrzania

1 — dla ścieków miejskich, 2 — dla ścieków o początkowej zawartości pirydyny: 100 mg/dm³, 3 — 200 mg/dm³, 4 — 300 mg/dm³, 5 — 400 mg/dm³, 6 — 500 mg/dm³, 7 — 600 mg/dm³, 8 — 700 mg/dm³
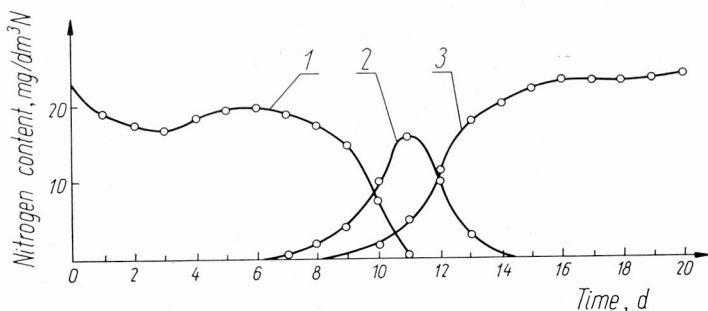

Fig. 19. Concentrations of nitrogen compounds in municipal wastewater vs. aeration time

1 — ammonium nitrogen, 2 — nitrite nitrogen, 3 — nitrate nitrogen

Rys. 19. Zależność zawartości związków azotowych w ściekach miejskich od czasu napowietrzania

1 — azot amonowy, 2 — azot azotynowy, 3 — azot azotanowy

During nitrification an increase in permanganate consumption can be seen for the municipal wastewater without and with addition of 100 mg/dm³ of pyridine, fig. 21. This is also manifested in the ammonium content in the wastewaters after 20 days of aeration (fig. 22, curve *3*). Curve *3* in fig. 22 presents the quantity of ammonium nitrogen in wastewater after 20 days of aeration versus the initial content of pyridine. Curve *1* presents the same
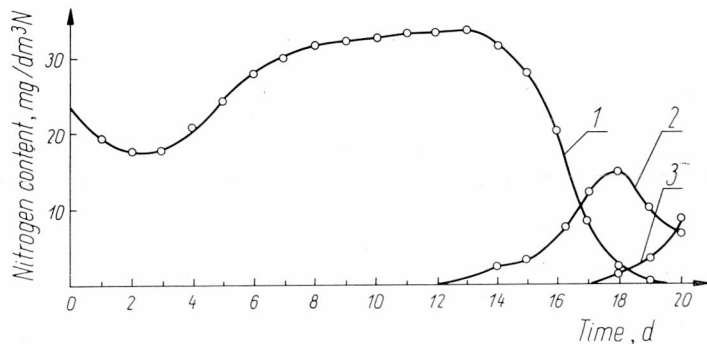
Fig. 20. Concentrations of nitrogen compounds in municipal wastewater with initial concentration of pyridine 700 mg/dm³ vs. aeration time

1 — ammonium nitrogen, *2* — nitrite nitrogen, *3* — nitrate nitrogen

Rys. 20. Zależność zawartości związków azotowych w ściekach miejskich o początkowej zawartości pirydyny 700 mg/dm³ od czasu napowietrzania

1 — azot amonowy, *2* — azot azotynowy, *3* — azot azotanowy
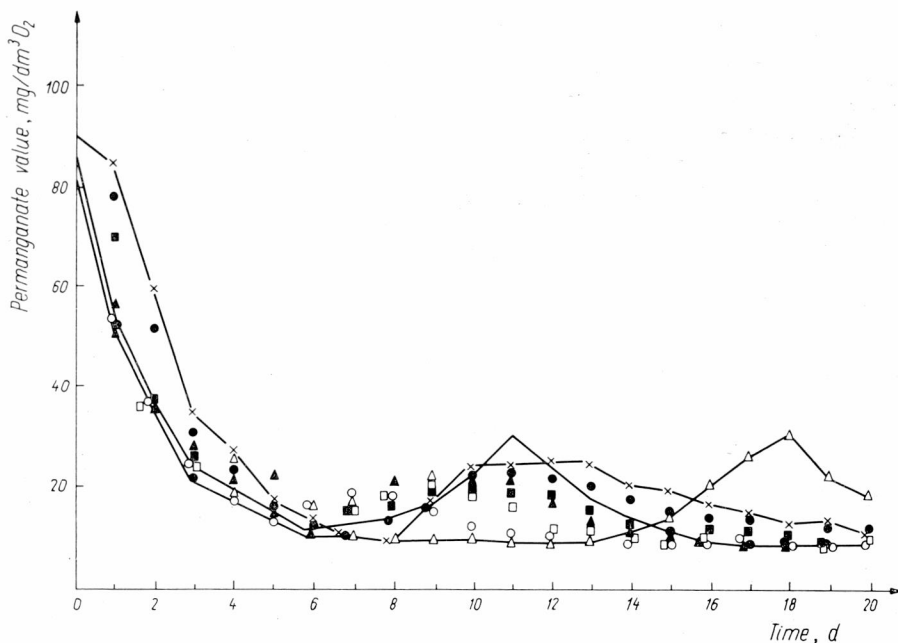
Fig. 21. Chemical oxygen demand of wastewater during aeration

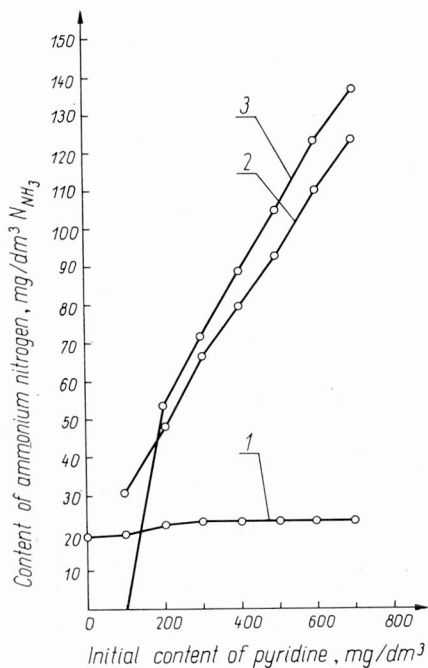Rys. 21. Przebieg utlenialności ścieków podczas ich napowietrzania

Fig. 22. Concentrations of ammonium nitrogen vs. initial concentration of pyridine in wastewater

1 — before aeration, *2* — at the moment of pyridine decay, *3* — after 20 days of aeration

Rys. 22. Przebieg zawartości azotu amonowego w zależności od dawki początkowej pirydyny w ściekach

1 — przed napowietrzeniem, *2* — z chwilą usunięcia pirydyny, *3* — po 20 dobach napowietrzania

dependency but after the first day of aeration, and curve *2* at the moment of pyridine decay. In the latter case this dependence is linear. On the basis of the measurements of oxygen consumption and carbon dioxide production rates the respiratory index can be calculated as the numerical ratio of the produced moles of carbon dioxide produced to the moles of oxygen absorbed. This ratio called also a respiratory quotient is characteristic for the type of the organic substrate biodegraded by microorganisms. From theoretical calculations is follows that at the oxidation of hydrocarbons respiratory index is equal to unity, since from n moles of oxygen consumed n moles of carbon dioxide are formed:

$$(CH_2O)n+nCO_2 = nCO_2+nH_2O$$
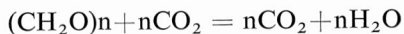
while in the case of pyridine theoretical value of respiratory index calculated from the equation

$$C_5H_5N+5\tfrac{1}{2}O_2 = 5CO_2+H_2O+NH_3$$

amounts to: $5.5 = 0.91$.

The values of the indices for wastewater of different pyridine concentrations amount to 75–96 % of the theoretical values calculated above. This should indicate that the quantity of CO_2 produced in wastewater is lower than this resulting from the pyridine oxidation. This difference is partially due to biosynthesis of cellular material (which is not entirely oxidized), and to the secondary process in which CO_2 is combined with ammonium produced as a result of pyridine degradation. Carbon dioxide in presence of ammonium can

be bounded in form of bicarbonate, and at higher pH in form of ammonium carbonate, according to reactions:

$$NH_3 + H_2O = NH_4OH,$$

$$NH_4OH + CO_2 = NH_4HCO_3,$$

$$2NH_4OH + CO_2 = (NH_4)_2CO_3 + H_2O.$$
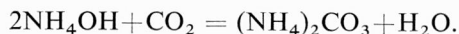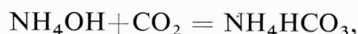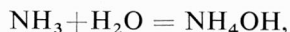
Formation of ammonium salts of carbonic acid is justified by the increasing basicity in wastewaters after 20 days of aeration, being the greater the higher was pyridine dose, as well as by slightly basic pH of this wastewater (table 1). Formation of bicarbonates and ammonium carbonates in basic medium is also followed by other chemical reactions, resulting in the precipitation of calciu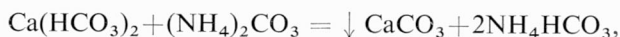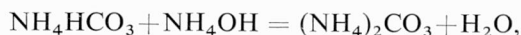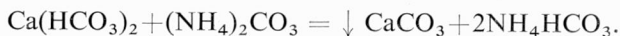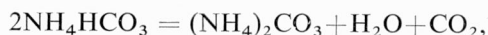m carbonate. Production of CO_2 in wastewater in which pyridine is biodegraded can occur, according to different reactions; via hydroxide, carbonates or bicarbonates. Bicarbonates present in wastewater and responsible for its temporary hardness can react according to the following pathways:

$$NH_3 + H_2O = NH_4OH,$$

$$Ca(HCO_3)_2 + NH_4OH = \downarrow CaCO_3 + NH_4HCO_3 + H_2O,$$

or

$$NH_4HCO_3 + NH_4OH = (NH_4)_2CO_3 + H_2O,$$

$$Ca(HCO_3)_2 + (NH_4)_2CO_3 = \downarrow CaCO_3 + 2NH_4HCO_3,$$

or else

$$NH_3 + H_2O + CO_2 = NH_4HCO_3,$$

$$2NH_4HCO_3 = (NH_4)_2CO_3 + H_2O + CO_2,$$

$$Ca(HCO_3)_2 + (NH_4)_2CO_3 = \downarrow CaCO_3 + 2NH_4HCO_3.$$
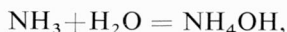
The precipitation of calcium carbonate from wastewater is intensive during the degradation of organic substances being at colloidal state, i.e. during the flocculation and bio-coagulation of activated sludge. The disappearance of the colloidal substances promotes the precipitation of low solubility calcium carbonate. In the case of wastewater investigated precipitation of the carbonates occurs when pyridine disappears in wastewater, i.e. after its degradation. It is confirmed also by the decrease in the total wastewater hardness in presence of pyridine, after 20 days of aeration. In the wastewater with initial concentration of pyridine exceeding 500 mg/dm^3 total hardness decreased from 5.29 meq/dm^3 to 2.8 meq/dm^3. Precipitation of calcium carbonate results in high content of mineral solids in the biomass. Fig. 23 represents SVI (sludge volume index) and mineral solids content in the biomass after 20 days of the wastewater aeration with different initial pyridine concentrations. The content of mineral solids in the biomass from wastewater with pyridine is much higher than in sludge from municipal wastewater, but it decreases at the highest pyridine doses. This may be explained by the fact that on one hand, the quantity of preci-
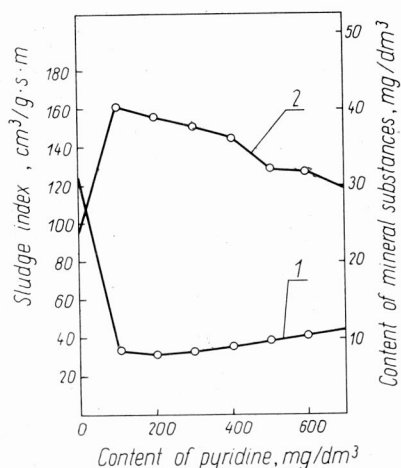
Fig. 23. Activated sludge volume index and concentrations of mineral compounds vs. initial concentration of pyridine in wastewater
1 — SVI, 2 — percentage of the mineral solids
Rys. 23. Zależność indeksu osadowego oraz zawartości ciał mineralnych od dawki początkowej pirydyny w ściekach
1 — indeks osadowy, 2 — procent substancji mineralnej

pitated calcium carbonate for the pyridine-containing wastewater in concentrations higher than 400 mg/dm³ is constant, as the remaining hardness of these wastewaters is the same (table 1), and on the other hand, the amount of synthetized biomass increases with the increasing dose of pyridine degraded. The adaptation period is also a factor being longer for higher concentrations of pyridine. As a result the process of pyridine degradation is shifted, and consequently, for higher concentrations of pyridine the mineralization degree of synthetized cellular substance (biomass) till the 20th day of aeration was lower, compared with wastewater with smaller content of pyridine. Considering settling properties of the biomass degradation of large doses of pyridine promotes the decrease in SVI due to precipitation of calcium carbonate, i.e. due to the decarbonization of wastewater.

The changes in the composition of wastewater after biochemical degradation of different concentrations of pyridine are given in table 1. The wastewater treated is characterized by weak colour, high basicity (whose increase depends on pyridine degradation), high concentrations of ammonium compounds, and dry residue lower than in crude wastewater, due to decarbonization (precipitation of calcium carbonate) as well as to accumulation of ammonium salts, unstable at the temperature at which volatile solids are determined, since they are decomposed according to the reactions:

$$NH_4HCO_3 = \uparrow NH_3 + \uparrow H_2O + \uparrow CO_2,$$
$$(NH_4)_2CO_3 = \uparrow 2NH_3 + \uparrow H_2O + \uparrow CO_2.$$
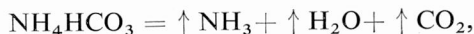
4. CONCLUSIONS

1. Under conditions in which permanganate consumption, COD and degradable organics are determined pyridine is relatively resistant both to chemical oxidation and to biodegradation under condition of BOD test by dilution method. Hence, these indices cannot be used as the measures of the pyridine concentrations in wastewater.

2. From the quantities of oxygen consumed and carbon dioxide produced at the first day of wastewater aeration (figs 7 and 8) it should be stated that initial contents of pyridine in municipal wastewater below 400 mg/dm³ do not inhibit the biodegradation rate of the easily biodegraded wastewater organics, whereas its higher initial concentrations hinder this process.

3. The adaptation period of the bacteria present in raw municipal wastewater to pyridine biodegradation is the longer the higher is initial content of pyridine.

4. Adaptation period is followed by pyridine biodegradation, its rate is time and initial dose dependent, whereas the biodegradation time is not a function of the pyridine concentration.

5. The constant rate of pyridine degradation within the examined range of concentrations varies from 0.07 to 0.08 mg/dm³·d·mg.

6. Pyridine concentrations in wastewater up to 100 mg/dm³ C_5H_5N does not affect the nitrification of ammonium to nitrites but it is shifted in time (fig. 18), hence this process starts after the degradation of pyridine. The pyridine concentrations higher than 200 mg/dm³ eliminate totally the nitrification process.

7. Biodegradation of pyridine is accompanied by the formation of ammonium salts (bicarbonates and carbonates) which increase the pH value (basicity) and cause precipitation of calcium carbonate.

8. Formation of calcium carbonate improves the settling properties of the biomass, by decreasing the value of SVI.

REFERENCES

[1] BERNACKI K., *Phenol wastewater* (in Polish), Arkady, Warszawa 1975.

[2] CEBULA J., KEMPA E., *Analysis of solid wastes and compost.*, (in Polish) edited by Wrocław Technical University, Wrocław 1971.

[3] DIALTOVSKAYA P., *Methods of piridine homologues determination in industrial wastes* (in Polish), Higiena i Sanitaria 6/60, Gaz, Woda i Technika Sanitarna Vol. 7, p. 270, 1961.

[4] DUTKIEWICZ T., *Toxicological chemistry* (in Polish), PZWZ, Warszawa 1974, p. 199.

[5] GOMÓŁKA B., KEMPA E., *RSO − a rapid method for pollutant determination in wastes* (in Polish), Materiały na XVIII Konferencję Naukowo-Techniczną „Postęp techniczny w dziedzinie oczyszczania ścieków", Katowice 1975.

[6] GOMÓŁKA E., SZYPOWSKI W. et al., *Respirometers for studying detergents biodegradation* (in Polish), Scientific Papers of the Institute of Environment Protection Engineering of Wrocław Technical University No. 11, Studies and Research No. 10, p. 135, 1971.

[7] HERMANOWICZ W., DOŻAŃSKA W. et al., *Physico-chemical analyses of municipal sewage and sludge* (in Polish), Arkady, Warszawa 1967.

[8] HERMANOWICZ W. et al., *Physico-chemical analyses of water and wastes* (in Polish), Arkady, Warszawa 1976.

[9] JUST J., HERMANOWICZ W., *Physico-chemical analyses of water* (in Polish), PZWL, Warszawa 1971.

[10] KALABINA M. M., *Industrial waste treatment in Soviet* Union, Trudy instituta WODGEO, 20 th editon, Moscow 1968, p. 7.

[11] LUDZAK F., ETTINGER M., *Chemical structures resistant to aerobic biochemical stabilization*, Jour. Water Pollution Control Federation **32**, 11, 1173, 1960.

[12] ŁAZANIEV N. V., *Toxic industrial substances* (in Polish), PWN, Warszawa 1954.

[13] MALANEY G. W., Jour. Water Pollution Control Federation **32**, 12, p. 1300, 1960.
[14] MEINCK F., STOFF H., et al., *Industrial wastes* (in Polish), Arkady, Warszawa 1975.
[15] Polski Komitet Normalizacyjny: BN/6215-14 BOD determination by dilution. Polish Standards.
[16] Polski Komitet Normalizacyjny BN/6215-28 COD determination in wastewater. Polish Standards.
[17] SHIRLEY D. A., *Organic chemistry* (in Polish), WNT, Warszawa 1964.
[18] STASIAK M., *Harmful effect of toxic organics on biotreatment of wastes* (in Polish), Biuletyn Informacji Technicznej „Biprowod" No. 12, p. 29, 1968.
[19] ZDYBIEWSKA M., KWIATKOWSKA K., *Effect of benzene and pirydine on biotreatment of coke wastes on trickling filters* (in Polish), Scientific Papers of Silesian Politechnic No. 8, 1965.

WPŁYW KOŃCOWYCH PRODUKTÓW BIODEGRADACJI PIRYDYNY NA ZMIANĘ CHEMICZNEGO SKŁADU NAPOWIETRZANYCH ŚCIEKÓW MIEJSKICH

Pirydyna znajduje szerokie zastosowanie jako surowiec w przemyśle chemicznym do syntezy wielu związków organicznych i barwników, w przemyśle farmaceutycznym do produkcji leków, i w przemyśle skórzanym, gumowym i drukarstwie tkanin jako rozpuszczalnik. Jest ona związkiem toksycznym i jej obecność w ściekach wywiera szkodliwy wpływ na odbiornik, powoduje zatruwanie ryb, mikroorganizmów osadu czynnego i błony biologicznej na oczyszczalniach, oraz pogarsza własności organoleptyczne wody przez swój specyficzny, odrażający zapach wyczuwalny już przy stężeniach 0,0004 mg/dm^3.

Dane literaturowe krajowe i zagraniczne podają optymalne stężenie pirydyny w ściekach miejskich oczyszczanych biologicznie — 200–400 mg/dm^3. W naszych badaniach rozszerzyliśmy zakres stężenia od 100 do 700 mg/dm^3.

Badania prowadzono w respirometrach o dużych pojemnościach kolb (ponad 2 dm^3), co pozwalało na pobór prób do kontroli składu fizyczno-chemicznego i bakteriologicznego napowietrzanych ścieków. Aparatura umożliwiała ponadto równoczesny pomiar ilości zużytego tlenu na manometrach i wydzielanego dwutlenku węgla, który oznaczano miareczkując nadmiar nie przereagowanego KOH pochłaniającego w zamkniętej kolbie wydzielany dwutlenek węgla.

Biochemiczny rozkład pirydyny prowadzono w zestawie respirometrów składającym się z 8 kolb, co pozwoliło na równoczesne przebadanie różnych stężeń. Doświadczenia trwały 20 dni, środowiskiem reakcji były ścieki miejskie, jako naturalne źródło mikroorganizmów adaptujących się do rozkładu pirydyny.

Na podstawie badań stwierdzono, że zawartości początkowe pirydyny w ściekach miejskich poniżej 400 mg/dm^3 nie wpływają hamująco na szybkość biochemicznego rozkładu związków organicznych zawartych w ściekach, natomiast większe dawki pirydyny hamują ten proces. Świadczą o tym ilości zużytego tlenu i wydzielonego dwutlenku węgla z procesów biochemicznych.

Rozkład pirydyny w ściekach następuje dopiero po pewnym zastoju i adaptacji bakterii do rozkładu tego związku. Czas adaptacji jest tym dłuższy im wyższa jest zawartość początkowa pirydyny w ściekach i dla przebadanych stężeń wynosił od 4 do 8 dni. Po tym okresie zawartość pirydyny w ściekach szybko malała aż do całkowitego jej zaniku (5–7 dni), a czas rozkładu praktycznie nie zależał od dawki początkowej.

Biochemiczny rozkład pirydyn powoduje rozerwanie pierścienia pirydynowego i uwolnienie atomu azotu, a zatem w miarę postępującego procesu zawartość azotu amonowego w ściekach wzrasta. Wydzielający się amoniak wchodzi w reakcję z dwutlenkiem węgla w środowisku wodnym, skutkiem czego powstają jego sole: wodorowęglany i węglany. Następuje zatem wzrost zasadowości i odczynu ścieków, oraz obniżenie twardości ogólnej na skutek wytrącania się węglanu wapniowego. To ostatnie zjawisko wpływa korzystnie na zdolność sedymentacyjną osadu czynnego, gdyż obniża wartość indeksu osadowego.

Zawartość pirydyny w ściekach do 100 mg/dm^3 nie hamuje procesu nitryfikacji amoniaku do azotynów, natomiast przesuwa go w czasie z 6. dnia w ściekach miejskich bez pirydyny do 12. dnia dla ścieków z 100 mg/dm^3 tego związku. Oznacza to, że nitryfikacja następuje dopiero po rozłożeniu całej dawki pirydyny. Stężenia pirydyny powyżej 200 mg/dm^3 całkowicie eliminują proces nitryfikacji.

EINFLUSS DER ABBAUPRODUKTE DES PYRIDINS AUF DIE CHEMISCHE ZUSAMMENSETZUNG DER BELÜFTETEN ABWÄSSER

Im Beitrag wird der Einfluß des Pyridins auf den Abbauverlauf der im Abwasser anwesenden organischen Inhaltsstoffe erörtert. Die Versuche wurden in statischer Weise in entsprechenden Großvolumen--Respirometern durchgeführt. Die Konzentration des Pyridins wurde im städtischen Abwasser bis zu 700 mg/dm^3 stufenweise künstlich angereichert.

Die Versuche ergaben, daß eine Konzentration des Pyridins von mehr als 100 mg/dm^3 die Nitrifikation praktisch eliminierte, eine Konzentration von mehr als 400 mg/dm^3 hemmte stark den biochemischen Abbau der organischen Abwasserinhaltsstoffe in der Anfangsphase. Nachdem sich die Mikroorganismen an Pyridin gewöhnt haben (Adaptationsperiode), wurde diese auch abgebaut wobei u.a. Ammoniumsalze der Kohlensäure entstehen. Diese bewirken einen Ausfall des Calziumkarbonats und dies zieht eine bessere Sedimentation des Belebtschlammes nach sich.

Zur Ermittlung der Abbaubarkeit des Pyridins, wurden sowohl chemische (COD, KMnO$_4$-Verbrauch, AOS) wie biochemische Kriterien (BSB$_5$) angewandt.

ВЛИЯНИЕ КОНЕЧНЫХ ПРОДУКТОВ БИОРАСПАДА ПИРИДИНА НА ИЗМЕНЕНИЕ ХИМИЧЕСКОГО СОСТАВА ОТКРЫТЫХ ГОРОДСКИХ СТОКОВ

В работе исследовано влияние пиридина на процесс минерализации органических веществ, содержащихся в городских стоках. Эксперимент выполнен в статических условиях с использованием респирометра для городских стоков с большим содержанием пиридина (до 700 мг/дм^3). Установлено, что содержание пиридина выше 100 мг/дм^3 тормозит процесс биохимического распада органических соединений на начальной стадии. После адаптации бактерий пиридин поддается биохимическому распаду. При этом образуются амонийные соли углекислоты, которые вызывают осаждение карбонатного углерода.

Исследована восприимчивость пиридина к химическому окислению в условиях, обозначенных ChZT и RSO, а также к биохимическому распаду в условиях, определенных методом разбавления BZT$_5$.