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BIODEGRADABILITY OF MUNICIPAL WASTEWATER ORGANIC CONTAMINANTS

Biodegradation of the organic contaminants in the municipal wastewater of Opole after conventional treatment as a result of aeration is presented. Rate coefficient k_1 and velocity of reaction V have been evaluated on the basis of Streeter–Phelps first order equation. Reduction of COD, TOC and BOD_5 during aeration process and indices of pollution to BOD_5 ratio were investigated. Correlation between kinetic parameters and COD, TOC, BOD_5 removal percent and the factor determined as pollution indices to BOD_5 ratio have been defined.

1. INTRODUCTION

The dynamics of changes occurring in polluted surface water is manifested in its self-purification ability. Self-purification is a complex of natural physical, chemical and biological processes in which organic substances are transformed into simpler forms, the oxygen required for these reactions is uptaken from water and atmosphere with cooperation of microorganisms.

The efficiency of self-purification process depends on the accompanying physical, chemical and biological factors of which water temperature, degree of oxygenation, volume and rate of flow, turbulence, kind and concentration of pollutants, their biochemical oxidation ability, presence of toxic substances, composition and the number of organisms living in the river are of special importance [9]. The review of the previous results of studies on self-purification of Polish rivers [4] has shown that the degree of loading with organic matter and the kind of introduced contaminants are the main factors affecting the intensity of self-purification. Biodegradability of wastewaters depends in a considerable degree on their kind and the degree of their treatment [8]. Hence, it is necessary to evaluate the biodegradation kinetics of pollutants introduced to the receiving water bodies and to determine the coefficient

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characterizing the self-purification process. The latter can be determined either by a direct analysis of biodegradation rate k_1 indirectly considering the parameter characterizing the degradation rate in relation to BOD and COD tests and to organic carbon concentrations.

The curves representing the concentration of dissolved oxygen and its consumption serve as the numerical evaluation of waters self-purification process, according to the oxygen criterion [9], [18]. In examining the rate of biochemical oxidation of organics in wastewater and surface water, as well as in modelling water systems, the basic Streeter–Phelps equation is most frequently applied, assuming that the changes of biochemical oxygen demands (COD) follow the equation of first order reaction [2], [5], [6], [10], [14], [19]

$$y_t = L_0(1-e^{-kt}) \tag{1}$$

where:

y_t — BOD in time t, mg/dm^3,
L_0 — final BOD, mg/dm^3,
k — reaction rate, d^{-1}.

There is a number of papers in which attempts are made to evaluate pollution biodegradation and to model the water quality taking into consideration higher reaction orders of the organic matter decomposition [6], [14], [16], [21]. For instance, attempts were made to use the modified first order equation in determining the rate constant of BOD changes, having assumed multi-order reactions ranging from 1 to 4 [6]. The alternative model, in which the second order reaction is included, is the one in which the rate of organic matter decay is proportional to the second power of concentration [20]:

$$Yt = \frac{L_0^2 Kt}{1+L_0 Kt}. \tag{2}$$

All the quantities are the same as those in equation (1) except for the constant K, expressed in (mg/dm^3)$^{-1}t^{-1}$.

The purpose of the paper is to evaluate the degree of biodegradation by determining the coefficient characterizing the decomposition of pollutants in the municipal wastewater depending on the degree of its treatment. The sewage-treatment plant in Opole is an example.

In the so-far-made studies on the kinetics of the self-purification process in Polish rivers and on determining the coefficient characterizing this process, Streeter–Phelps equation has been used [4], [9]. Hence, the biodegradation rate of organic pollutants in wastewater was calculated by applying the same method. Such a procedure enables to compare and possibly to correct the coefficients of self-purification intensity by the predicted degradability of organic pollutants introduced with municipal wastewater into water receivers.

The results of experiments may be a contribution to complex research works on the mathematical modelling of the quality of Polish water systems which would make it possible to evaluate and forecast the changes of water quality as well as rational management of the water resources. The experiments were performed in 1981–1983 within the Research Development Governmental Programme PR-7 "The modelling and utilization of water resources" coordinated by the Institute of Meteorology and Water Management in Warsaw. This programme included the 07 trend "Foundations of comlex management of the Odra water resources", coordinated by the Silesian Institute in Opole.

2. SCOPE AND DIRECTIONS OF THE RESEARCH

The investigations included the municipal wastewater from the sewage treatment plant in Opole after the subsequent phases of conventional treatment, i.e., raw wastewater (grid), mechanically treated wastewater (primary settling tank) and biologically treated wastewater on the activated sludge (secondary settling tank).

Wastewaters in the Odra river include the municipal and industrial ones. The most troublesome industrial wastewaters constitute 19% [22] of the whole. 90% to 95% of municipal wastewaters undergo treatment. Raw wastewaters are characterized by average pollution indices BOD_5 — 215 mg O_2/dm^3, oxidation indices — 105 mg O_2/dm^3 and adequately purified — 83 mg O_2/dm^3 and 38 mg O_2/dm^3, respectively. The experiments performed aimed at determining coefficients characterizing biochemical changes which affect organic contaminants in water with the presence of oxygen. In relation to this, on the basis of BOD studies, BOD curves were made and the average value characterizing biodegradation kinetics was calculated.

After testing the changes of chosen pollution indices, as a result of aeration, removal state was determined as well as coefficients expressed by indices to BOD ratio. Correlation among these values and parameters of decomposition kinetics k_1 and V was determined (k_1 is the rate coefficient in d^{-1}, V is the rate of decomposition coefficient in mg/dm^3/d).

3. METHODS OF THE RESEARCH

Studies of BOD were conducted in an apparatus Sapromat A6, made by Voith. It recorded results of BOD changes every hour. On the basis of the results obtained during five days the values characterizing biodegradiation rate of organic pollutants were calculated using a programme for digital computer in the Algol 1900 language. The programme, constructed in the Wrocław Unit of the Institute of Meteorology and Water Management, made it possible to calculate the reaction rate constant

k_1 [1] and reaction rate V [4] of the BOD changes as a function of time [12]

$$f_{j(t)} = La_j(1-10^{-k}j(t)), \tag{3}$$

hence

$$V_j = La_j k_j 10^{-kj} \ln 10 \tag{4}$$

where:

V_j — reaction rate in the final moment of the j-th day, mg/dm^3/d,
La_j — asymptotic value of BOD, mg/dm^3,
k_j — value of k parameter in the j-th day, d^{-1},
j — successive day number.

The five day period of testing corresponded to the first degradation phase of pollutants [2], [15], i.e., to biochemical reactions of carbon organic compounds. The changes in BOD, COD, oxygen consumption and the content of organic carbon due to 6, 24, 48, 72 96 and 120 h aeration have been examined, applying two variants of the principle method. In variant I the experiments were performed in Sapromat apparatus which assured constant temperature and mixing conditions. In variant II wastewater in laboratory bulbs was intensely aerated by means of aquarium pumps in the ambinet conditions. In samples prior to and after the given oxidation time, BOD$_5$, COD, oxygen consumption, organic carbon concentration and suspended matter were determined (the latter only in the non-aerated sample). In the tests performed in Sapromat (variant I) the values of BOD were read for each previously assumed period of oxidation (BOD$_1$, BOD$_2$, etc). The samples were analysed immediately after they had been taken (or fixed) according to the required standards: PN-74/C-04578 Polish Standards.

4. DISCUSSION OF RESULTS

The results discussed are given for both variants of experiments performed in Sapromat (oxygenation) and in laboratory bulbs (intensive aeration).

Figure 1 shows a typical course of BOD changes for raw wastewater after its mechanical and biological treatment and biodegradation. The parameters of biodegradation kinetics k_1 and V, calculated from the data set, for the 2 and 5 days are shown in table 1. Besides the typical period of 120 hours, the first 48 h period was taken as characteristic, since basic pollution removal occurs within 48 to 72 hours (see fig. 2, variant I and fig. 3, variant II). The average reaction rate constant k_1 for raw and mechanically treated wastewater for a 5 day period ranges from 0.25 d^{-1} to 0.27 d^{-1} and that for biologically treated wastewater amounts to 0.033 d^{-1}.

The kinetics of changes occurring in the examined wastewater is more distinctly characterized by the reaction rate V. The average value of V for raw wastewater

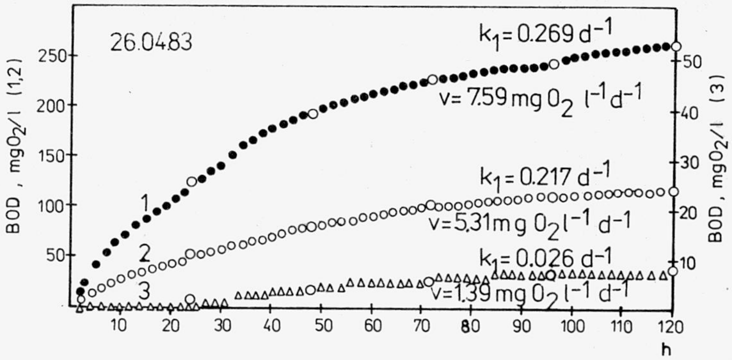

Fig. 1. Biochemical oxygen demand

1 — raw wastewater, 2 — mechanically treated wastewater, 3 — biologically treated wastewater

Table 1

Characteristic parameters of the biodegradation rate

Rate parameters	Raw wastewater		Mechanically treated wastewater		Biologically treated wastewater	
	2 days	5 days	2 days	5 days	2 days	5 days
reaction rate coefficient k_1 day^{-1}						
average	0.28	0.25	0.39	0.29	0.065	0.035
minimum	0.141	0.159	0.110	0.122	0.013	0.014
maximum	0.495	0.327	0.785	0.483	0.191	0.087
probability						
50%	0.27	0.25	0.33	0.27	0.052	0.033
90%	0.40	0.30	0.64	0.43	0.155	0.075
reaction rate V mg $O_2/dm^3/d$						
average	61.04	12.78	17.85	4.31	1.13	1.75
minimum	30.91	6.13	6.10	1.86	0.05	0.25
maximum	130.01	41.70	29.28	18.71	2.97	8.77
probability						
50%	57.0	12.0	20.0	4.40	1.43	1.30
90%	126.5	32.0	32.0	11.0	2.95	3.60

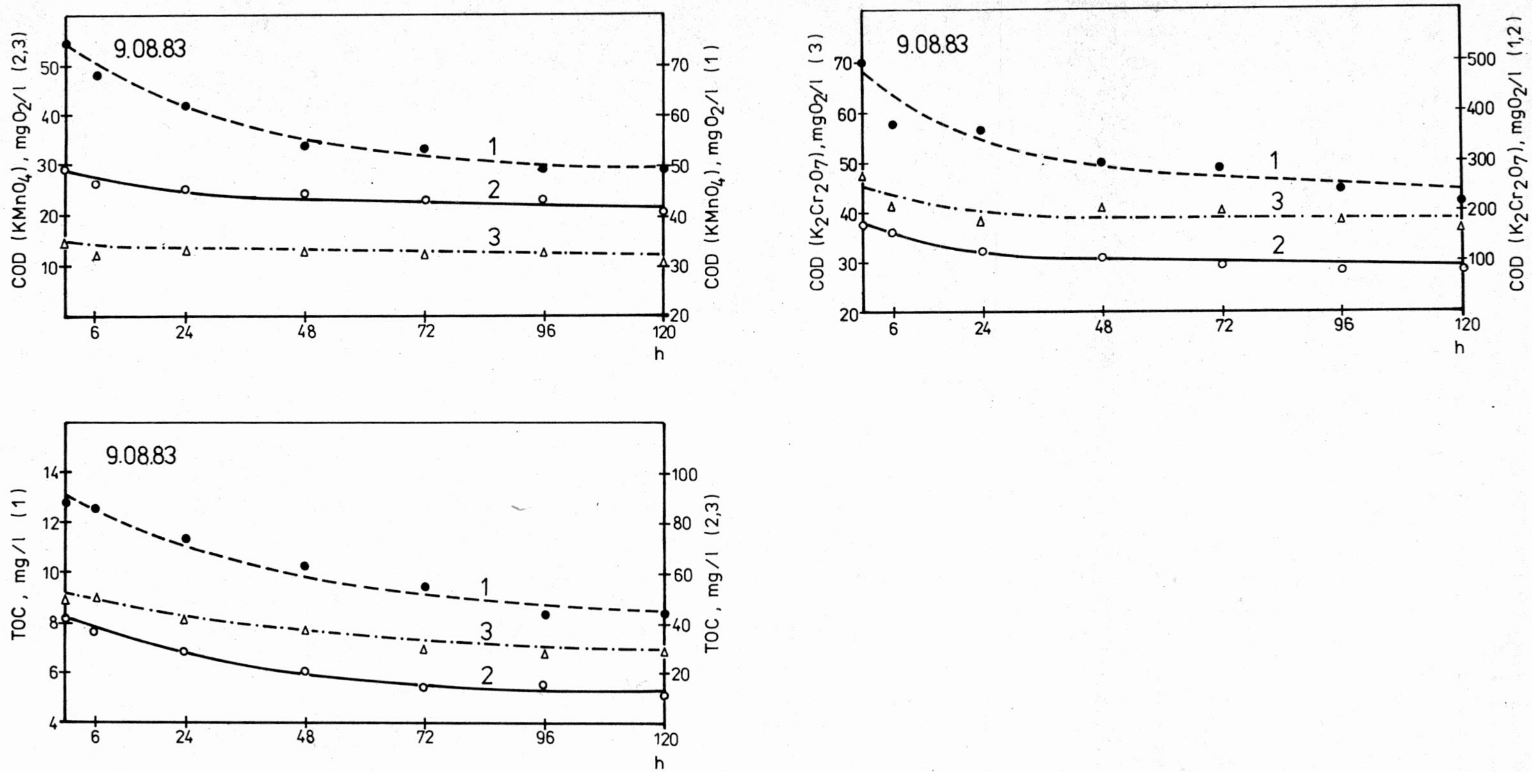

Fig. 2. COD and TOC versus oxidation time

for explanations see fig. 1

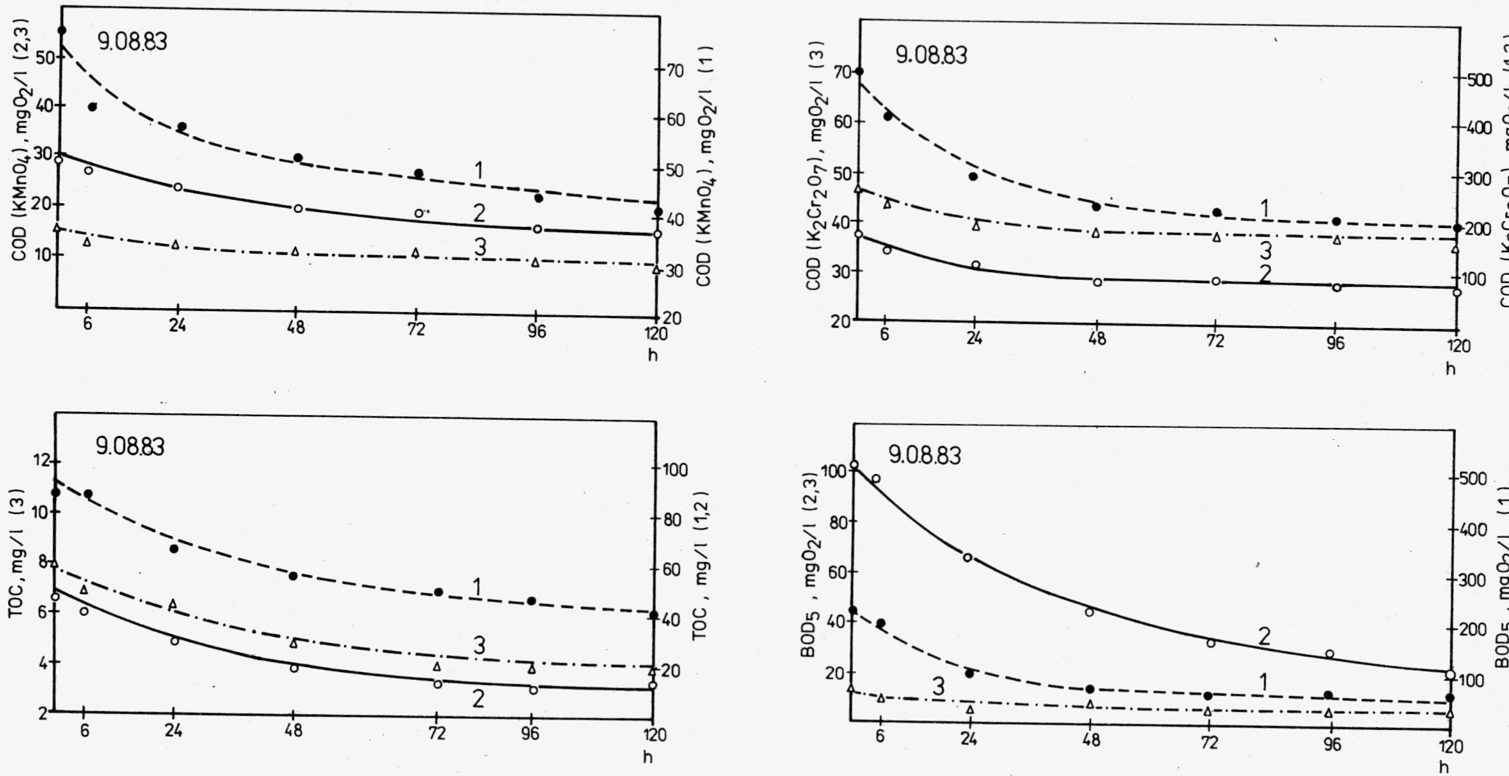

Fig. 3. COD, TOC and BOD_5 versus aeration time

for explanations see fig. 1

Table 2

Characteristic results of the pollutions removal percent

Reduction, %	Raw wastewater		Mechanically treated wastewater		Biologically treated wastewater	
	2 day aeration	5 day aeration	2 day aeration	5 day aeration	2 day aeration	5 day aeration
COD ($K_2Cr_2O_7$)						
values: minimum	25.6	36.6	32.4	50.0	12.8	16.3
maximum	50.0	65.7	52.8	63.8	33.3	37.5
avervge	40.6	54.9	43.5	55.5	23.5	28.6
probability						
50%	39.0	54.0	42.0	54.0	23.0	29.0
90%	52.0	64.0	55.0	63.0	45.5	45.0
COD ($KMnO_4$)						
values: minimum	20.5	27.6	15.5	24.1	5.3	10.5
maximum	47.5	72.5	41.5	52.5	31.0	33.3
average	30.3	42.0	30.0	40.8	21.4	24.7
probability						
50%	30.0	40.0	29.0	39.0	16.8	20.0
90%	44.0	63.0	44.5	55.0	32.2	32.5
TOC						
values: minimum	35.5	48.3	29.1	41.9	11.6	14.3
maximum	55.3	87.7	53.8	69.7	47.4	50.0
average	42.6	63.4	46.4	59.6	26.3	31.7
probability						
50%	46.0	65.0	50.0	64.0	23.0	32.0
90%	60.0	84.0	60.0	75.0	42.0	51.5

equals 12 $mg/dm^3/d$, and for mechanically and biologically treated wastewaters — 4.4 and 1.3 $mg/dm^3/d$, respectively (table 1).

The obtained results are consistent with the basic principle of kinetics, i.e., the reaction rate depends on substrates concentration [11].

Degree of pollution removal expressed in COD, oxygen consumption, organic carbon content during 5 day oxygenation (variant I, table 2 and variant II, table 3) for raw wastewater and after its mechanical treatment, referred to average values, reached 52–54%, and after biological treatment 28%. During the first two days the average reduction of the selected indices with respect to the average reduction during 5 days amount to 76%. By expressing the results of biodegradation process in pollution indices to BOD ratio, wastewater could be classified depending on the degree of its pollution.

The experimental results given in table 4 (variant 1) and table 5 (variant II) show that during the characteristic periods of aeration, the coefficients expressed by COD, oxygen consumption and organic carbon to BOD_5 ratios for raw wastewater and

Table 3

Characteristic results of the pollutions removal percent

Reduction, %	Raw wastewater		Mechanically treated wastewater		Biologically treated wastewater	
	2 day aeration	5 day aeration	2 day aeration	5 day aeration	2 day aeration	5 day aeration
COD ($K_2Cr_2O_7$)						
values: minimum	38.8	51.1	40.6	50.4	9.1	15.2
maximum	54.2	68.3	56.5	74.3	35.5	48.8
average	48.5	61.0	48.5	61.3	22.9	31.8
probability						
50%	50.0	62.0	49.0	62.0	23.0	29.0
90%	56.0	71.0	55.5	72.0	36.5	49.0
COD ($KMnO_4$)						
values: minimum	18.9	31.6	27.7	38.6	3.81	7.70
maximum	36.1	45.7	42.4	56.5	30.2	34.8
avervge	29.4	38.0	34.0	44.3	15.4	21.3
probability						
50%	30.5	40.0	34.0	43.0	13.8	18.3
90%	45.0	56.0	42.0	53.0	30.0	35.5
TOC						
values: minimum	34.5	45.5	34.2	48.3	15.8	21.1
maximum	55.5	65.0	57.1	77.5	50.0	59.5
average	41.0	53.2	47.5	58.5	26.3	43.0
probability						
50%	42.0	55.0	50.0	58.5	29.0	40.0
90%	60.0	73.0	63.0	72.0	52.0	59.0
BOD_5						
values: minimum	44.6	57.1	48.1	69.2	14.9	18.8
maximum	77.0	88.7	75.0	87.1	50.0	57.1
average	62.5	77.3	63.4	77.5	28.6	34.0
probability						
50%	63.0	79.5	64.0	78.0	27.0	32.0
90%	74.0	87.0	72.0	86.0	49.0	56.0

after its mechanical treatment are low and slightly differ from one another, being higher after its biological treatment. For raw and mechanically treated wastewaters the mean value of such a coefficient (table 4) is 6 times higher than for a biologically treated wastewater. E.g., for the selected ratios of COD to BOD_5, oxygen consumption to BOD_5 and C_{org} to BOD_5 it is on average 4.3 times, 7.7 times (raw wastewater), 6.5 times (mechanically treated wastewater), C_{org} to BOD_5 7.4 times (raw wastewater), 5.6 times (mechanically treated wastewater) higher than the corresponding average values calculated for biologically treated wastewater. In variant II (table 5) the average values of coefficients characterizing raw and

Table 4

Characteristic data for the coefficients expressed by the rate of pollution indices to BOD

	Raw wastewater		Mechanically treated wastewater		Biologically treated wastewater	
	Probability					
	50%	90%	50%	90%	50%	90%
Cr–$COD_{(0)}/BOD_{5(0)}$	1.70	2.10	1.80	2.20	4.60	21.00
Mn–$COD_{(0)}/BOD_{5(0)}$	0.24	0.33	0.30	0.44	1.50	5.00
$TOC_{(0)}/BOD_{5(0)}$	0.31	0.58	0.40	0.66	1.10	8.00
Cr–$COD_{(0)}/BOD_2$	2.40	3.20	2.50	3.50	10.50	55.00
Mn–$COD_{(0)}/BOD_2$	0.33	0.46	0.42	0.60	3.40	9.50
$TOC_{(0)}/BOD_2$	0.42	0.80	0.52	0.83	3.30	15.00
Cr–$COD_{(2)}/BOD_2$	1.50	2.70	1.40	1.90	7.70	36.00
Mn–$COD_{(2)}/BOD_2$	0.26	0.32	0.29	0.38	2.30	9.50
$TOC_{(2)}/BOD_2$	0.23	0.37	0.29	0.44	2.40	9.00
Cr–$COD_{(5)}/BOD_{5(0)}$	0.80	0.90	0.80	1.00	3.60	13.00
Mn–$COD_{(5)}/BOD_{5(0)}$	0.16	0.19	0.17	0.25	1.00	4.40
$TOC_{(5)}/BOD_{5(0)}$	0.11	0.20	0.17	0.27	0.95	4.20
Cr–$COD_{(2)}/BOD_{5(0)}$	1.00	1.25	1.00	1.40	5.00	20.00
Mn–$COD_{(2)}/BOD_{5(0)}$	0.18	0.23	0.21	0.28	1.20	3.10
$TOC_{(2)}/BOD_{5(0)}$	0.16	0.27	0.20	0.30	1.05	5.70

Index in parantheses is aeration time in days.
Cr–COD is dichromate COD, and Mn–COD is permanganate COD.

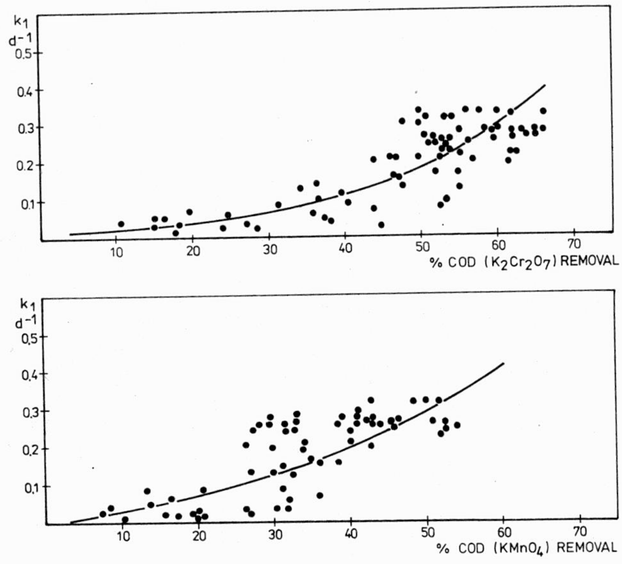

Fig. 4. Reaction rate coefficient constant k_1 versus the degrees of COD removals

Table 5

Characteristic data for the coefficients expressed by the rate of pollution indices to BOD_5

	Raw wastewater		Mechanically treated wastewater		Biologically treated wastewater	
	Probability					
	50%	90%	50%	90%	50%	90%
$Cr–COD_{(0)}/BOD_{5(0)}$	2.20	2.90	2.40	3.60	4.70	8.20
$Mn–COD_{(0)}/BOD_{5(0)}$	0.29	0.38	0.36	0.64	1.40	2.15
$TOC_{(0)}/BOD_{5(0)}$	0.46	0.94	0.62	1.00	1.60	4.80
$Cr–COD_{(5)}/BOD_{5(0)}$	0.82	1.20	0.90	1.35	2.90	4.40
$Mn–COD_{(5)}/BOD_{5(0)}$	0.18	0.25	0.20	0.31	1.00	1.95
$TOC_{(5)}/BOD_{5(0)}$	0.19	0.33	0.23	0.40	0.90	2.70
$Cr–COD_{(5)}/BOD_{5(5)}$	3.80	10.00	3.80	7.00	5.00	8.30
$Mn–COD_{(5)}/BOD_{5(5)}$	0.75	1.52	0.90	1.48	1.80	3.00
$TOC_{(5)}/BOD_{5(5)}$	0.85	2.00	1.15	1.80	1.80	2.95
$Cr–COD_{(0)}/BOD_{5(2)}$	5.80	9.50	6.20	8.50	8.40	13.50
$Mn–COD_{(0)}/BOD_{5(2)}$	0.90	1.25	0.97	1.42	2.10	3.20
$TOC_{(0)}/BOD_{5(2)}$	1.30	2.50	1.60	2.30	2.60	6.10
$Cr–COD_{(2)}/BOD_{5(2)}$	3.10	4.50	3.25	4.20	5.20	7.50
$Mn–COD_{(2)}/BOD_{5(2)}$	0.60	0.88	0.66	0.90	1.75	2.70
$TOC_{(2)}/BOD_{5(2)}$	0.70	1.25	0.83	1.15	2.00	3.25
$Cr–COD_{(2)}/BOD_{5(0)}$	1.12	1.60	1.20	1.80	3.40	5.20
$Mn–COD_{(2)}/BOD_{5(0)}$	0.21	0.29	0.25	0.40	1.10	2.00
$TOC_{(2)}/BOD_{5(0)}$	0.23	0.43	0.28	0.56	1.10	3.30

Index in parantheses is aeration time in days.
Cr–COD is dichromate COD, and Mn–COD is permanganate COD.

mechanically treated wastewater, referred to those for biologically treated water, are higher. Thus COD to BOD_5 ratio is 2 times higher for both the kinds of wastewater, oxygen consumption to BOD_5 for raw and mechanically treated wastewaters 2.1 and 3.4 times higher, respectively, for C_{org} to BOD_5 ratio being correspondingly 3.3 and 2.7 times higher.

Based on the curves presented in figs. 4–6 and representing some of the analysed correlations between the parameters of the kinetics of biodegradation and the ratios of the separate indices to biochemical oxygen demand, the quantities characteristic of these relations can be determined. According to literature data [2] and the obtained results biodegradation rate constant k_1 for raw wastewater does not exceed 0.3/d. Then the degrees of COD, oxygen consumption, C_{org} and BOD_5 removal are smaller than 60%, 52%, 78%, and 83%, respectively, while the COD_5 to $BOD_{5(0)}$, oxygen consumption$_{(5)}$ to $BOD_{5(0)}$ and $C_{org(5)}$ to $BOD_{5(0)}$ ratios are higher than 0.64, 0.12 and 0.04, respectively.

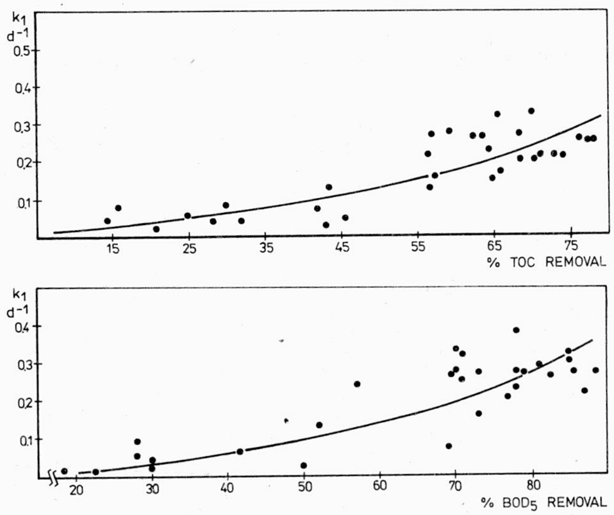

Fig. 5. Reaction rate coefficient constant k_1 versus the degrees of TOC and BOD_5 removals

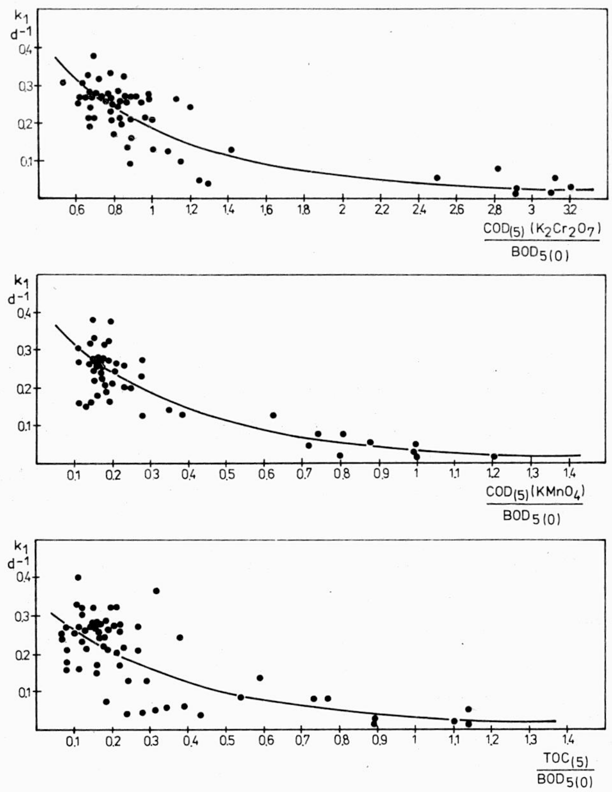

Fig. 6. Reaction rate coefficient constant k_1 versus the ratios of COD and TOC (after five days of aeration) to BOD_5 (non-treated samples)

When k_1 exceeds the statistically determined mean value, the removal degree of indices after 5 day aeration will increase and the coefficients expressed by indices to BOD_5 ratio will decrease with the increasing values of k_1. For the biologically treated wastewater, for which the average value of k_1 does not exceed 0.1/d, the removal degrees of COD, oxygen consumption, C_{org}, BOD_5 are smaller than 39%, 26%, 39% and 50%, respectively, while the COD_5 to $BOD_{5(0)}$, oxygen consumption to $BOD_{5(0)}$ and C_{org} to $BOD_{5(0)}$ ratios are higher than 1.48, 0.55 and 0.5, respectively. From the analysis of data given in tables 1–5 it follows that the degradation rate of pollutants and the percent of their removal with the degree of wastewater treatment decreases, while the indices to BOD ratios increase.

5. CONCLUSIONS

1. In order to forecast and evaluate the quality of water resources it seems advisable to extend the analyses of wastewater by including the parameters characterizing the kinetics of organic matter decomposition, i.e., degradation rate constant k_1, reaction rate V as well as to establish the coefficients expressed in the ratios of the selected pollution indices to BOD_5.

2. The transformations of organic matter expressed by a degree of COD, oxygen consumption, C_{org} concentration and BOD_5 reductions as well as the analyses of parameters of degradation kinetics show that most pollutants are subject to biodegradation during two or three days of aeration.

3. In the designing and future-oriented works concerning municipal wastewater of similar characteristics it would be possible to assume the reducing coefficient of 0.6 for raw and biologically treated ones. The applied multiplier will allow us to determine approximately the quantities of pollutants remaining in the municipal wastewater after its biodegradation.

4. Coefficients expressed by the ratio of pollution indices, after 5 day aeration, to BOD_5 of the non-treated sample characterize the degree of wastewater treatment.

In the case of raw and mechanically treated municipal wastewater for which the average values of k_1 amount to 0.25 d^{-1} and 0.27 d^{-1} the corresponding $COD_{(5)}$ to $BOD_{5(0)}$, oxygen consumption to BOD_5 and C_{org} to $BOD_{5(0)}$ ratios read from the plot are 0.76 and 0.70, 0.18 and 0.15, as well as 0.11 and 0.08, respectively. Analogical values for biologically treated wastewater of the average value of $k = 0.033$ d^{-1} are 2.66, 1.02, and 1.00, respectively.

5. With the proceeding decomposition of organic componds the biodegradability of substances remaining in the wastewater decreases, hence the value of k_1 decreases, while the COD to BOD_5 ratio distinctly increases.

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PODATNOŚĆ ZANIECZYSZCZEŃ ORGANICZNYCH WYSTĘPUJĄCYCH W ŚCIEKACH MIEJSKICH NA BIODEGRADACJĘ W ZALEŻNOŚCI OD STOPNIA ICH OCZYSZCZENIA

Przedstawiono wyniki badań nad biodegradacją zanieczyszczeń organicznych w ściekach miejskich po kolejnych etapach oczyszczania w oczyszczalni w Opolu. Po oznaczeniu BZT obliczono na podstawie równania Streetera–Phelpsa parametry k_1 i V określające szybkość degradacji. Określono stopień

redukcji wybranych wskaźników, tj. utlenialności, ChZT, węgla organicznego i BZT_5, w procesie napowietrzania. Spróbowano ustalić korelacje pomiędzy parametrami kinetyki a stopniem redukcji wskaźników zanieczyszczenia i współczynnikiem wyrażonym stosunkiem tych wskaźników do BZT_5 dla ścieków zależnie od stopnia ich oczyszczenia.

СПОСОБНОСТЬ К БИОДЕГРАДАЦИИ ОРГАНИЧЕСКИХ ЗАГРЯЗНЕНИЙ, ВЫСТУПАЮЩИХ В ГОРОДСКИХ СТОЧНЫХ ВОДАХ, В ЗАВИСИМОСТИ ОТ СТЕПЕНИ ИХ ОЧИСТКИ

Представлены результаты исследований способности к биодеградации органических загрязнений в городских сточных водах после очередных этапов очистки в очистной станции в Ополе. После обозначения БПК были вычислены параметры, определяющие быстроту деградации k_1 и V на основе уравнения Стритера–Фельпса. Исследована степень редукции избранных указателей, т.е. окисляемости, ХПК, органического угля и $БПК_5$ в процессе аэрации. Был предпринят опыт установления корреляции между параметрами кинетики и степенью редукции указателей загрязнения и коэффициентом, выраженным отношением этих указателей к $БПК_5$ для сточных вод в зависимости от степени их очистки.