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Original Research Article

ZAHN-WELLENS TEST IN INDUSTRIAL WASTEWATER BIODEGRADABILITY ASSESSMENT

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Abstract

Biodegradability of pollution contained in examined industrial wastewater was assessed according to methodology based on Zahn-Wellens (OECD 302B) test. The following kinds of wastewater were examined:

- metal industry wastewater from aluminium pressure foundry;
- wastewater from industrial waste treatment processes, such as: filtration waste, chemical reagents, coolants, water emulsions, oil wastes and other industrial wastes, galvanising waste treatment processes sludge.

Samples COD value decrease in the subsequent days of the experiment proves that organic substances contained in the examined wastewater undergo gradual biodegradability in aerobic conditions. The highest biodegradability degree of aluminium pressure foundry wastewater equal 65.7% was noted during 28 day of the experiment. However, the minimum biodegradability degree equal 80% after 13 aeration days, which in Zahn-Wellens test allows to determine the examined substance to be biodegradable, has not been achieved. Meanwhile, Zahn-Wellens test conducted for wastewater from industrial waste treatment processes showed that in the day 14 of the process, high (87.1%) organic substance degradation degree, measured with COD value decrease, was achieved. Further aeration of the samples did not increase biodegradability, which equalled 87.9% after 28 days.

Keywords: COD, organic substances, industrial wastewater, liquids

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1. INTRODUCTION

Simultaneous treatment of industrial and municipal wastewater is limited by industrial wastewater biodegradability degree [Myszograj, 2008].
Wastewater biodegradability may be estimated through value of COD/BOD_5 quotient. It is assumed that quotient $COD/BOD_5 > 2.5$ points to slow degradation and large amount of non-degradable substances, while value <1.8 shows substance biodegradability. However, this interpretation of the results has merely illustrative character, since it prove reliable for substrates consisting of only bio-oxidizable substances which may be oxidise quantitatively with chemical substances. In regards to wastewater containing also non-degradable compounds, slowly degradable compounds, or biodegradable compounds not marked with the dichromate method, such assessment of contents is frequently misleading. In the aforementioned cases, COD fractions calculation provides better wastewater content characteristics. The basic division is based on determining biodegradable and non-biodegradable COD fractions in the total COD of the wastewater [Myszograj et al., 2017].
Wastewater COD with division of fractions may be calculated in a simplified way using the following formula [Płuciennik-Koropczuk et al., 2017]:

$$COD = S_S + S_I + X_S + X_I, mgO_2 / dm^3 \quad (1)$$

where:
S_S – COD of solved organic easily biodegradable compound,
S_I – COD of solved organic non-biodegradable compound,
X_S – COD of organic degradable suspension,
X_I – COD of organic non-biodegradable suspension.

Biochemical tests offer more options of wastewater biodegradability assessment. A correct test type is selected depending on the analysis objective. Examined compound low concentration and biomass inoculation are used to assess organic compounds processing in surface water and its influence on sewage self-treatment. Examined compound concentration and microflora inoculation will be significantly higher, however, if test purpose is a prognosis of biochemical degradation of the examined substance in biological wastewater treatment plant. Biodegradation tests may be conducted in both water and ground environments [Klimiuk, Łebkowska, 2004].
Research on biochemical degradability of non-volatile organic compounds solved in water should be conducted utilising screening, confirmation, and simulation tests. Screening tests utilise low inoculation and typical analytical methods to assess biochemical degradability. Substance is considered biodegradable if solved organic carbon value decreases by 70%, and BOD_5 or produced CO_2 by 60%, after 28 days of the experiment. In the case of negative

tests results or low results precision, additional confirmation tests are conducted, the duration of which must not exceed 28 days. Initially, a compound should be considered biodegradable if its concentration decreases at least by 20%. If the decrease does not reach this value, the examined substance should be considered non-biodegradable and constant in the environment. Biodegradation simulation tests consist primarily of tests presenting degradation in reactors with active sludge [Klimiuk and Łebkowska, 2004]. Table 1 presents biodegradation standards for screening, confirmation, and simulation tests acc. to OECD ((Organisation for Economic Cooperation and Development).

Table. 1. Biodegradation standards of biochemical tests acc. to OECD [Klimiuk, Łebkowska, 2004]

Standard No.	Title
	'Screening' tests
301A	RWO die-Away
301B	Modified Sturm test (CO2 emission)
301C	MITI*
301D	Closed Bottle test
301E	Modified OECD 'screening' test
301F	Manometric Respiratory Test
	Confirmation tests
302A	Modified SCAS** examination
302B	Zahn-Wellens test / EMPA***
302C	Modified MITI (II) test
	Simulation tests
303A	Aerobic wastewater treatment. Examination using connected devices
303B	Susceptibility to ground-specific biodegradation

* Ministry of International Trade and Industry, Japan

** Simulation half-constant test with active sludge,

*** Swiss Federal Laboratories for Materials Science and Technology, Switzerland

2. ZAHN-WELLENS TEST

Zahn-Wellens test is one of the methods of substance susceptibility to degradation by microorganism, occurring in large quantities during the conducted test. The examination lasts for 28 days and consist of regular control of COD or TOC indicator value. Zahn-Wellens test is conducted in reactors of volume from 1 to 4 dm^3. The containers should be air-tight and equipped in

aeration and mixing devices. The contain the examined substance, nutrients, and the sludge. Reactors contents are incubated for 28 days. Test stand should be placed in diffuse light or darkness, and environment temperature should equal 20-25ºC. The results are presents as biodegradation over time curve.
Degradation percentage value, achieved after 28 days, is called "biodegradation in Zahn-Wellens test" and expressed by the following formula:

$$R_{t(\%)} = \left[1 - \frac{C_T - C_B}{C_A - C_{BA}}\right] \cdot 100 \tag{2}$$

where:
C_r – COD or TOC value in sludge supernatant of the examined sample at the end of aeration period, mg/dm^3;
C_B – COD or TOC value in the zero sample during sample gathering, mg/dm^3;
C_A – COD or TOC value in the examined mixture, marked 3h after start of the experiment, mg/dm^3;
C_{BA} – COD or TOC value in the zero sample, marked 3h after start of the experiment, mg/dm^3.

The method is utilised in the case of organic substances which in concentration used in the test:
- are water-solvable in experimental conditions,
- have very low vapor pressure value in experimental conditions,
- do not inhibit bacteria growth,
- absorb only in limited range in the experimental conditions,
- do not undergo foaming losses.

3. METHODOLOGY

Biodegradability of pollution contained in examined industrial wastewater was assessed according to methodology based on Zahn-Wellens (OECD 302B) test.
The examined samples consisted of:
- metal industry wastewater from aluminium pressure foundry. Production processes, besides aluminium alloys, utilise also lubricants, form separators, adhesion preventers, cleaning agents, and synthetic varnishes;
- wastewater from industrial waste treatment processes, such as: filtration waste, chemical reagents, coolants, water emulsions, oil wastes and other industrial wastes, galvanising waste treatment processes sludge.

Biodegradation tests were conducted on the following samples:
- sample 1 - examined wastewater from aluminium pressure foundry, mixed in 1:1 volume ratio with dewatered active sludge from biological wastewater treatment plant, washed in a basic solution of the examined substrates;
- sample 2 - examined wastewater from industrial waste treatment processes, mixed in 1:1 volume ratio with dewatered active sludge from biological wastewater treatment plant, washed in a basic solution of the examined substrates;
- sample 3 - examined wastewater from aluminium pressure foundry of theoretical oxygen demand equal ca. 1200 mg/dm^3, mixed with a nutrient solution.

In order to control test procedure simultaneously with the conducted test, a control substance meeting criteria of considerable biodegradability was being examined:
- sample 4 - solution with test substance, glucose, of theoretical oxygen demand equal ca. 1200 mg/dm^3.

The examined samples were aerated for 28 days at temperature 20-25ºC. Organic substances degradation process was monitored by marking COD in samples on day 1, 2, 3, 5, 7, 9, 11, 14, 19, 21, and 28 of the experiment. The process was additionally controlled through solved oxygen content, pH, and specific conductance measurements.
Analytic marking was conducted in accordance with the applicable methodology.

4. RESULTS

Samples of the examined substrates characterised with high concentration of organic pollution, COD of respectively 33500 and 6943 mg/dm^3, BOD_5 respectively of 5124 and 1580 mg/dm^3, and low concentration of nitrogen and phosphorus. Solutions pH value was within neutral range and did not point to necessity of pH correcting before conducting the test.
Pollution biodegradability, estimated on the basis of COD/BOD_5 quotient value, showed substrates resistance to biochemical degradation. In both cases, values of the calculated COD/BOD_5 quotient was higher than 2.5 and equalled 6.5 for wastewater from aluminium foundry and 4.4 for industrial waste treatment processes wastewater. Tables 2 and 3 present physical and chemical characteristics of wastewater from aluminium pressure foundry and wastewater from industrial waste treatment processes.

Table 2. Physical and chemical characteristics of mixed raw wastewater from aluminium pressure foundry (sample 1)

parameter	pH	Conductivity	Total suspension	BOD_5	COD	N_{og}	Cl^-	$P_{og.}$
unit	-	µS/cm	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3
value	7.10	1106	520	5124	33500	98.3	11.2	7.5

Table 3. Physical and chemical characteristics of wastewater from industrial waste treatment processes (sample 2)

parameter	pH	Conductivity	$TOC_{soluble}$	BOD_5	COD	$N\text{-}NH_4$	$P\text{-}PO_4^{3-}$	$P_{og.}$
unit	-	µS/cm	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3
value	7.51	14330	2009	1580	6943	90.3	0.01	0.49

In order to unequivocally determine substrates biochemical degradability, Zahn-Wellens test was conducted. Tests results are presented by tables 4 and 5.

Table 4. Physical and chemical parameters of wastewater from aluminium foundry (sample 1) in the subsequent days of Zahn-Wellens test

Parameter	Start	Test, day									
		1	2	3	5	7	11	13	19	21	28
COD mg/dm^3	14068	12737	12366	11924	10638	9289	8812	6057	5103	4909	4823
pH	7.10	7.11	7.11	7.12	7.11	7.12	7.11	7.10	7.12	7.14	7.15
Condictivity µS/cm	1106	1103	1065	1063	1058	1045	1038	1032	1023	1009	998

Table 5. Physical and chemical parameters of wastewater from industrial waste treatment processes (sample 2) in the subsequent days of Zahn-Wellens test

Parameter	Start	Test, day									
		1	2	3	5	7	11	14	19	21	28
COD mg/dm^3	3395	2843	2665	2474	1099	878	667	368	464	449	398
pH	6.85	7.66	7.57	7.42	7.67	7.47	6.92	7.10	6.84	6.97	7.10
Conductivity µS/cm	8130	8130	8130	8390	8450	8420	8560	8600	9050	9260	10150

In the subsequent days of the experiment, samples COD values decreased, which proves that organic substances in the examined substrates undergo gradual biodegradation in aerobic conditions. COD value in wastewater from the foundry decreased from initial 14068 mg/dm^3 to 4823 mg/dm^3, while COD of industrial waste treatment processes wastewater decreased from 3395 to 398 mg/dm^3. Substrates degradation process curves presents Fig. 1.

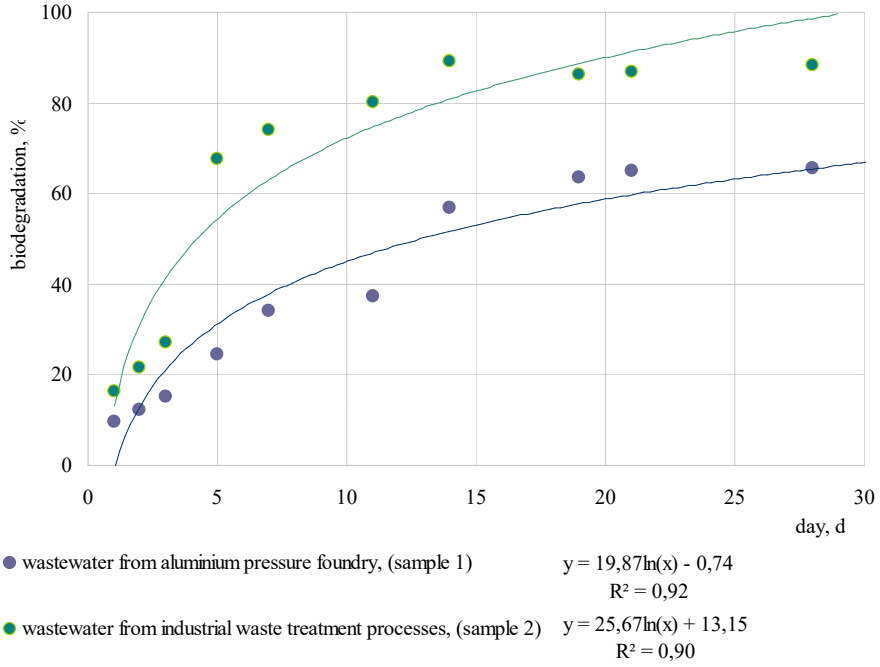

Fig. 1. Substrates degradation curves during Zahn-Wellens test (samples 1 and 2)

Received substrates biodegradation curves (Fig. 1) present biodegradation degree increase in the subsequent days of the experiment. The highest biodegradation degree of aluminium pressure foundry wastewater equal 65.7% was noted during day 28 of the experiment. Meanwhile, Zahn-Wellens test conducted for wastewater from industrial waste treatment processes showed that in the day 14 of the process, high (87.1%) organic substance degradation degree, measured with COD value decrease, was achieved. Further aeration of the samples did not increase biodegradability. During Zahn-Wellens test, the examined substance is considered biodegradable if after 13 days of aeration, its degradation equals minimum 80%. In the case of wastewater from industrial waste treatment processes, degradation during day 14 equalled 89.1%, thus reaching its maximum value, while the aluminium pressure foundry wastewater did not achieve minimum degradability degree. On day 14 of the experiment, its biodegradability degree equalled 56.9%. Test results of samples 3 an 4 present tables 6 and 7. Aluminium pressure foundry wastewater biodegradation degree in a sample of initial COD content equal 1200 mg/dm^3 changed within range from 20 to about 4% during test duration.

Table 6. Physical and chemical parameters of aluminium pressure foundry wastewater (sample 3) in the subsequent days of Zahn-Wellens test

Parameter	Start	Test, day									
		1	2	3	4	7	9	11	15	24	28
COD mg/dm^3	1200	974	963	936	900	893	848	786	780	748	654
pH	7.03	7.22	7.26	7.27	7.33	7.34	7.39	7.40	7.43	7.45	7.45
Conductivity mS/cm	45.3	43.4	43.2	44.6	45.2	44.4	44.1	44.6	44.9	44.8	45.3

Table 7. Physical and chemical parameters of control sample with glucose reference solution (sample 4) in the subsequent days of Zahn-Wellens test

Parameter	Start	Test, day									
		1	2	3	5	7	9	11	15	24	28
COD mg/dm^3	1282	1201	1190	1090	1036	825	752	577	551	429	399
pH	7.23	7.28	7.26	7.25	7.19	7.05	6.98	7.02	7.03	7.04	7.04
Conductivity mS/cm	44.6	44.8	45.2	47.0	48.3	55.0	57.5	58.5	58.5	58.2	58.2

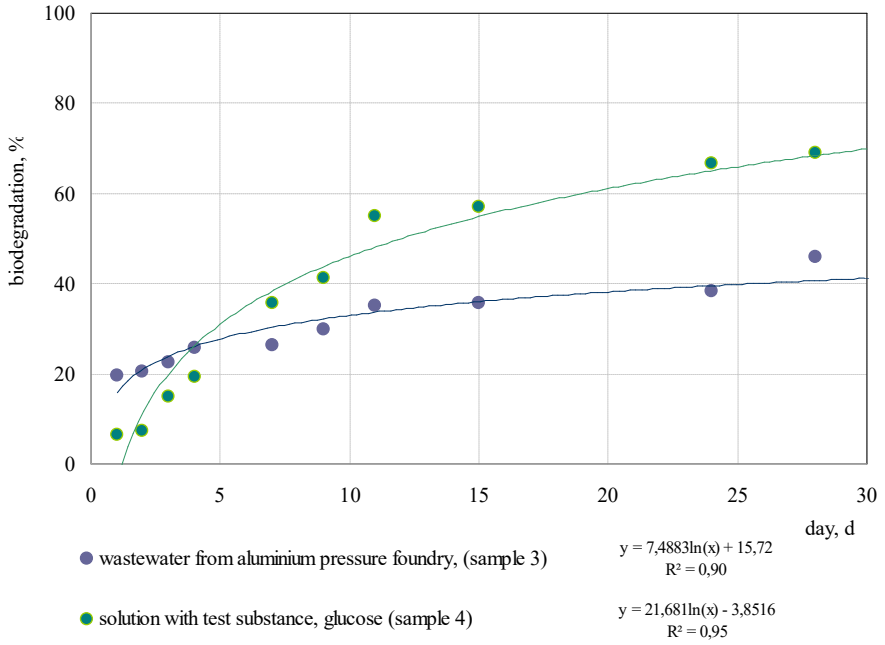

Fig. 2. Substrates biodegradation curves during Zahn-Wellens test (samples 3 and 4)

However, COD decrease speed was the highest during the first 10 days of the experiment. In subsequent days, it increased very slightly, eventually reaching the maximum value. Meanwhile for the glucose test solution sample of the same initial COD value equal 1282 mg/dm^3, biodegradation degree equal around 70% during the last day of the process (Fig. 2).

5. CONCLUSIONS

1. The conducted Zahn-Wellens test proved degradability of aluminium pressure foundry wastewater and of wastewater from industrial waste treatment processes in aerobic conditions.
2. Biodegradability degree after 28 test days equalled 65.7% for aluminium pressure foundry wastewater, and 88.3% for wastewater from industrial waste treatment processes.
3. Substance is considered degradable if it undergoes biodegradation in at least 80% after 13 days of aeration. This condition was fulfilled by wastewater from industrial waste treatment processes.

On the basis of laboratory tests, process conditions of aerobic treatment of wastewater from industrial waste treatment processes were determined. Biodegradation on industrial scale conducted in a system of submerged fixed-bed rotating-discs reactors confirmed high effectiveness of the method.

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TEST ZAHN-WELLENSA W OCENIE BIODEGRADOWALNOŚCI ŚCIEKÓW PRZEMYSŁOWYCH

S t r e s z c z e n i e

Podatność na biodegradację zanieczyszczeń zawartych w badanych ściekach przemysłowych oceniono zgodnie z metodyką opracowaną na podstawie testu OECD - Test Zahn –Wellens'a (OECD 302B). Badaniom poddano:

- ścieki z przemysłu metalowego z odlewni ciśnieniowej aluminium. W procesie produkcyjnym oprócz stopów aluminium wykorzystywane są środki smarne, oddzielacze od form, środki zapobiegające przyleganiu, substancje czyszczące oraz lakiery syntetyczne;
- odcieki z procesów unieszkodliwiania odpadów przemysłowych, takich jak: odpady pofiltracyjne, odczynniki chemiczne, chłodziwa, emulsje wodne, odpady olejowe i inne pochodzenia przemysłowego, osady z oczyszczania ścieków galwanizerskich.

Zmniejszenie wartości ChZT w próbkach w kolejnych dobach prowadzenia testu świadczy o tym, że substancje organiczne zawarte w badanych ściekach ulegają stopniowej biodegradacji w warunkach tlenowych. Najwyższy stopień biodegradacji ścieków z odlewni ciśnieniowej aluminium wynoszący 65,7% stwierdzono w 28 dobie prowadzenia testu. Nie uzyskano jednak progu minimalnego stopnia biodegradacji wynoszącego 80% po 13 dobach napowietrzania, który w teście Zahn-Welens'a pozwala uznać badaną substancję za podatną na rozkład biologiczny. Natomiast test Zahn-Wellens'a przeprowadzony dla odcieków z procesów unieszkodliwiania odpadów przemysłowych wykazał, że w 14 dobie procesu uzyskano wysoki (87,1 %) stopień rozkładu substancji organicznej, mierzony obniżeniem wartości ChZT. Dalsze napowietrzanie próbek nie wpłynęło na zwiększenie biodegradacji i po 28 dobach wskaźnik ten wynosił 87,9%.

Słowa kluczowe: ChZT, substancje organiczne, ścieki przemysłowe, odcieki

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