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ESTIMATION OF TOXICITY AND BIODEGRADABILITY OF WASTES FROM PRODUCTION OF ACRYLIC POLYMERS

The investigations were performed to determine the toxicity of wastewater from production of acrylic polymers as well as the possibility of biodegradation in activated sludge process. It has been stated that acrylates are susceptible to biodegradation expressed in reduction of BOD and COD values.

It seems that acrylates exert an advantageous effect on the efficiency of activated sludge, which can be explained by the presence of nitrogen from acrylate resin.

The greatest number of organisms in activated sludge has been stated during the treatment of combined wastes from the production of the all kinds of acrylates. Toxicity of wastewater was tested by using the following aquatic organisms: *Lebistes reticulatus*, *Gammarus pulex*, *Daphnia magna* and *Lemmna minor*.

Threshold concentrations and LC_{50} and PC_{50} values wered etermined after 24 and 48 h of observations. For *L. minor* the lethal zone and that of inhibition of their green mass increment were determined.

Results of experiments allowed to determine the admissible concentrations of wastewater from acrylate production in water.

1. INTRODUCTION

A dynamic increase in the production of wastewaters containing polymers of acrylic acid and its derivatives as well as copolymers of those compounds with vinyl compounds started in the 70ties. Acrylic polymers have been more and more commonly used for production and refining of fabrics, paper, varnish, leather, rubber as well as for production of floor-cleaners, coating agents for metal and other products, replacing the so far applied classical natural agents. In general, about 20 kinds of acrylic resins are produced in the factory being now investigated [1].

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Removal of acrylic polymers from the wastewaters was investigated by Japanese scientists. The method of coagulation and flocculation with copper sulphate yielded the COD removal exceeding 90% [5, 6].

In Poland the literature dealing with the properties of the wastewaters containing acrylic polymers and the methods of their treatment are limited. There is no basic information about the toxicity of these compounds, their effect on water organisms, and about their biodegradation. It is due to the fact that the production of acrylates was developed not earlier than in the 70ties [2, 10].

The purpose of the present paper is to determine the toxicity of wastes for the selected and most representative kinds of polymers and to state the possibilities of their biodegradation in activated sludge process.

2. CHARACTERISTICS OF WASTEWATER FROM PRODUCTION OF ACRYLIC POLYMERS

Industrial wastes from production of acrylic polymers come from periodical washing of the apparatus with demineralized water and 7% solution of sodium hydroxide. The average physicochemical composition of wastewaters is presented in table 1.

Table 1

The average physicochemical composition of wastewaters
Średni skład fizykochemiczny ścieków

Notation	Unit	Wastewater from washing the reactors with demineralized water	Wastewater from leaching the reactors	Mixed wastewater
pH	—	6.5	13.6	13.1
BOD_5	mg/m³ O_2	2596	2300	2250
ether extract	mg/dm³	102	25	91
nonionic surfactants	mg/dm³	227	100	145
anionic surfactants	mg/dm³	36	12	25
total suspension	mg/dm³	85.8	69.8	81.6

3. TREATMENT OF ACRYLATE WASTES BY PHYSICOCHEMICAL METHODS

Mixed wastes (from washing the reactors with demineralized water and sodium hydroxide) were treated by coagulation method using 1% solutions of aluminium sulphate and by acidification with hydrochloric acid to $pH < 3$.

For the wastes of pH 2.2 the acidification method reduced chemical oxygen demand $(COD)_{KMnO_4}$ to 71.0%, K_2CrO_7 to 80.0%, and biological oxygen demand (BOD_5) to 72.5%.

Coagulation with aluminium sulphate gave the following results: COD_{KMnO_4} — 75%, $COD_{K_2CrO_7}$ — 61%, BOD_5 — 75%.

4. BIODEGRADATION OF ACRYLATES

The following kinds of wastewaters were tested: 1. wastes from production of rokryl SW-9, 2. wastes from production of rokryl TW-3, 3. combined wastes from production of all kinds of acrylates — flocculants and coagulant acids, etc.

Acrylates were removed from municipal wastes in the activated sludge chamber of the volume of 10 dm^3. Concentrations of acrylates in the chamber amounted to 100, 300, and 500 mg of active substance in 1 dm^3 of wastes. The control of the treatment process consisted in hydrobiological analyses of activated sludge and in determining of the suspended solids concentrations and of the basic indicators of pollution in raw and treated wastewaters.

Table 2 shows the effects of biodegration of the acrylate wastes at the aeration time of 12 hours and the concentration of active substance equal to 500 mg/dm^3 of wastes.

4.1. BIOLOGICAL CHARACTERISTICS OF THE ACTIVATED SLUDGE DURING BIODEGRADATION OF ROKRYL SW-9

In all experimental chambers and in the control one the biocenoses developed during the investigations were very similar with respect to their quality and quantity. During the investigation total number of the organisms in 1 cm^3 of sludge, determined by hydrobiological analysis, ranged within 5×10^3-8.5×10^3 [3]. Bacteriological analysis was not performed.

Sedentary species of the *Vorticella* and *Opercularia* genera were the dominant organisms, with co-dominant floating species of *Lionotus* genus. Rotifers and rhizopoda occurred in small numbers.

4.2. BIOLOGICAL CHARACTERISTICS OF THE ACTIVATED SLUDGE DURING BIODEGRADATION OF ROKRYL TW-3

Total numbers of organisms in 1 cm^3 of the sludge, varying from 4×10^3-9×10^3, did not changed distinctly with the acrylic doses.

Rotifers, mainly *Diglena* sp., *Rotifer* sp. and amoebas (*Amoeba* sp., *Arcella* sp.), were dominant and co-dominant species.

Table 2

Effects of the acrylic wastes biodegradation, at 500 mg of active substance in 1 dm^3 of wastewaters, and parameters of the activated sludge
Efekty biodegradacji ścieków akrylanowych przy stężeniu 500 mg substancji aktywnej w 1 dm^3 ścieków oraz parametry pracy osadu czynnego

Indicator	SW-9		Control		TW-3		Control		Combined wastes		Control	
	min	max	min	max	min	max	min	max	min	max	min	max
pH of the raw wastes	6.05	8.4	7.15	8.6	7.6	8.3	7.6	8.3	7.6	9.1	7.7	9.1
pH of the treated wastes	6.8	7.5	6.6	7.65	7.45	8.35	7.3	8.2	8.2	8.7	7.5	8.5
reduction of BOD_5 (%)	95.9	98.1	95.5	97.7	88.1	98.2	89.4	97.2	98.2	99.2	92.2	98.6
reduction of COD (%)	91.2	94.4	84.6	93.2	83.6	91.4	69.6	91.3	78.5	89.3	81.6	91
concentration of activated sludge (g/dm^3)	3.2	4.51	2.79	4.14	3.31	5.95	3.52	4.26	2.92	5.32	2.73	3.83
sludge index	46.5	54.2	61.3	68.2	37.2	52.6	70.8	84.9	46.9	64.4	62	80.4
activated sludge loading with BOD_5 g (g of dry weight/24h)	0.23	0.43	0.25	0.50	0.2	0.45	0.19	0.39	0.62	1.19	0.25	0.46
chamber loading with BOD_5 ($g/m^3/24h$)	100	177	89	167	120	266	76	141	266	416	98	138

4.3. BIOLOGICAL CHARACTERISTICS OF THE ACTIVATED SLUDGE DURING BIODEGRADATION OF THE COMBINED WASTES

Wastewaters neutralized to pH 8.5 were added to the chambers with activated sludge. Total numbers of the organisms ranged within 13×10^3-21×10^3 in 1 cm^3 of the sludge with a succesive development of *Ciliata* whose percentage amounted to 89-95% of the total number of organisms in 1 cm^3 of the sludge.

The growth of floating organisms in biocenosis, giving the evidence of the proper course of treatment process, has been also observed.

5. ESTIMATION OF TOXICITY DEGREE OF ROKRYL SW-9 AND TW-3 AND COMBINED WASTES FROM PRODUCTION OF ACRYLATES

5.1. HIGH TOXICITY WITH RESPECT TO AQUATIC FAUNA AND FLORA

Toxicity tests were performed on *Lebistes reticulatus*, *Gammarus pulex*, *Daphnia magna* (fauna) and *Lemna minor* (flora).

The tests on water animals and nutrient analyses were performed according to the methods given by Polish Standards [7, 8].

The aim of the investigations was to determine the threshold as well as lethal (LC_{50}) and permissible (PC_{50}) concentrations after 24 and 48 hours of the experiment [4]. For *L. minor* lethal concentrations and those at which green mass increment is inhibited have been determined. The experiment was carried out for 10 days [9]. Results of the toxicity tests, especially PC and LC, were used to determine the admissible concentrations of the substances investigated. Series of dilutions were prepared, using the titre equal to 2 for the preliminary experiments and the titres equal to 1.5, 1.3, 1.15 for the proper experiments.

Water for dilutions was taken from natural stream of a known physicochemical composition or from aquarium. Demineralized water, used for washing the columns and which later contributed to the combined wastes, was characterized by low hardness and small buffer capacity. It brought about a higher mortality rate of the tested organisms than pure SW-9 and TW-3 complexes.

Readings of the results were done after 1, 3, 6, 12, 24, 48, and 72 hours. Each time the number of dead, injured and unchanged individuals was recorded.

While analyzing the $LC_{50/24}$ $PC_{50/24}$, and $LC_{50/48}$, $PC_{50/48}$ values of Rokryl SW-9, it has been stated that the most safe concentration (safety factor — 0.1) [10] for *G. pulex* amounts to 0.4 ml/dm^3 (table 3). This amount of Rokryl SW-9 can be safely introduced into surface waters, thus it must be diluted in the ratio 1:2 500 with water of the receiving body. Rokryl SW-9 in concentrations equal to/or higher than 13 ml/dm^3 was lethal to plants growing

Table 3

Results from investigations on the high toxicity tests of Rokryl SW-9
Przegląd wyników doświadczeń nad toksycznością ostrą rokrylu SW-9

Date	Test organism	Range of concentrations (ml/dm^3)	Water for dilution	Titre of dilution	Values of concentrations (ml/dm^3) after time		
					LC_{50}	PC_{50}	Threshold
8 IV 76	*Gammarus pulex*	50.0–3.17	from the stream	2	—	—	after 24h in the concentration above 125 ml/dm^3–100% of dead individuals
12 IV 76	*Gammarus pulex*	150.0–6.44	from the stream	1.3	—	—	24h — below 6.44
21 IV 76	*Gammarus pulex*	30.0–2.83	from the stream	1.3	24h — 6.97 48h — 5.54	24h — 4.35 48h — 4.00	24h — 3.78 48h — below 2.83
27 IV 76	*Gammarus pulex*	10.0–1.70	from the stream	1.15	24h — 8.34 48h — 4.67	24h — 5.29 48h — 4.55	24h — 4.30 48h — 2.83
27 IV 76	*Lebistes reticulatus*	3.74–1.80	aquarium water	1.15	—	—	24h — 2.14 48h — 2.14
27 IV 76	*Daphnia magna*	3.74–1.70	aquarium water	1.15	—	—	24h — 1.95 48h — 1.95

Table 4

Results from the investigations on the high toxicity tests of Rokryl TW–3

Przegląd wyników doświadczeń nad toksycznością ostrą rokrylu TW–3

Date	Test organism	Range of concentrations (ml/dm^3)	Water for dilution	Titre of dilution	Values of concentrations (ml/dm^3) after time		
					LC_{50}	PC_{50}	Threshold
8 IV 76	*Gammarus pulex*	200.0–5.0	from the stream	2	—	—	24h above
12 IV 76	*Gammarus pulex*	450.0–19.1	from the stream	1.3	24h – 83.15 48h – 51.69	24h – 52.05 48h – 40.14	24h – 25.1 48h – 25.1
21 IV 76	*Gammarus pulex*	150.0–14.4	from the stream	1.3	— 48h – 38.4	— 48h – 32.0	24h – 68.27 48h – 23.9
27 IV 76	*Gammarus pulex*	80.0–17.9	—	1.15	— 48h – 53.84	24h – 51.42 48h – 44.40	24h – 34.59 48h – 34.59
27 IV 76	*Lebistes reticulatus*	30.0–17.2	aquarium water	1.15	—	—	24h – 26.15
27 IV 76	*Daphnia magna*	30.0–17.2	aquarium water	1.15	—	—	24h – 22.7 48h – 19.17

Table 5

Results from investigations on the high toxicity tests of the combined wastes
Przegląd wyników doświadczeń nad toksycznością ostrą ścieków oddziałowych

Date	Test organism	Range of concentrations (ml/dm^3)	Water for dilution	Titre of dilution	Values of concentrations (ml/dm^3) after time			Remarks
					LC_{50}	PC_{50}	Threshold	
7 IV 76	*Lebistes reticulatus*	2.0—0.06	distilled	2	—	—	24h — 0.10	alkaline reaction
7 IV 76	*Gammarus pulex*	2.0—0.06	distilled	2	—	—	—	alkaline reaction, death of the organisms in the control sample
8 IV 76	*Gammarus pulex*	10.0—0.03	from the stream	2	24h — 11.49	24h — 5.45	24h — below 0.311 48h — 2.5	alkaline reaction
8 IV 76	*Lebistes reticulatus*	10.0—0.03	aquarium water	2	—	—	24h — 0.311 72h — 0.15	alkaline reaction
9 IV 76	*Lebistes reticulatus*	160.0—20.0	aquarium water	2	—	—	toxicity threshold below 20 ml/dm^3	after preliminary neutralization still alkaline

12 IV 76	*Gammarus pulex*	150.0—6.44	from the stream	1.3	—	—	toxicity threshold below 6.44 ml/dm³	after preliminary neutralization still alkaline
21 IV 76	*Gammarus pulex*	500.0—47.1	from the stream	1.3	24h — 208.5 48h — 148.5	—	24h — 175.0 48h — 103.6	neutralized wastes
26 IV 76	*Lebistes reticulatus*	105.26—60.18	aquarium water	1.15	—	—	toxicity threshold below 105 ml/dm³	neutralized wastes
26 IV 76	*Gammarus pulex*	280.0—60.18	from the stream	1.15	24h — 227.8	24h — 219.6	24h — 105.2	neutralized wastes
27 IV 76	*Gammarus pulex*	280.0—60.18	from the stream	1.15	24h — 155.1	24h — 130.3	24h — 105.26	neutralized wastes
27 IV 76	*Lebistes reticulatus*	105.26—60.18	aquarium water	1.15	—	—	24h — 105.2 48h — 91.5	neutralized wastes
27 IV 76	*Daphnia magna*	105.26—60.18	aquarium water	1.15	—	—	24h — 105.2 48h — 74.59	neutralized wastes

in nutrients solution as well as in aquarium water. In the concentrations lower than 10 ml/dm^3 the blooms of algae (green algae) were started.

Assuming the safety factor equal to 0.1 of the $PC_{50/48}$ value, the permissible concentration of Rokryl TW-3 in the receiving body water amounted to 3.2 ml/dm^3 (table 4). To this end the compound introduced into the receiving body should be diluted with river water in 1:312 ratio. Such a concentration of this compound should not exert a negative effect on *L. minor*, since stimulation of plant mass increment has been observed at higher concentrations of this compound (12.5-25.0 ml/dm^3).

It has been stated that the values of LC_{50} and PC_{50} varied within 130.3-227.8 ml/dm^3 after 24 and 48 hours, while threshold concentrations varied from 74.6 for *D. magna* (after 48 hours) to 175.0 ml/dm^3 for *G. pulex* (after 24 hours).

Safe and permissible concentrations of the combined wastes in river water should range within 13-23 ml/dm^3 (wastes should be diluted in 1:77 ratio) [1]. Such a concentration stimulates the growth of *L. minor* and green algae.

Estimation of the degree of the wastewater toxicity was based on the analyses of neutralized wastewater (table 5).

6. CONCLUSIONS

The experiments performed lead to the following conclusions:

1. Degradation of acrylates expressed in reduced values of BOD, COD and BOD_5 proceeded efficiently and these substances may be regarded as biodegradable.

2. Basing on the number of organisms in the activated sludge, it has been stated that the most advantageous conditions for their growth occurred during biodegradation of the combined wastes.

3. A high degree of pollutant removal occurring in the experimental chambers as well as positive estimation of the composition of the activated sludge biocenosis indicate the positive effect of acrylates on the activated sludge activity. It seems that acrylates become a nutrient due to nitrogen present in acrylate resin.

4. The values of permissible concentrations of the particular substances are as follows: Rokryl SW-9 — 0.4 ml/dm^3, Rokryl TW-3 — 3.2 ml/dm^3, neutralized combined wastes — 13.0 ml/dm^3.

REFERENCES

[1] Collective work, *Informator Branży Chemicznych Środków Pomocniczych*, Zrzeszenie Producentów Środków Pomocniczych.

[2] HEBROWSKA A., MAJEWSKI R., RZEWUSKA E., *Ocena stopnia toksyczności substancji Rokryl SW-9*,

Rokryl TW-3 i ścieków produkcyjnych akrylanowych w odniesieniu do biocenozy środowiska wodnego (typescript), Instytut Kształtowania Środowiska, Wrocław 1976.
[3] JANKOWSKI M., *Badania nad technologią postępowania ze ściekami z wytwórni Roskoli i Rokryli*, Biprowod. V-VI, 1976.
[4] ŁUKJANIENKO W. J., *Toksykologia ryb*, PWRiL, Warszawa 1974.
[5] MASANOBU T., MAKOTO S., KAZIYI F., *Treatment of wastewater containing acryl resins*, Japan kokai 7455, 152; 29 May 1974, p. 2.
[6] MASANOBU T., MAKOTO S., KAZUSKI F., *Treatment of wastewater containing oils and antifoaming agents*, Japan kokai 7455, 155; 29 May 1974, p. 6.
[7] *Polska Norma PN-72 C-04610*, arkusz 03.
[8] *Polska Norma PB-72 C-04610*, arkusz 04.
[9] ŚWIĘTOCHOWSKI B., SKOWROŃSKA M., ŻURAWSKI M., *Studia nad działaniem na środowisko herbicydów dawanych na gleby*, II. *Modyfikacja metody biologicznej oceny zakażenia gleby Simazinem*, Zesz. Nauk. WSR, Wrocław 15 (46) (1962), pp. 83-89.
[10] U.S. National Technical Advisory Committee, *Report of National Techn. Adv. Com. on Water Quality Criteria to the Secretary of the Interior U.S.*, Fed. Wat. Poll. Control Adm., Wash. D.C., 1968, pp. 1-234.
[11] WIERZBICKI T., PIETRZYK H., *Próby biodegradacji ścieków z produkcji kwasu akrylowego i akrylanów*, Materiały Konferencji Nauk.-Techn. „Problemy oczyszczania ścieków przemysłowych", Kraków 1972.

OCENA TOKSYCZNOŚCI ORAZ PODATNOŚCI NA ROZKŁAD BIOLOGICZNY ŚCIEKÓW Z PRODUKCJI POLIMERÓW AKRYLOWYCH

Przeprowadzono badania nad określeniem toksyczności ścieków pochodzących z produkcji polimerów akrylowych — rokryli oraz określono możliwości rozkładu tych związków osadem biologicznym.

Stwierdzono, że akrylany są podatne na rozkład biologiczny wyrażony obniżeniem tlenowych wskaźników zanieczyszczeń.

Wydaje się, że akrylany wywierają korzystny wpływ na pracę osadu czynnego, co można prawdopodobnie tłumaczyć obecnością azotu z żywicy akrylanowej.

Największą liczbę organizmów w osadzie czynnym stwierdzono podczas oczyszczania ścieków oddziałowych z produkcji wszystkich rodzajów akrylanów. Do badania toksyczności ścieków zastosowano organizmy wodne: *Lebistes reticulatus*, *Gammarus pulex*, *Daphnia magna* oraz *Lemna minor*. Określono stężenia progowe oraz wartości LC_{50} i PC_{50} po 24 i 48 godzinach obserwacji. W odniesieniu do *L. minor* ustalono strefę śmierci roślin i hamowania przyrostu ich zielonej masy.

W oparciu o wyniki badań toksyczności ustalono wartości dopuszczalnych stężeń ścieków z produkcji akrylanów w środowisku wodnym.

ZUR BEWERTUNG DER TOXIZITÄT UND DER ABBAUBARKEIT VON ABWASSERINHALTSSTOFFEN AUS DER HERSTELLUNG VON AKRYLPOLYMEREN

Durchgeführt wurden Untersuchungen zur Bestimmung der Toxizität der Abwässer aus der Herstellung von Akryl-Rokryl-Polymeren sowie über deren Abbau mittels Belebtschlamm.

Anhand der Versuche kann man behaupten, daß Akrylate dem biochemischen Abbau zugänglich sind. Allem Anschein nach, wirken Akrylate auf den Belebtschlamm günstig ein, was durch die Anwesenheit von Stickstoff aus dem Akrylatharz erklärbar wäre.

Das massenhafte Vorkommen von Mikroorganismen im Belebtschlamm war bei der Reinigung von Abteilungsabwässer bei der Herstellung von allen Akrylatarten feststellbar.

Zur Bewertung der Toxizität dieser Abwässer wurden folgende Organismen verwendet: *Lebistes reticulatus*, *Gammarus pulex*, *Daphnia magna* und die Wasserpflanze *Lemna minor*. Festgelegt wurden Schwellenwerte sowie LC_{50} — und PC_{50} — Werte nach 24 und 48 Stunden Einwirkzeit. Für *Lemna minor* wurde die Sterbegrenze für Pflanzen und die Hemmung des Wachstums der grünen Masse erkannt.

Anhand der Versuche wurden für Gewässer die Konzentrationsgrenzen der Abwässer aus der Akrylatherstellung festgelegt.

ОЦЕНКА ТОКСИЧНОСТИ, А ТАКЖЕ ПОДАТЛИВОСТИ НА БИОЛОГИЧЕСКОЕ РАЗЛОЖЕНИЕ СТОЧНЫХ ВОД ОТ ПРОИЗВОДСТВА АКРИЛОВЫХ ПОЛИМЕРОВ

Проведены исследования по определению токсичности сточных вод, происходящих от производства акриловых полимеров — рокрилов, а также определены возможности разложения этих соединений биологическим илом.

Отмечено, что акрилаты податливы на биологическое разложение, выраженное снижением кислородных показателей загрязнений. Кажется, что акрилы оказывают благоприятное влияние на работу активного ила, что можно вероятно объяснить наличием в них азота из акрилатной смолы.

Наибольшее число организмов в активном иле обнаружено во время очистки цеховых сточных вод от производства всех видов акрилатов. Для испытания токсичности сточных вод были применены водные организмы: *Lebistes reticulatus*, *Gammarus pulex*, *Daphnia magna*, а также *Lemna minor*. Определены пороговые концентрации, а также значения LC_{50} и PC_{50} после 24 и 48 часов наблюдений. По отношению к маленькой ряске была определена зона смерти растений и торможения прироста зелёной массы.

На сонове результатов исследований токсичности были установлены значения допускаемых клицентраций сточных вод от производства акрилатов в водной среде.