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DEGRADABILITY OF SIMAZINE IN AEROBIC TREATMENT OF MUNICIPAL SEWAGE

Under standard conditions of permanganate COD determination the oxidation of simazine has not been stated, while according to dichromate COD method the oxidation took place approaching 73% of TOD. Simazine occurring in municipal sewage is resistant to biodegradation even when the intensive aeration is prolonged. Because of its low water-solubility simazine does not affect the rate of biodegradation of organic compounds contained in municipal sewage. Only nitrifying bacteria are sensitive to the toxic action of simazine.

1. INTRODUCTION

The use of chemicals to control pests has been practised in Poland. A number of synthetic organic compounds (insecticides) produced at the past decade killed effectively many insect pests. Other chemicals, produced and marketed in thousands formulations: the herbicides, fungicides and rodenticides, were widely used to control the growth of plants, fungi and small mammals, respectively. Not only arable lands, but also homes and gardens were covered abundantly with all these liquids, powders and granules. Consequently, the pollution level in natural waters has increased rapidly. Pesticides enter the waterways from a variety of sources which can be divided into three general classes: agricultural, industrial and domestic ones.

Concentrated pesticide residues being mostly highly toxic have harmful effects on the aquatic habitat. The selective action of these substances is not sufficiently well known. Apart from some benefits, such as increased food production due to the application of such chemicals, there are some possible side-effects as these substances are capable of disturbing the biological balance when entering the watercourse.

Needless to say that the production of any insecticide, herbicide, fungicide or other pesticide should be preceded by investigations proving the effectiveness of the product

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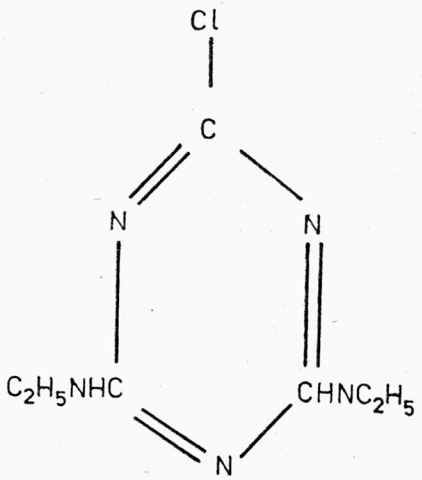
for the purpose intended and its harmlessness for any lifeforms, all safety precautions shown on the label are observed.

The purpose of the study presented here was to determine the influence of simazine on the efficiency of aerobic treatment methods.

2. CHARACTERISTICS OF SIMAZINE ($C_7H_{12}ClN_5$)

Simazine (2-chloro-4,6-diethylamine-1,3,5-triasine) of the following structural formula



is a weakly water-soluble (0.0005% at 295 K) herbicide of triasine type [6, 7] which was first synthesized in 1885 by HOFFMANN [7] and has been used in agriculture since 1955 [7]. Simazine is particularly useful when applied to maize cultures prior to seed germination [2]. Weeds are killed with no adverse effects on the crops. The chemical in question may also be safely used for orchard protection (especially apple and pear trees), for the protection of viticulture, sugar cane, asparagus shoots and pineapple crops, as well as for supporting shrubbery and tree growth. Large simazine doses are successfully applied in the soil disinfection [7]. Simazine itself acts as a photosynthesis inhibitor, in leguminous plants for instance photosynthesis is blocked at the concentration of 1.0 mg of simazine/kg.

Simazine being a strong herbicide is little toxic for rodents. DL_{50} doses administered orally to rats may be as high as 5000 mg/kg and higher, and repeated 100 mg/kg doses administered to the same rats during a two-year period were without any toxic effect [1].

LUDEMANN and KAYSER investigated the toxic influence of simazine on plankton (daphnia, *Corinogammarus*, *Asellus*, *Tubifex*, red larvas of *Chironomidae* and *Aedes* larvas) and stated its toxicity at concentrations as low as 20 to 50 g/m^3 [5].

3. EXPERIMENTAL

3.1. OXIDABILITY DETERMINATION

The determination of whether or not a given organic waste constituent is resistant to chemical oxidation (usually expressed in terms of permanganate and dichromate COD) is a problem of prime importance when estimating the pollution level in natural waters. Unfortunately, under conditions of permanganate and dichromate COD determinations not entire organic matter present in the wastewater undergoes a complete oxidation; some of those compounds are oxidized only partly, and some of them are not oxidized at all. The result is that the latter become underterminable under conventional conditions, since they do not influence either of the two COD values.

The oxidability of simazine was measured in terms of dichromate and permanganate COD. The experiments were run in distilled water treated with various doses of simazine by the method reported in [4]. The results are given in tabs. 1 and 2. The theoretical oxy-

Table 1

Degradation of simazine under conditions of permanganate COD determination

Rozkład symazyny w warunkach oznaczenia utlenialności nadmanganianowej

Simazine concentration g/m³	Permanganate COD g O_2/m³	TOD g O_2	TOD %
5	0.70	12.71	5.51
10	1.40	25.41	5.51
15	2.25	38.12	5.90
20	2.80	50.82	5.51
30	4.30	76.23	5.64
40	5.60	101.64	5.51
60	7.40	152.46	4.85
		average	5.49

Table 2

Degradation of simazine under conditions of dichromate COD determination

Rozkład symazyny w warunkach oznaczania utlenialności dwuchromianowej

Simazine concentration g/m³	Dichromate COD g O_2/m³	TOD g O_2	TOD %
10	23.2	25.40	90.94
20	38.5	50.82	75.76
30	56.8	76.23	74.51
40	77.5	101.64	76.25
60	100.0	152.46	65.59
80	132.1	203.28	64.98
200	318.8	508.20	62.73
		average	72. 97

gen demand (TOD) for oxidation of 1 g of simazine was calculated in terms of the stoichiometric equation:

$$C_7H_{12}N_5Cl + 16O_2 = 7CO_2 + 5HNO_3 + HCl + 3H_2O.$$

Under conditions of permanganate COD determination, the degree of simazine oxidation is insignificant (tab. 1), and the quantity of oxygen taken up from $KMnO_4$ is on the average 5.5% of TOD. Oxygen uptake from $K_2Cr_2O_7$ (when simazine is being oxidized under conditions of dichromate COD determination) usually approaches 73% (tab. 2). It follows that dichromate COD alone can be considered as an adequate indicator of water pollution from simazine.

3.2. BIOCHEMICAL DEGRADABILITY

BOD is an indirect indicator of biodegradable substances present in the water to be treated. Experiments show that if BOD_5 determination is carried out under standard conditions, simazine is not subject to biodegradation. Hence, BOD_5 cannot be considered either as an adequate indicator of water pollution with simazine. Laboratory investigations involving respirometers have additionally shown that simazine contained in municipal sewage is also resistant to biodegradation.

3.3. INFLUENCE OF SIMAZINE ON THE COURSE AND EFFICIENCY OF AEROBIC TREATMENT

The experiments were run for various concentrations of simazine. The experimental system consisted of respirometers with 2.4 dm^3 flasks (fig. 1). Samples were collected throughout the experiments. Analytical control included measurements of O_2 uptake and CO_2 production along with the determination of chemical composition during aeration. The design and operation of the respirometers as well as the calculation methods employed in the experiments are described in [3].

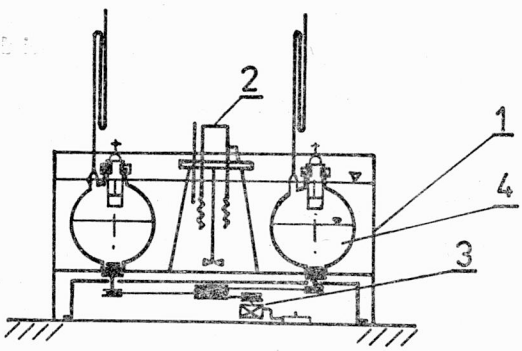


Fig. 1. Respirometer

1 — thermostatic tank, *2* — thermostat, *3* — magnetic stirrer, *4* — flask

Rys. 1. Respirometr

1 — zbiornik termostatyczny, *2* — termostat, *3* — mieszadło magnetyczne, *4* — kolba

The experiments reported here were conducted for raw municipal sewage of a composition given in tab. 3. The wastewaters to be tested were collected at an intermediate pumping station in a period of intensive rainfall. That is why their physicochemical and chemical characteristics differed from the composition of a typical municipal wastewater produced in the city of Wrocław (dichromate and permanganate COD, BOD_5 and organic nitrogen levels were very low; tab. 3). The wastewater under test was aerated simultaneously in 17 respirometers. Two of them contained municipal sewage alone (with

Table 3

Characteristics of experimental wastewater

Charakterystyka doświadczalnych ścieków

Parameter	Unit	Concentration
Turbidity	g SiO_2/m^3	110
Colour	g Pt/m^3	40
pH	pH	7.1
Total alkalinity	g $CaCO_3/m^3$	285
Total acidity	g $CaCO_3/m^3$	45
Permanganate COD	g O_2/m^3	31
Dichromate COD	g O_2/m^3	96.2
BOD_5 (dilution method 1:50)	g O_2/m^3	120
Ammonia nitrogen	g N/m^3	10.0
Nitrite nitrogen	g N/m^3	0.01
Nitrate nitrogen	g N/m^3	0
Organic nitrogen	g N/m^3	7.5
Phosphates	g PO_4^{-3}/m^3	15.0
Chlorides	g Cl^-/m^3	97.0
Sulphates	g SO_4^{-2}/m^3	81.0
Dry matter	g/m³	714
Mineral matter	g/m³	583
Total dissolved solids	g/m³	645
Mineral dissolved solids	g/m³	555
Total suspended solids	g/m³	69
Mineral suspended solids	g/m³	28

no simazine addition). In this report they will be treated as a control system. The remaining 15 were additionally treated with the following simazine doses: 0.5 (in two samples), 1.25, 2.5, 5, 12.5, 25, 37.5, 50, 75, 150, 250, 500, 750, and 1500 g/m³. At the beginning of each experimental run the volume of the wastewater to be aerated was 1000 cm³ in each of the respirometers. The experimental temperature as well as the number of revolutions of the magnetic stirrer were kept constant throughout the process (i.e. for 252.5 h).

Samples were taken from the respirometer bulbs to determine composition changes which occur in the course of the experiments. O_2 uptaken and CO_2 produced were also measured.

Simazine concentrations were measured by thin-layer chromatography [8]. The concentrations of other waste constituents were determined by Polish standard methods [4].

4. DISCUSSION OF RESULTS

The aeration of simazine-containing municipal sewage shows that the herbicide in question, even at relatively high concentrations (up to 500 g/m³), does not inhibit the rate of biochemical degradation. This fact is indicated by the quantities of O_2 consum-

Table 4

Oxygen uptake for degradation of symazine-containing municipal sewage
Pobranie tlenu do rozkładu ścieków miejskich zawierających symazynę

Initial concentration of simazine g/m³	Aeration time, h							
	17.5	43.0	63.5	86.5	157.5	180.5	204.5	252.5
0	46.9	97.1	106.3	116.1	161.3	212.1	224.3	234.5
0	47.2	97.6	106.4	117.3	162.2	214.0	226.5	235.9
0.5	46.5	99.1	108.6	118.4	163.2	216.2	228.5	238.0
0.5	46.4	99.8	108.4	116.5	161.7	214.5	—	—
1.25	46.4	100.7	109.1	118.6	161.8	214.0	227.4	235.4
2.5	44.8	98.7	109.1	118.3	167.9	219.2	232.1	243.8
5	45.8	94.8	106.6	116.4	168.8	218.2	231.7	241.2
12.5	47.3	98.3	108.5	119.1	169.4	222.2	235.2	244.2
25	47.4	97.6	108.3	118.0	170.2	224.3	237.0	247.1
37.5	48.2	101.7	113.1	124.3	175.1	231.3	242.9	251.4
50	49.5	98.9	109.9	120.0	175.8	231.5	246.0	257.2
75	47.4	100.3	109.3	119.7	166.2	216.5	230.3	239.5
150	47.2	101.0	111.8	122.7	155.0	208.4	220.7	235.3
250	46.9	99.3	111.3	116.5	149.5	156.5	206.3	239.6
500	47.4	95.6	107.2	115.1	144.2	148.7	160.9	224.1
750	43.2	88.6	105.0	114.9	141.2	146.4	155.8	197.5
1500	40.4	77.5	99.0	114.5	135.2	140.0	145.8	158.5

Table 5

Carbon dioxide production during degradation of simazine-containing municipal sewage
Produkcja dwutlenku węgla podczas rozkładu ścieków miejskich zawierających symazynę

Initial concentration of simazine g/m³	Aeration time, h							
	17.7	43.0	63.5	86.5	157.5	180.5	204.5	252.5
0	69.5	122.9	144.5	164.0	222.5	—	281.1	294.1
0	69.5	120.5	140.1	158.0	215.1	—	274.3	286.3
0.5	68.6	122.5	142.1	160.4	214.8	—	275.5	287.3
0.5	69.6	124.5	146.9	165.2	220.7	—	—	—
1.25	66.0	121.9	144.4	162.7	220.1	—	280.5	290.7
2.5	67.0	120.8	141.2	160.6	217.8	—	271.1	286.5
5	67.5	122.4	144.9	165.6	222.2	—	280.8	293.1
12.5	66.0	119.7	140.3	161.0	218.1	—	278.7	293.1
25	63.4	117.2	139.7	158.0	214.6	—	276.3	290.2
37.5	64.3	118.1	137.6	158.2	221.0	—	283.8	299.8
50	65.3	121.0	143.4	162.8	220.1	—	284.7	298.1
75	64.4	119.3	140.8	160.9	218.5	—	277.8	288.4
150	62.6	117.3	141.2	160.0	196.2	—	256.7	272.3
250	65.8	120.9	141.9	160.0	196.4	—	248.7	285.9
500	64.1	120.9	140.5	154.3	186.9	—	207.7	265.8
750	63.3	117.5	135.7	148.1	179.6	—	196.8	214.0
1500	58.2	108.1	134.2	150.4	180.8	—	192.3	198.7

ed (tab. 4) and CO_2 produced (tab. 5). As shown in these tables, O_2 uptake and CO_2 production decrease insignificantly even though the simazine doses have been markedly increased (750 and 1500 g/m^3). This inhibiting effect is, however, of a transient nature, because after a 86.5 h aeration the amount of O_2 consumed is almost identical with that obtained for the control (fig. 2). CO_2 production follows a somewhat different behavioral pattern, since in the control the amount of CO_2 produced during aeration is greater

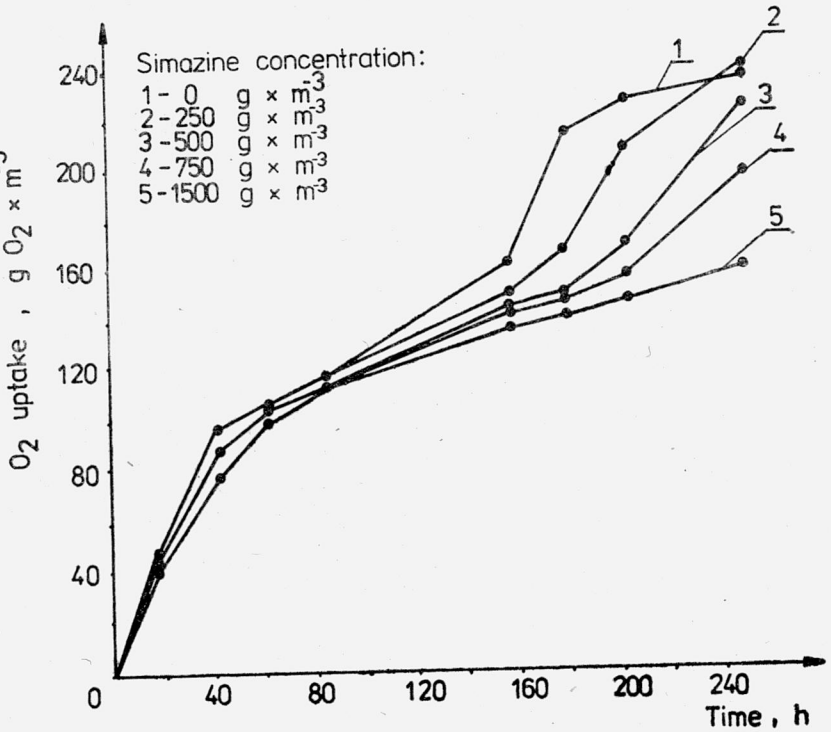


Fig. 2. Oxygen uptake versus time for various concentrations of simazine in municipal sewage

Rys. 2. Pobieranie tlenu dla różnych stężeń symazyny w ściekach miejskich jako funkcja czasu

(tab. 5, fig. 3). The inhibition effect of simazine on the microorganisms participating in the biodegradation of organic substances in municipal sewage is insignificant and can be attributed to the low water-solubility of this herbicide. That is why the portion of simazine added to the experimental sewage remained in dispersed solid phase.

A higher toxic effect of simazine has been stated in nitrifying bacteria. Thus, in the control the oxidation of ammonia nitrogen to nitrite nitrogen is initiated after 86.5 h of aeration; since then, ammonia nitrogen content tends to decrease (fig. 4), while that of nitrite nitrogen increases (fig. 5). Again, the nitrification of ammonia nitrogen in simazine-containing wastewater proceeds via the same route as in the control, provided that the concentration of simazine does not exceed 150 g/m^3. At higher concentrations, the

initiation of the nitrification process will be delayed or even inhibited (figs. 4 and 5). Hence, the increasing concentration of simazine accompanied with the increasing toxic effect on nitrifying bacteria are followed by the increasing concentration of ammonia nitrogen (fig. 4) and decreasing O_2 uptake (fig. 2) and CO_2 production (fig. 3).

Figs. 6 and 7 show the relationship between concentration of simazine and the efficiency of ammonia nitrogen nitrification. In fig. 6 O_2 uptake and CO_2 production (obtained during 252.5 h aeration) are plotted for various initial concentrations of simazine. Ammonia nitrogen and nitrite nitrogen contents (determined after completion of experiments, i.e. after 252.5 h aeration) are given in fig. 7. However, the shape of curve *2* representing ammonia nitrogen in this figure (and especially its segment referring to simazine concentrations from 0 to 250 g/m^3) requires additional comments.

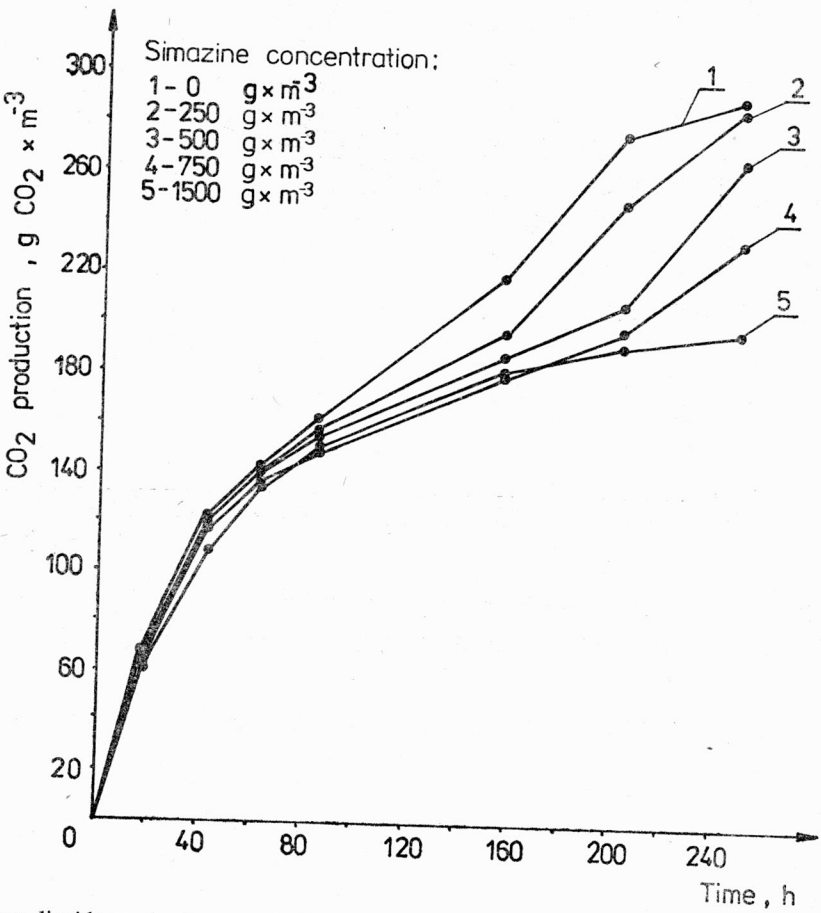


Fig. 3. Carbon dioxide production versus time for various concentrations of simazine in municipal sewage

Rys. 3. Produkcja dwutlenku węgla dla różnych stężeń symazyny w ściekach miejskich jako funkcja czasu

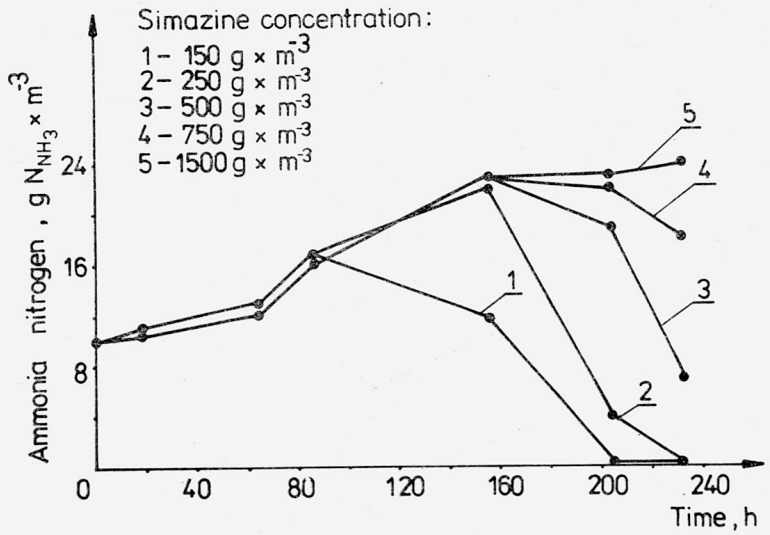


Fig. 4. Ammonia nitrogen concentration versus aeration time for various concentrations of simazine in municipal sewage

Rys. 4. Stężenie azotu amonowego dla różnych stężeń symazyny w ściekach miejskich w zależności od czasu aeracji

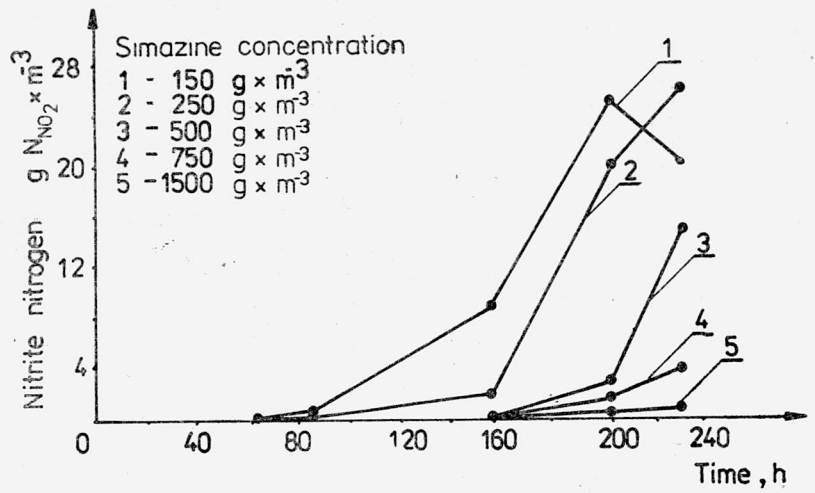


Fig. 5. Nitrite nitrogen concentration versus aeration time for various concentrations of simazine in municipal sewage

Rys. 5. Stężenie azotu azotynowego dla różnych stężeń symazyny w ściekach miejskich w zależności od czasu aeracji

Thus, the unusual shape of this segment is due to a partial oxidation of nitrogen to nitrate nitrogen that takes place at initial concentrations of simazine from zero (control system) to 150 g/m^3. This process does not occur when the initial concentration of simazine is 250 g/m^3 (or higher).

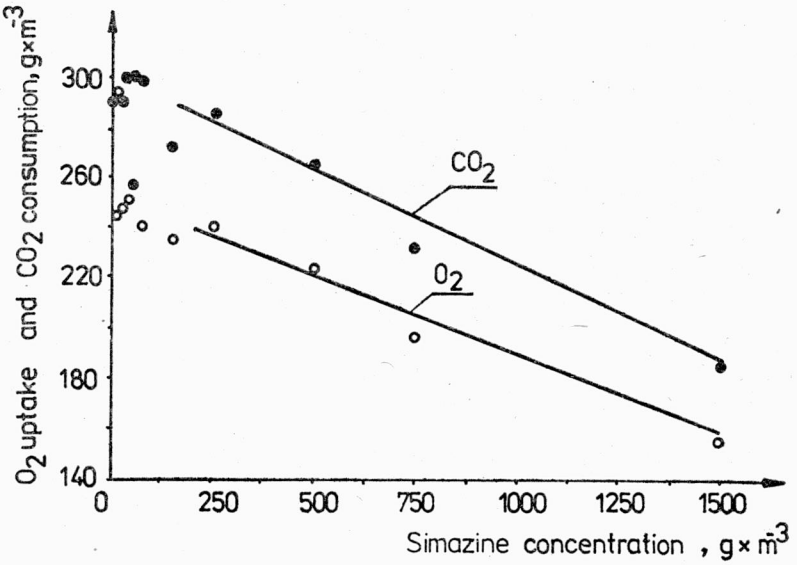


Fig. 6. Oxygen uptake and carbon dioxide production versus initial concentrations of simazine (measurements conducted after 252.5 h of aeration)

Rys. 6. Pobieranie tlenu i produkcja dwutlenku węgla w zależności od początkowego stężenia symazyny (pomiary wykonano po 252,5 h aeracji)

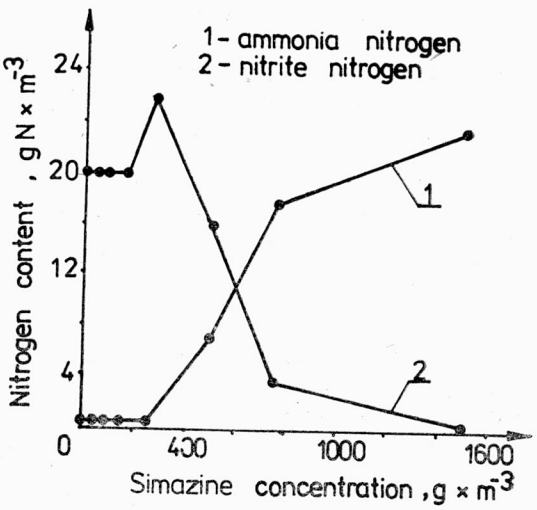


Fig. 7. Ammonia nitrogen (*1*) and nitrite nitrogen (*2*) contents versus initial concentration of simazine (measurements conducted after 252.5 h of aeration)

Rys. 7. Zawartości azotu amonowego (*1*) i azotynowego (*2*) w zależności od początkowego stężenia symazyny (pomiary wykonano po 252,5 h aeracji)

5. CONCLUSIONS

1. Under standard conditions of permanganate COD determination the oxidation of simazine has not been stated, while according to dichromate COD method the oxidation took place approaching 73% of TOD.

2. Under standard conditions of BOD_5 determination simazine appears to be resistant to biodegradation. Thus, BOD_5 and permanganate COD values cannot be considered as reliable indicators of simazine contents in natural water or wastewaters.

3. Simazine occurring in municipal sewage is resistant to biodegradation even when the intensive aeration is prolonged. Hence, simazine behaves as a refractory compound both in the biological treatment of wastewaters and in the process of self-purification in natural waters.

4. Because of its low water-solubility, simazine does not affect the rate of biodegradation of organic compounds contained in municipal sewage. Only nitrifying bacteria are sensitive to the toxic action of simazine.

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ROZKŁAD SYMAZYNY PODCZAS AEROBOWEGO OCZYSZCZANIA ŚCIEKÓW MIEJSKICH

Symazyna (2-chloro-4,6-dwumetyloamina-1,3,5-triazyna) nie ulega utlenieniu w standardowych warunkach oznaczania utlenialności nadmanganianowej. W warunkach oznaczenia utlenialności dwuchromianowej stopień utlenienia symazyny osiąga 73% całkowitego zapotrzebowania tlenu. Symazyna występująca w ściekach miejskich jest odporna na rozkład biochemiczny nawet w przypadkach przedłużonego czasu napowietrzania. Nie wpływa ona niekorzystnie na tempo biochemicznego rozkładu związków organicznych zawartych w ściekach miejskich. Jedynie bakterie nitryfikacyjne są wrażliwe na działanie symazyny, która jest toksyczna tylko dla tych organizmów.

AEROBER ABBAU VON SIMAZIN IN KOMMUNALEN ABWÄSSERN

Simazin (2-Chlor-4,6-Dimethylamin-1,3,5-Triazin) wird durch die Wirkung von Kaliumpermanganat (siehe: Bestimmung der Oxydierbarkeit) nicht oxydiert. Das Kaliumdichromat oxydiert Simazin zum 73% des theoretischen Sauerstoffbedarfs. Wenn Simazin im kommunalen Abwasser vorkommt, ist sie für den

biologischen Abbau resistent — auch bei Überbelüftung. Ihre Gegenwart wirkt sich auf den biologischen Reinigungsverlauf kaum aus. Die toxische Wirkung von Simazin macht sich jedoch gegenüber Nitrifikationsbakterien bemerkbar.

РАСПРЕДЕЛЕНИЕ СИМАЗИНА ПРИ АЭРОБНОЙ ОЧИСТКЕ ГОРОДСКИХ СТОЧНЫХ ВОД

Симазин (2-хлор-4,6-диметиламин-1,3,5-тризин) не подвергается окислению в стандартных условиях определения перманганатной окисляемости. В условиях определения бихроматной окисляемости степень окисления симазина достигает 73% полной потребности в кислороде. Симазин, выступающий в городских сточных водах, является стойким к биологическому разложению даже в случаях продлённого времени аэрации. Он не влияет неблагоприятно на темпы биологического разложения органических соединений, содержащихся в городских сточных водах. Только нитрифицирующие бактерии чувствительны к действию симазина, который токсичен только для этих организмов.