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IMPACT OF PYRETHROIDS ON METHANE DIGESTION

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The process of methane digestion is very sensitive to any changes in the environment. In the group of compounds exerting a toxic effect on the process a special notice should be taken to pesticides – agricultural chemicals, set purposely into the environment to destroy both animal and floral parasites. The remains of these xenobiotics may impede or delay the processes applied at treatment plants or in treatment of sewage sludge. The study presents the results of experimental tests made on the influence of a representative member of pyrethroid insecticides on the methane digestion process.

Keywords: pyrethroids, methane digestion process, sewage sludge

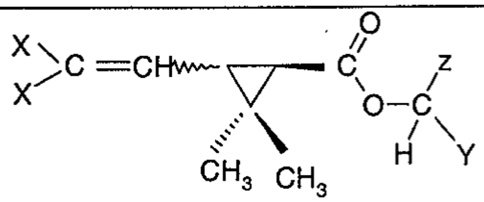
1. INTRODUCTION

Pyrethroids were a group of insecticides introduced into agricultural practice at the end of 1970s. These compounds are synthetic derivatives of natural pyrethrins, insecticidal media contained in flowers of plants belonging to *Chrysanthemum* genus and *Pyrethrum* subgenus [2,5].
The most often used among pyrethroids for fighting harmful species of insects are preparations based on permethrin, cypermethrin, deltamethrin and fenvalerat, that is on the earliest synthesized substances. Chemical structures of synthetic pyrethroids are presented in table 1. In Poland there are about 15 preparations based on these compounds registered.

The speed of pesticide degradation in environment depends not only on chemical structure of the compounds but also, to considerable extent, on physical, chemical and biological features and these are characterised by great variety. Physical-chemical features of Polish priority insecticides are presented in table 2.

Table 1. Chemical structures of pyrethroid insecticides [2,5].

Chemical constitution



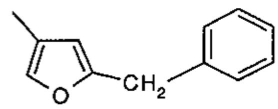
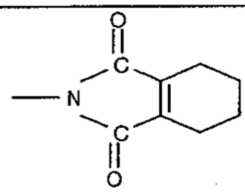
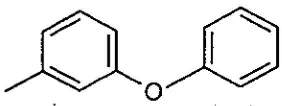
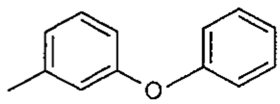
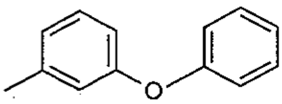
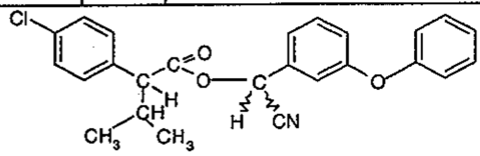
Compound group	Insecticide name	X	Y	Z
Esters of chrysanthenum acid	resmethrin	$-CH_3$	-H	
	tetramethrin	$-CH_3$	-H	
Esters of 3-(2',2'-dihalogenovinyl)- cyclopropane-1,1- dicarboxylic acid	permethrin	-Cl	-H	
	cypermethrin	-Cl	-CN	
	deltamethrin	-Br	-CN	
Fenvalerat				

Table 2. Polish priority insecticides – physical-chemical features

Insecticide	Molecular weight	Molecular formula	Solubility in water	
			mg/dm^3	^0C
γHCH	290,8	$C_6H_6Cl_6$	10,0	20
Metoxychlor (DMDT)	341,5	$C_{16}H_{11}O_2Cl_3$	0,1	25
Chlorfenvinphos	359,5	$C_{12}H_{14}Cl_3O_4P$	124,0	20
Fenitrothion	277,2	$C_9H_{12}NO_5PS$	30,0	20
Malathion	330,4	$C_{10}H_{19}O_6PS_2$	145,0	25
Karbaryl	201,2	$C_{12}H_{11}NO_2$	104,0	20
Cypermethrin	416,3	$C_{22}H_{19}Cl_2NO_3$	0,01-0,2	20
Permethrin	391,3	$C_{21}H_{20}Cl_2O_3$	0,2	30

First compounds of pyrethroid group having considerable anti-pest significance were synthesised in 1954. In spite of small durability they are characterised by good anti-pest functioning. Selectivity of action not found in other groups of insecticides, high anti-pest activity with minimum harmfulness towards humans and other organisms causes big interest in this group of compounds and enables to eliminate or limit application of many chlorine-organic and phosphor-organic insecticides.

Due to the fact that toxicity of pyrethroids increases with temperature drop, they are more toxic for cold-blooded organisms than for homoeothermic animals. Pyrethroids do not show tendencies to get accumulated in living organisms, in which, in general, they undergo quick metabolic changes and get purged. Acute toxicity of some synthetic pyrethroids is presented in table 3.

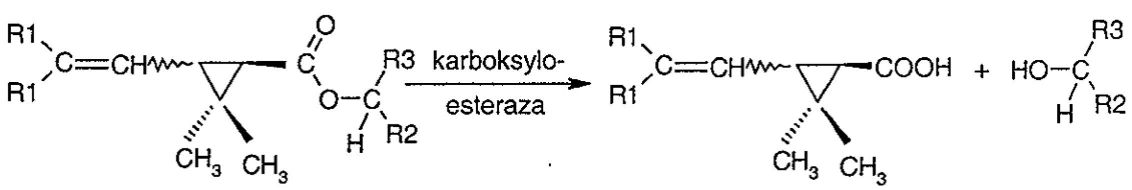
Table 3. Acute toxicity of synthetic pyrethroids [5]

Customary and commercial name	LD_{50} dose *per os* for a rat, mg/kg
Fenvalerat (Susicidin)	450
Cypermethrin (Ripcort)	251-500
Permethrin (Ambush)	1500-4000
Rozmetryna (Sintrin)	1400-1600

Apart from toxicity, an important feature of pesticides is durability and the related time of persistence of compounds in environment. Persistence in soil and water depends mainly on physical-chemical features of individual compounds and sensitivity to environmental factors. These factors decisive for efficiency of proceeding reactions and time in which processes of natural decay take place.

Transformation of pyrethroids changes starts with reactions of splitting ester bonding and/or oxidation, which occur either alternatively or simultaneously. The course of hydrolytic split of ester binding, decomposition of cypermethrins may consist in hydration of cyan group and hydrolysis of created amide and oxidation reactions.

Analysing ways of cypermethrin transformation in environment one should note that two most important reactions – oxidation and hydrolysis – supplement each other.



R1 - CH_3, -Cl lub –Br
R2 - H lub –CN
R3 – fenoksyfenyl; 5-(fenylometylo)-furyl lub 3,4,5,6-tetrahydroftalimidyl

Fig. 1. Hydrolysis of ester bonding in particles of pyrethroid.

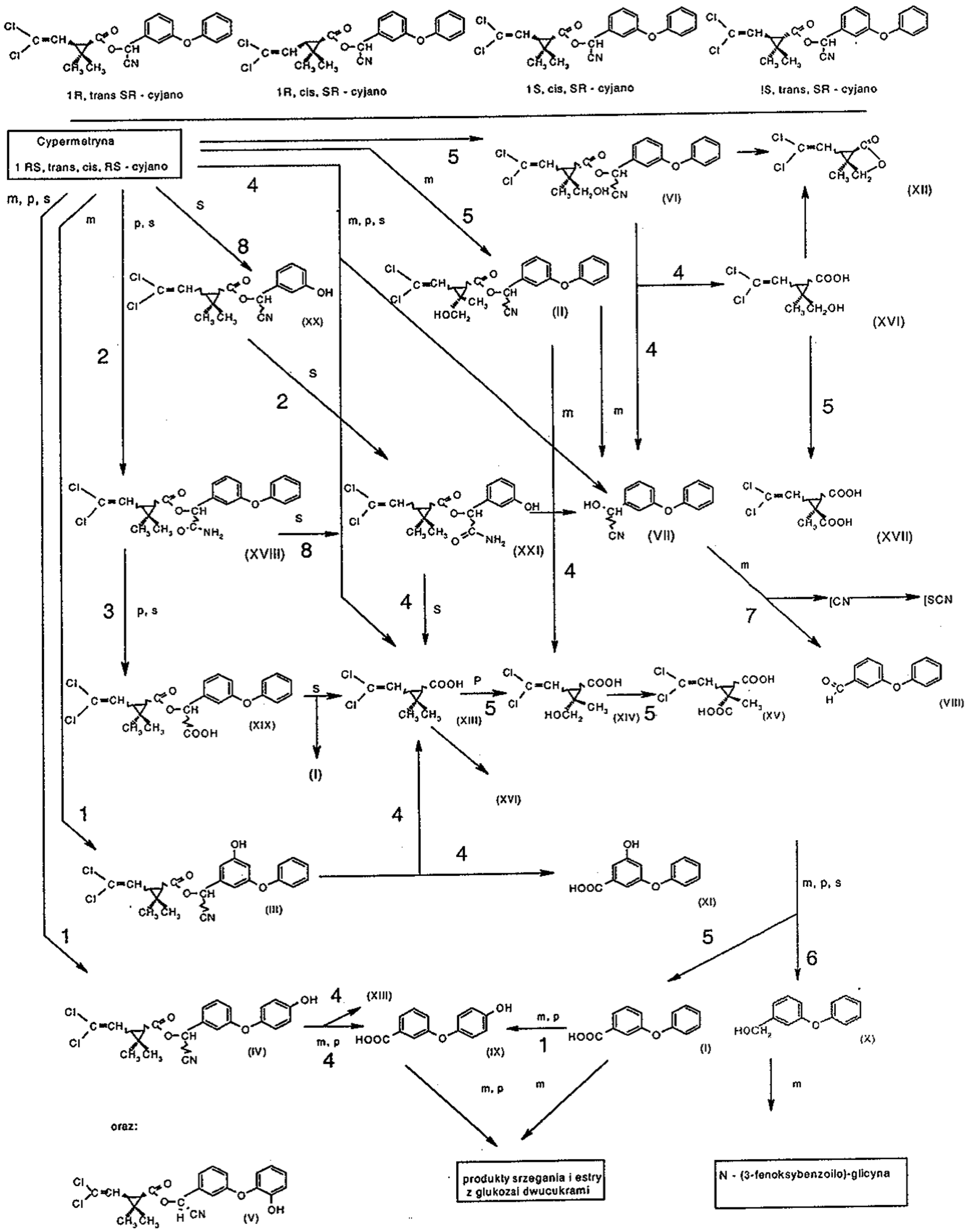


Fig. 2. Possible transformations of cypermethrin in aerobic and anaerobic conditions.

Summarising, transformations of cypermethrin, taking into consideration possibility of occurrence of transformations in aerobic and anaerobic conditions, one should say that oxygen reactions predominate. From anaerobic reactions only one has been separated – reduction of 3-phenylo-ksylo-benzene-aldehyd (VIII) to 3-fenylo-ksyleno-benzyl alcohol (X) (Fig. 2).

2. PURPOSE AND SCOPE OF TESTS

The objective of the present paper is to prove whether pyrethroids have a toxic impact on the process of methane digestion of sewage sludge and to determine their chemical durability in anaerobic conditions.

3. CHARACTERISTICS OF SEWAGE SLUDGE

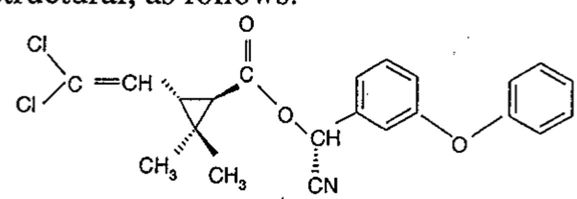
An input substrate for methane digestion was excess sludge from the wastewater treatment plant in Świebodzin. The sludge was inoculated at proportion of 3:1 using digested sludge taken from separated digestion chambers in wastewater treatment plants in Poznań or in Świebodzin.

The mixture of sludge was characterized by the content of dry mass from 5 to 55 g/dm^3(including 64 – 75 % was dry organic mass) and pH value of 6.8 – 7.4. The sludge before being introduced to laboratory fermentation chambers was filtered using a sieve and then carefully mixed. A possibly homogenous mixture was subjectto fermentation process.

4. CHARACTERISTICS OF INSECTICIDE USED IN TESTS

The tests carried out in order to determine influence of perythroids on methane digestion process used the preparation with commercial name: **Fury 100EC.** A biologically active substance in the preparation **Fury 100EC** is *zeta*-cypermethrin.

Cypermethrin is included into esters of 3-(2.2-dichlorine-tartaric)-2.2-dimethylo-cyclo-propane-carboxylic acid with the summary formula as follows: $C_{22}H_{19}Cl_2NO_3$ and structural, as follows:



Solubility of cypermethrin in water at temperature of 20 ° C is of 0.01 – 0.2 mg/dm^3.

LD_{50} *per os* for a rat is of 251 – 500 mg/kg. FURY 100EC is included into III class of toxicity.

5. DESCRIPTION OF TESTING EQUIPMENT USED, METHODOLOGY OF DETERMINATION

Methane digestion of sewage sludge with tested pesticides was made on a laboratory scale, using periodic method (not flow system). Glass bottles of 3 dm^3 each, placed in 12-stands water thermostat, were used as digestion chambers . The bottles were connected to calibrated gas burettes filled with saturated solution of NaCl. These burettes served as measurement devices to check fermentation gas. The pictorial diagram of the testing stand is presented in Fig. 3.

The course of the process was observed in accordance with the Polish standard PN-75/0-04616.07 by daily monitoring the volume of emitted gas, temperature and pressure. Preliminary tests proved that the greatest gas output was obtained in the tests carried out on 4 – 6 day of the process, therefore at that time suitable doses of pesticides were added to the sewage sludge. The digestion process was conducted at the temperature of 35 ± 2 ° C, during 28 – 30 days. Sums of daily gas increments and gas output are referred to normal conditions, i.e. p = 1013 hPa and T = 273 K.

In dozen series of tests aimed at determining the influence of selected insecticides on methane digestion process, the obtained volumes of gas in series with various doses of individual insecticides were compared to control tests, i.e. the tests on sewage sludge digestion carried out simultaneously but without addition of insecticides.

Before digestion the following values were determined in the sludge: dry mass of sludge, dry organic mass, pH value, volatile gases, in accordance with standards in force.

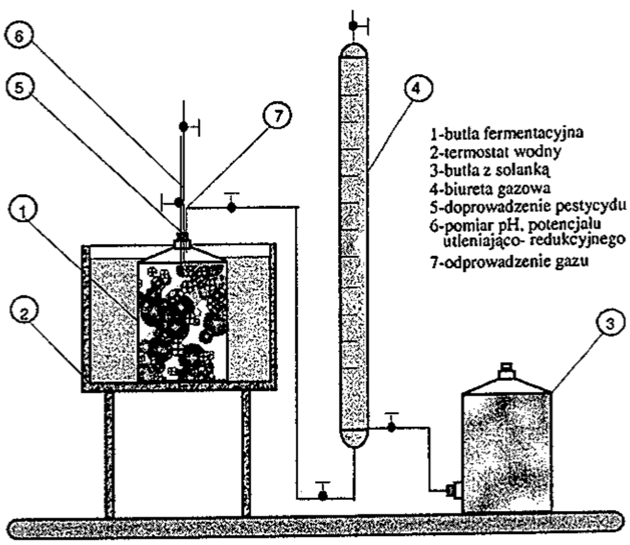


Fig. 3. Diagram of testing stand.

6. INFLUENCE OF ZETA-CYPERMETHRIN (FURY 100EC) ON METHANE DIGESTION PROCESS

Tests determining influence of cypermethrin on methane digestion process used commercial preparation named Fury 100 EC, This preparation contained active substance named *zeta*-cypermethrin. The preparation of the concentration ranging from 0.5 to 100 mg/dm^3 was used in tests [1], which corresponded to the values of 0.74 x 10^{-4} to 1.48 x 10^{-3} g act/g of organic dry mass. The results obtained are shown in Table 4. Symptoms of considerable process braking were noted at concentration of 0.5 mg/dm^3, i.e. 0.74 x 10^{-4} g/g of organic dry mass. The total gas production was reduced by 66 % In relation to the control sample and the average output of gas was reduced from 298 to 113 dm^3/kg of organic dry mass. pH value was also considerably reduced to 6.85 in the sample under analysis.

In the samples with the content of Fury of 1, 2, 5, 10 mg/dm^3, symptoms of process braking were at the similar level – daily volumes of gas in comparison to the control sample were reduced successively by: 62.1: 72.2 and 63.7 %. pH value in the samples was from 6.47 – 6.87.

Increase of Fury 100 EC dose to 20, 50 and 100 mg/dm^3 resulted in total stop of methanegenesis – the gas output was only: 35; 27 and 14 dm^3/kg of organic dry mass. Also considerable increase of volatile acids concentration took place, up to 967.1 mg/dm^3 of CH_3COOH which reduced pH value to 6.57, thus below the optimum scope for normal activity of methane producing bacteria.

Graphic representation of the relation between the sum of daily gas volume increase and time of digestion for selected samples is presented in Fig. 4. Fig. 5 presents exemplary relations between gas production during sewage sludge digestion and content of Fury preparation.

Table 4. Production of gas (dm^3 * 10^{-3}) during digestion of sewage sludge with content of FURY 100 EC insecticide.

Pesticide dose mg/dm^3 g act /g of sludge dry mass / Process parameters	Control sample	0,5 0,74* 10^{-4}	1,0 1,4* 10^{-4}	2,0 2,9* 10^{-4}	5,0 7,4* 10^{-4}	10,0 1,5* 10^{-3}	20,0 3,0* 10^{-2}	50,0 7,4* 10^{-3}	100,0 14,8* 10^{-3}
Daily fermentation time	Gas production dm^3*10^{-3}								
1	633	414	346	405	391	583	587	388	367
2	947	706	929	920	1076	1254	1114	975	855
3	479	321	323	342	371	452	427	395	307
4	325	255	283	255	333	251	320	283	269

Pesticide dose mg/dm^3 g act /g of sludge dry mass / Process parameters	Control sample	0,5 0,74* 10^{-4}	1,0 1,4* 10^{-4}	2,0 2,9* 10^{-4}	5,0 7,4* 10^{-4}	10,0 1,5* 10^{-3}	20,0 3,0* 10^{-2}	50,0 7,4* 10^{-3}	100,0 14,8* 10^{-3}
Daily fermentation time	Gas production dm^3*10^{-3}								
5	233	193	224	191	163	186	65	214	189
6	254	176	185	180	152	185	189	194	153
7	97	107	130	121	93	116	56	27	0
8	98	61	32	99	23	70	9	0	4
9	181	74	74	27	65	93	18	5	0
10	162	65	65	44	34	69	0	28	9
11	157	65	74	50	55	74	0	9	9
12	162	55	65	61	46	74	14	9	9
13	139	92	46	33	40	46	9	0	0
14	116	18	18	9	0	28	4	9	4
15	117	14	18	0	14	18	0	0	0
16	118	28	28	28	0	28	0	0	0
17	121	19	46	0	19	47	0	0	0
18	132	18	47	28	18	18	0	0	0
19	101	23	28	23	28	0	0	0	0
20	95	0	41	0	0	0	0	0	0
21	82	0	0	0	18	0	0	0	0
Sum of daily gas volumes calculated from time of pesticide additi dm^3*10^{-3}	1878	639	712	523	453	681	110	87	35
Sum of daily gas volumes referred to the control sample, %	100	34,0	37,9	27,8	24,1	36,3	5,9	4,6	1,9
Average gas output dm^3/kg s.m.	298	113	101	108	97	72	35	27	14
pH value	7,18	6,65	6,65	6,47	6,61	6,87	6,55	6,73	6,57
Concentration of volati acids, mg/dm^3 CH_3COOH	240,0	668,6	677,1	805,7	637,1	695,7	694,3	934,3	967,1

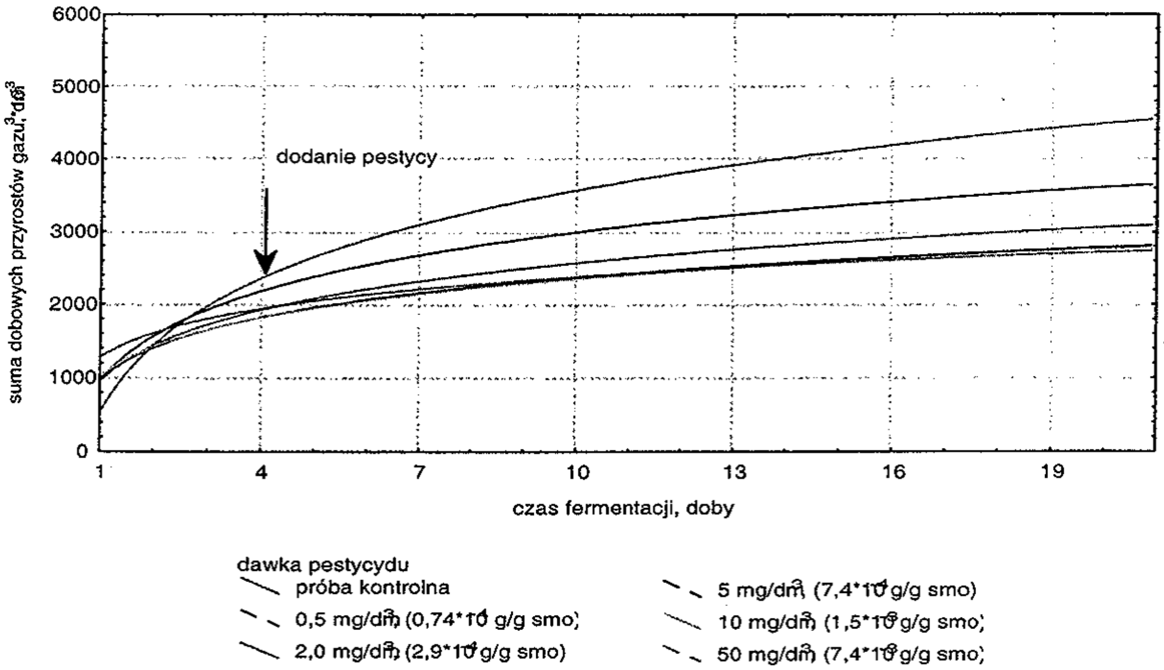


Fig. 4. Sum of daily increments of gas volume during digestion of sewage sludge with Fury 100 preparation.

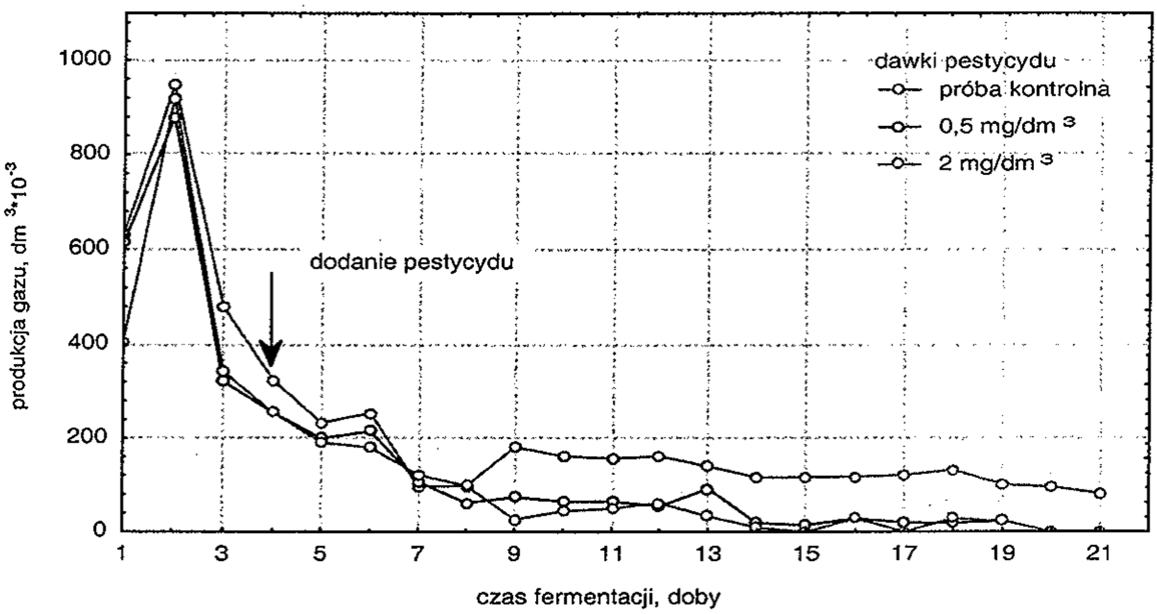


Fig. 5. Gas production during digestion of sewage sludge with Fury 100 preparation.

7. SUMMARY

The results of laboratory tests determining influence of Fury 100EC on methane digestion process prove high toxicity of this preparation. Concentration of 0.5 mg/dm^3 caused reduction of gas production by 50 % in comparison to the control sample. In accordance with Malina [3] such concentration should be recognized as toxic. Concentration of 0.5 mg/dm^3 of Fury corresponds to 0.74×10^{-4} g/g of organic dry mass what calculated for active substance in preparation gives the dose of 0.74×10^{-4} g act/g of organic dry mass. Therefore it may lead to the conclusion that cypermethrin acts on digestion process toxically at concentration of 0.74×10^{-4} g act/g of organic dry mass. Such low toxic concentration confirms low susceptibility of this selected pyrethroid for biodegradation in terms of methane digestion bacteria action. Such conclusion is confirmed by information of other authors [2, 5] (compare Fig. 2) that in the processes of pyrethroids degradation dominate oxygen reactions dominate.

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WPŁYW PYRETROIDÓW NA PROCES FERMENTACJI METANOWEJ

Streszczenie

Proces fermentacji metanowej jest procesem bardzo czułym na wszelkiego rodzaju zmiany środowiska. Wśród związków toksycznie działających na proces należy zwrócić uwagę na pestycydy-chemiczne środki ochrony roślin, które celowo wprowadzamy do środowiska w celu zniszczenia pasożytów roślinnych i zwierzęcych. Pozostałości tych ksenobiotyków mogą utrudniać lub hamować procesy stosowane w oczyszczalniach ścieków lub przeróbce osadów ściekowych. W pracy przedstawiono wyniki badań dotyczące wpływu przedstawiciela grupy insektycydów pyretroidowych na przebieg procesu fermentacji metanowej.