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KINETICS OF AEROBIC, THERMOPHILIC STABILIZATION PROCESS OF CONCENTRATED ORGANIC SEWAGE

The analysis of the kinetics of aerobic, thermophilic stabilization of the condensed sewage has proved that various stages of this process can be represented by the zero, first or second orders of reactions according to the transformation of the constituents of the substrate examined.

In a large scale plant it is advisable to maintain the first phase of the process that corresponds to the zero reaction order for which the rate constant k takes the greatest values. These conditions may be satisfied in a steady-state process.

1. INTRODUCTION

Biodegradation processes of organic matter contained in sewage result from aerobic and anaerobic metabolic processes occurring under mesophilic or thermophilic conditions. Biodegradation takes, however, different courses depending on the kind of metabolic processes. Schematic course of biodegradation in aerobic conditions, according to MUDRACK [7], is shown in fig. 1.

This simplified scheme is presented in different forms by many authors, its substance, however, remains unchanged. Biodegradation processes are namely iniciated by aerobic bacteria and, being aimed at a) production of energy and b) synthesis of constituents of bacterial cells, proceeds in two directions. First process consists in oxidation and partial combustion of carbon and hydrogene resulting in CO_2 and H_2O, respectively. Second one consists in partial decomposition of organic compounds and the synthesis of new compounds.

The course of biodegradation in aerobic conditions depends on numerous factors [3]:

concentration of biodegradable organic matter,

temperature,

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concentration of microorganisms (i. e. number of microorganisms in a unit of volume),
kind of microorganisms,
physiological properties of microorganisms,
chemical composition of organic matter.

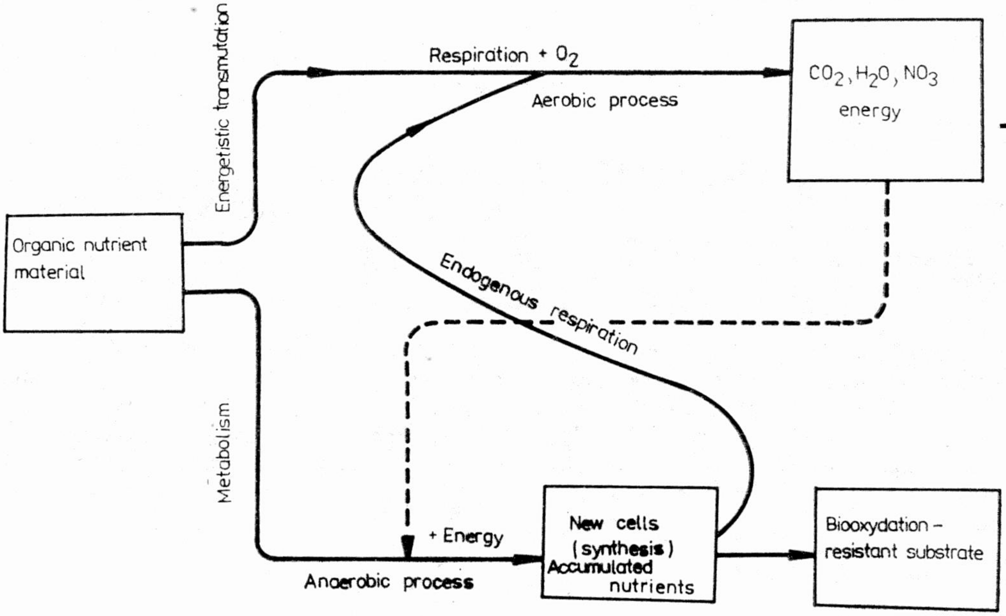

Fig. 1. Biodegradation of organic material under aerobic conditions

Rys. 1. Biodegradacja substancji organicznych w warunkach aerobowych

Ecto- and endoenzymes are the biocatalysts of organic matter oxidation; they accelerate or direct adequately the reactions proceeding within or outside the living cell. The enzymatic activity, i. e. the reaction rate, is mainly the function of temperature, pH, and the substrate concentration.

PÖPEL [8] in his research of fluid composting has stated that biodegradation reactions proceed according to the reactions of the 1st order. BRAUN [1] and Wilderer [11] have established that biochemical processes occurring in sewage can be interpreted according to the Michaelis-Menten equation

$$t = \frac{km}{V_{\max}} \ln \frac{L_0}{L_t} + \frac{L_0 - L_t}{V_{\max}} \tag{1}$$

where:

t — reaction time (days or hours),

km — constant of reaction rate corresponding to such a concentration of substrate L at which the value of reaction rate is equal to half of its limit value, i. e. $V_{\max}$,

L_0 — initial substrate concentration,

L_t — substrate concentration after the time t.

According to LOLL [4] the Michaelis-Menten equation can be transformed into equation of the 1st order, chiefly for a highly concentrated sewage containing a large number of easily biodegradable organic substances, that brings about self-heating of substrates and creates thermophilic conditions, hence increases reaction rate proceeding there. Then $(L_0-L_t)/V_{\max}$ takes a very small value and can be neglected.

If $V_{\max}/km$ in equation (1) is substituted with k_1, we obtain

$$t=\frac{1}{k_1}\ln\frac{L_0}{L_t}, \tag{2}$$

$$k_1\cdot t=\ln\frac{L_0}{L_t}, \tag{3}$$

$$e^{k_1\cdot t}=\frac{L_0}{L_t}, \tag{4}$$

hence

$$L_t=L_0e^{-k_1\cdot t}. \tag{5}$$

HARTMAN [2] has stated that the biodegradation process of mixed substrates, such as sewage, proceeds mostly (over 60%) according to the 1st order reactions and that the remaining part proceeds according to the 2nd order reactions following the equation

$$L_t=\frac{L_0}{L_0k_2t+1} \tag{6}$$

where k_2 is constant of reaction rate of the 2nd order.

Biodegradation processes depend not only on the substrates, but also on the "concentration", type and physiological properties of microorganisms inducing the above processes. As a result of aeration (supply of oxygen to aerobic systems), the number of bacteria increases. To define the bacterial growth in time MONOD [6] gave the following formula:

$$\frac{dx}{dt}=x\mu_{\max}\left(\frac{L}{k_s+L}\right) \tag{7}$$

where:

x — number or mass of bacterial cells,
$\mu_{\max}$ — maximum growth rate (d^{-1} or h^{-1}),
k_s — substrate concentration at the half of the maximum growth.

Having introduced the efficiency coefficient y defining the ratio of the cell mass produced to the mass of oxygen consumed

$$y=\frac{dx/dt}{dy/dt}, \tag{8}$$

we can calculate the rate of substrate loss:

$$\frac{dL}{dt} = -\mu_{\max}\frac{x}{y}\left(\frac{L}{k_s+L}\right). \tag{9}$$

If we assume that $k_s = k_m$, we will get

$$\frac{dL}{dt} = -\mu_{\max}\frac{x}{y}\left(\frac{L}{k_m+L}\right). \tag{10}$$

If we deal with concentrated sewage and with sludges stabilization, the process is the most efficient when carried out at the maximum logarithmic growth phase, connected with the maximum bacterial activity and according to the dispersed growth rule, i. e. under the conditions of dispersed bacteria growth.

McKINNEY's research [5] has confirmed the fact that the energy of bacteria is the highest at the phase of their logarithmic growth; that is why they do not flocculate, but overcoming even the adsorption forces they separate themselves from the existing suspended matter flocs and decaying bacterial cells. The observations of several dozen species of bacteria isolated from different sewage samples have shown that these microorganisms become a part of a floc only when they lack the energy to get out of it.

The decline in the cell energy leads to the domination of colloidal forces during the endogenous respiration phase. In thermophilic conditions all the processes both the metabolic ones as well as the bacterial reproduction are accelerated. The analysis of thermophilic growth at the optimum temperature has revealed that the reproduction begins almost immediately after the inoculation of the culture medium. The lag-phase is so short that it cannot be described analytically, whereas the course of logarithmic growth phase is more abrupt than in the case of mesophilic bacteria. Cell decay proceeds also very quickly being accompanied by autolytic process [9].

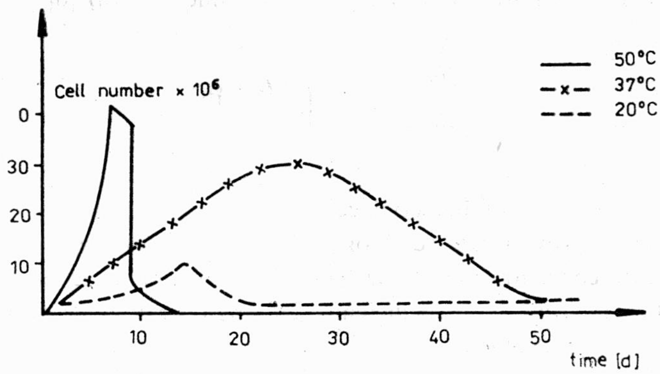

Fig. 2. Growth of thermophilic bacteria number

Rys. 2. Wzrost liczby bakterii termofilnych

This steep increase of the logarithmic phase and great activity of bacteria make it possible to shorten considerably the biodegradation time of highly concentrated sewage. The growth of thermophilic bacteria is presented in fig. 2.

In highly concentrated sewage the reaction rate is independent of the concentration and for the limit value, i. e. $V = V_{\max}$, it can be maintained for a long time. The maximum rate lasts until the most easily biodegradable substrate in the mixture of substrates contained in the sewage is depleted. Then, the general reaction rate diminishes and approximates the kinetics of reactions of the 1 st order.

The initial phase of biodegradation can be described mathematically by reactions of the 0 order:

$$L_t = L_0 - k_0 \cdot t \tag{11}$$

where k_0 is the constant reaction rate of the 0 order.

2. ANALYSIS OF THERMOPHILIC STABILIZATION OF CONCENTRATED SEWAGE ACCORDING TO THE ORDER OF REACTION. ESTABLISHING THE REACTION RATE IN PARTICULAR PHASES OF THE PROCESS

Equations of reactions of the 0, 1 st and 2nd orders were transformed in order to evaluate the results of research on stabilization of concentrated sewage under static conditions (batch operation) and allow us to determine the reaction rate constants k_0, k_1, k_2, as well as the load of pollution remaining after a time t, as compared with the input load.

Equations of the 0 order

$$L_t = L_0 - k_0 \cdot t / L_0,$$

$$\frac{L_t}{L_0} = 1 - \frac{k_0}{L_0} t, \tag{12}$$

where $L_t/L_0 = L$ (the residual load after a time t as compared to the input), and $k_0/L_0 = k'_0$, yield

$$L = 1 - k'_0 t. \tag{13}$$

Equations of the 1 st order

$$L_t = L_0 e^{-k_1 \cdot t} / L_0,$$

$$\frac{Lt}{L_0} = e^{-k_1 \cdot t}, \tag{14}$$

$$L = e^{-k'_1 \cdot t} \tag{15}$$

where $k_1 = k'_1$.

Equations of the 2nd order

$$L_t = \frac{L_0}{L_0 k_2 t+1} / L_0,$$

$$\frac{L_t}{L_0} = \frac{1}{L_0 k_2 t+1}, \tag{16}$$

$$L = \frac{1}{k_2' t+1} \tag{17}$$

where $k_2' = L_0 k_2$.

Diagrams (figs. 3–5) for evaluation of various reaction rate constants were based on the transformed equations. Then, it has been checked what values are, according to the order of reaction, assumed by the constants k_0, k_1, k_2 for a particular series of examinations. The course of the process is presented in tab. 1.

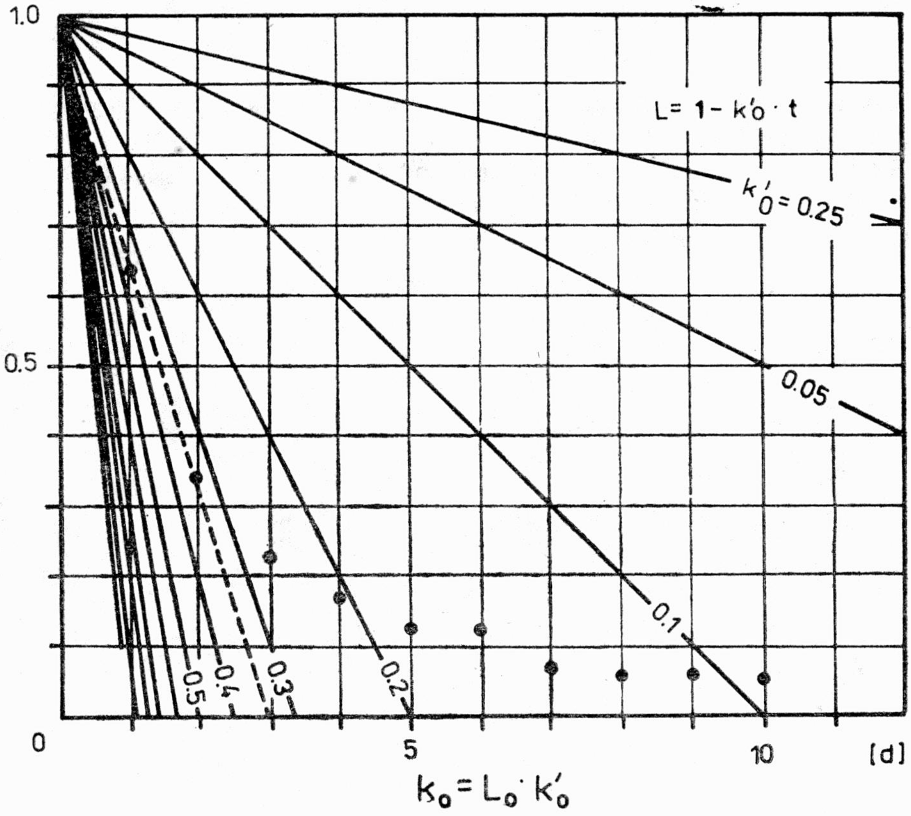

Fig. 3. Evaluation of rate constant k_0 (reaction of the zero order)

Rys. 3. Oszacowanie stałej szybkości k_0 (reakcja zerowego rzędu)

Table 1

Course of aerobic thermophilic stabilization of manure ($L_0 = 19.8$ g O_2/dm^3)
Przebieg procesu tlenowej stabilizacji termofilowej gnojowicy ($L_0 = 19.8$ g O_2/dm^3)

Time t	0	1	2	3	4	5	6	7	8	9	10
BOD_5 g O_2/dm^3	19.8	12.6	7.4	4.5	3.6	2.1	2.1	1.6	1.4	1.4	1.2
Load after time t referred to L_0	1	0.64	0.35	0.22	0.18	0.11	0.11	0.08	0.07	0.07	0.06
Activity of dehydrogenase μ MTF/dm^3	210	1890	1110	860	360	310	340	260	120	80	80

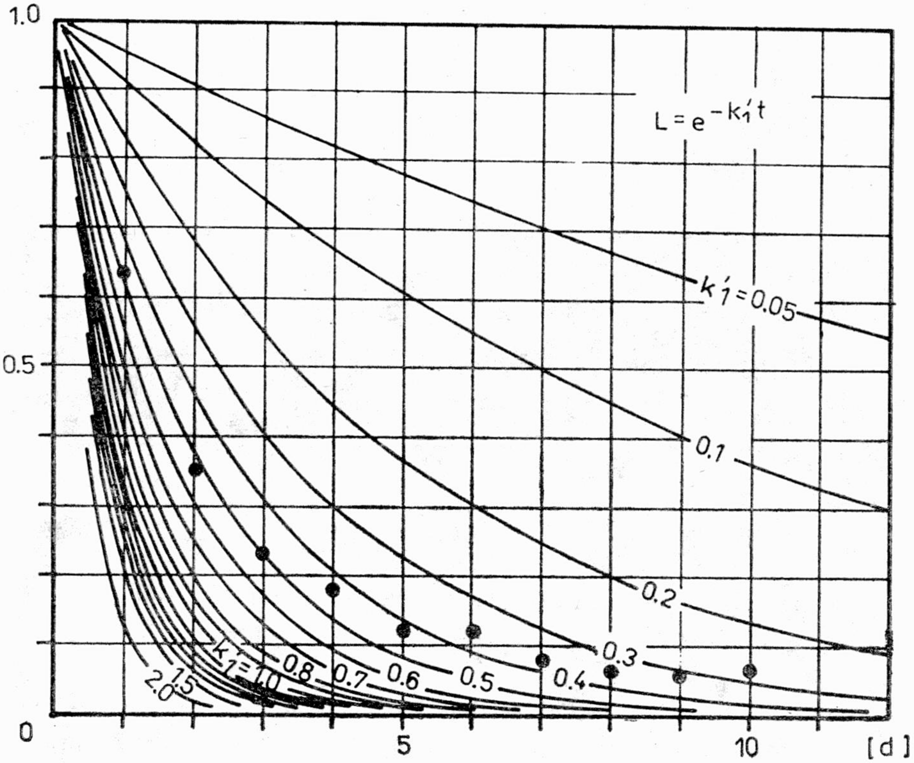

Fig. 4. Evaluation of rate constant k_1 (reaction of the first order)
Rys. 4. Oszacowanie stałej szybkości k_1 (reakcja pierwszego rzędu)

The results plotted in the diagrams allow us to state that during the first two days the biodegradation process can be interpreted according to the reaction of the 0 order where $k'_0 = 0.35$ (d^{-1}) and $k_0 = k'_0 L_0 = 0.35 \times 19.8 = 6.93$ ($g/dm^3 \cdot d$).

If, however, the course of the process is interpreted according to the reaction of the 1 st order, it may be assumed that during the first three days $k'_1 = 0.5$ (d^{-1}), which corresponds to the constant of reaction rate $k_1 = 0.5$ (d^{-1}). During these three days 77% of the total BOD_5 load diminished. For the 2nd order the reaction rate constant is given by $k'_2 = 0.5$ (d^{-1}) not earlier than after five days and corresponds to the value $k_2 = 1.5/19.8 = 0.075$ ($dm^3/g \cdot d$).

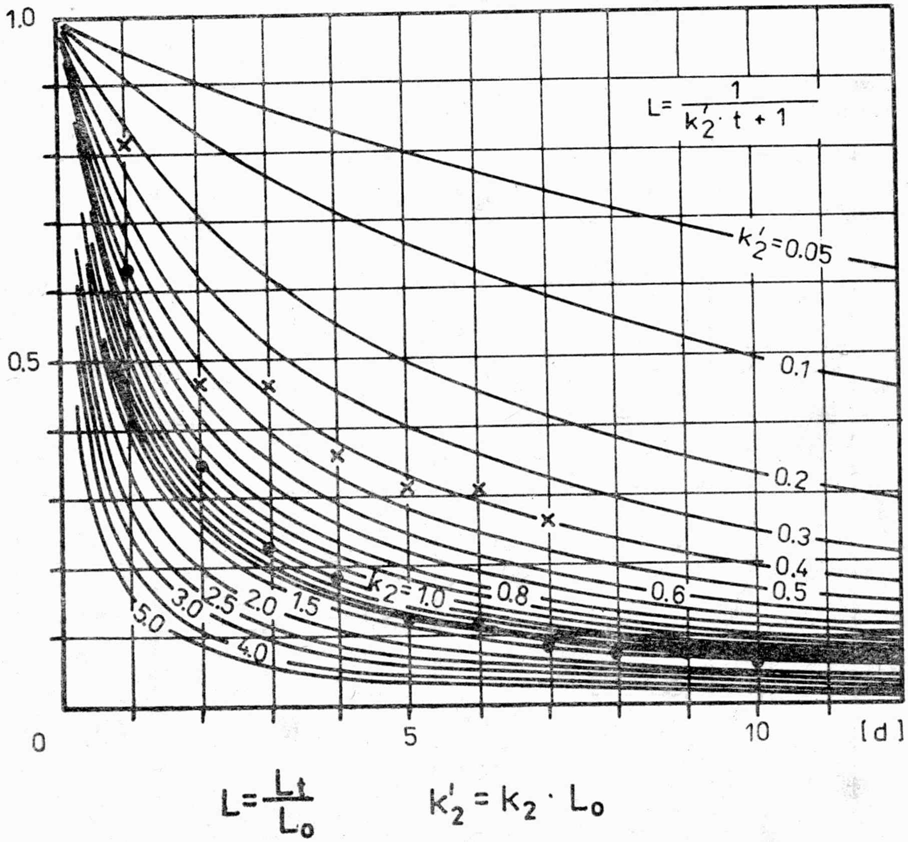

Fig. 5. Evaluation of rate constant k_2 (reaction of the second order)

Rys. 5. Oszacowanie stałej szybkości k_2 (reakcja drugiego rzędu)

Assuming that during the first three days biodegradation proceeds according to the reactions of the 1 st order, and later on according to the reaction of the 2nd order, it was possible to determine the constant of reaction rate for the residual load. The initial value of BOD_5 for the residual load was calculated as follows:

$$L_{or} = L_3 = 19.8e^{-0.5 \cdot 3} = 4.42 \text{ (g } O_2/dm^3\text{)}.$$

The course of the biodegradation process for the residual load is presented in tab. 2.

The values of the residual load calculated with respect to the input load for twenty-four hours, being plotted in the diagram of the reactions of the 2nd order, enabled us to determine k_2' for the residual load

$$k_2' = 0.4\ (\mathrm{d}^{-1}) \text{ and } k_2 = k_2'/L_{or} = 0.40/4.42 = 0.09\ (\mathrm{dm}^3/\mathrm{g}\cdot\mathrm{d}).$$

Table 2

Course of aerobic thermophilic stabilization for the residual load L_{or} ($L_{or} = 4.42$ g O_2/dm^3)

Przebieg procesu tlenowej stabilizacji termofilowej dla ładunku resztkowego L_{or} ($L_{or} = 4{,}42$ g O_2/dm^3)

Time t α	0(3)	1(4)	2(5)	3(6)	4(7)	5(8)	6(9)	7(10)
BOD_5 g O_2/dm^3	4.42	3.6	2.1	2.1	1.6	1.4	1.4	1.2
Residual load after time t referred to L_{or}	1	0.81	0.47	0.47	0.36	0.31	0.31	0.27

Reaction rate was calculated from determined constants [10]. The results are presented in tab. 3.

While analysing the reaction rate in the case of highly concentrated substrates at the initial phase of stabilization, it can be stated that the reaction rate is independent of

Table 3

Reaction rate and constant rates for the reactions of the 0, 1st and 2nd orders

Szybkość reakcji i stała szybkości dla reakcji 0, I i II rzędu

Reaction order	Reaction constant rate	Reaction rate, g/dm³·d
0	$k_0 = x^*/t (\mathrm{g/dm^3}\cdot d)$ $k_0 = 6.93$	$V_0 = k_0$ $V_0 = 6.93$
1	$k_1 = (1/t)\left(\ln \frac{C_0^{**}}{(C_0^{**}-x^*)}\right) \mathrm{d}^{-1}$ $k_1 = 0.5$	$V_1 = k_1(C_0^{**}-x^*)$ $V_1 = 2.2$
2	$k_2 = x/C_0^{**}t(C_0^{**}-x^*)$ $k_2 = 0.09\ (\mathrm{dm^3/g}\cdot d)$	$V_2 = k(C_0^{**}-x^*)^2$ $V_2 = 0.13$

$x^* = L_0 - L_t$ — loss of BOD_5 after time t (g O_2/dm^3).

$C_0^{**} = L_0$ — input BOD_5 (g O_2/dm^3).

concentration; biodegradation proceeds according to the reaction of the 0 order assuming the highest value $V_0 = 6.93$ g/dm$^3\cdot$d. As the most easily biodegradable substrates are depleted (after 48 h), the 1st order reactions prevail and their rate V_1 is only 2.2 g/dm$^3\cdot$d. At this phase of the process the effect of substrate concentration becomes visible. The reactions of the 2nd order prevail not earlier than after four days, when the reaction rate V_2 continues to diminish due to the depletion of biodegradable substrates, and is 0.13 g/dm$^3\cdot$d.

Decreasing rate with changing concentration of the substrate is in conformity with the TTC test, used to determine the activity of thermophilic bacteria in the biodegradation process.

The highest activity is observed within the first twenty-four hours; then — on the second and third days — it slightly decreases, and beginning with the fourth day a considerable drop of microorganism activity is noted.

According to figs. 3, 4 and 5 the course of the process in the initial phase may be interpreted according to the reactions of the 0 and the 1st orders; therefore it was agreed to find out the difference between oxygen consumption practically determined and its theoretical values calculated according to the reactions of the 0 and 1st orders. The difference thus obtained expressed in percent makes it possible to determine which of the kinetic models assumed here agrees with the real course of the process. The above differences are shown in tabs. 4 and 5.

Table 4

Differences between oxygen consumption determined practically and its theoretical values — the 1st and 2nd days of the process according to the reactions of the 0 order

Różnice między praktycznie wyznaczonym zużyciem tlenu a wartościami teoretycznymi — pierwsza i druga doba procesu zgodnie z reakcją 0 rzędu

Time d	Reaction order	Practical consumption		Theoretical consumption		Difference
		g O_2/dm^3	%	g O_2/dm^3	%	%
1	0	7.2	36.36	6.90	34.84	1.52
2	0	12.4	62.62	13.90	70.20	7.58
3	1	15.3	77.20	15.32	77.37	0.17
4	2	16.2	81.82	17.36	87.67	5.85
5	2	17.7	89.40	17.89	89.90	0.50
6	2	17.7	89.40	17.95	90.65	1.25
7	2	18.2	91.90	18.22	92.00	0.10
8	2	18.4	92.20	18.42	93.00	0.08
9	2	18.4	92.20	18.64	94.14	1.22
10	2	19.8	100.00	19.80	100.0	0

The slightest discrepancies between practical and theoretical oxygen consumption are obtained in the case of a kinetic model in which during the first twenty-four hours the reactions proceed according to the 0 order (the highest microorganism activity — 1890

μ MTF/dm^3), on the second and third days — according to the 1st order (microorganism activity — 1110 and 860 μ MTF/dm^3), and beginning with the fourth day according to the 2nd order (microorganism activity is within 300 μ MTF/dm^3).

After three days the load decreases by about 78% and this fact corresponds well with the high reaction rate observed in this period.

Table 5

Differences between oxygen consumption determined practically and its theoretical values, the 1st, 2nd and 3rd days of the process according to the reactions of the 1st order

Różnice między praktycznie wyznaczonym zużyciem tlenu a wartościami teoretycznymi — pierwsza, druga i trzecia doba procesu zgodnie z reakcją I rzędu

Time d	Reaction order	Practical consumption		Theoretical consumption		Difference %
		g O_2/dm^3	%	g O_2/dm^3	%	
1	1	7.2	36.36	7.80	39.40	2.8
3	1	12.4	62.62	12.52	63.20	0.60
3	1	15.3	77.20	15.32	79.37	0.17
4	2	16.2	81.82	17.36	87.67	5.85
5	2	17.7	89.40	17.80	89.90	0.50
6	2	17.7	89.40	17.95	90.65	1.25
7	2	18.2	91.90	18.22	92.00	0.10
8	2	18.4	92.92	18.42	93.00	0.08
9	2	18.4	92.92	18.64	94.14	1.25
10	2	19.8	100.00	19.80	100.0	0.0

3. CONCLUSIONS

1. In thermophilic conditions at highly concentrated substrates the biodegradation process in its initial phase proceeds according to the reactions of the 0 order, the reaction rate being independent of the concentration. Thermophilic bacteria are adapted to the high concentration, thus no initial phase (lag-phase) is observed.

2. With the depletion of substrates the reaction rate decreases and becomes dependent on the concentration. The process proceeds according to the reactions of the 1st order.

3. Depletion of easily biodegradable substrates diminishes the activity of microorganisms, the reaction rate decreases very distinctly, after three days being scarcely 0.13 g/m$^3\cdot$d. The process proceeds according to the reactions of the 2nd order.

4. On a technical scale and under steady state conditions it is the most beneficial to maintain the first phase of the process (reactions of the 0 order, the highest reaction rate) as then a large (about 70%) loss of the load is obtained in a short time. Biodegradation process may be continued in e. g. water receiver or soil, since then no rapid consumption of oxygen takes place (a low reaction rate).

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KINETYKA PROCESU AEROBOWEJ STABILIZACJI TERMOFILOWEJ STĘŻONYCH ŚCIEKÓW ORGANICZNYCH

Analiza kinetyki procesu aerobowej stabilizacji termofilowej stężonych ścieków wykazała, że różne fazy tego procesu mogą być opisane reakcjami zerowego, pierwszego i drugiego rzędu w miarę, jak zachodzi przemiana różnych składników substratu. W skali technicznej pożądane byłoby utrzymywanie pierwszej fazy procesu, odpowiadającej reakcji zerowego rzędu, dla której stała szybkości *k* przybiera największe wartości. Warunki te mogą być spełnione w układzie przepływowym.

ZUR KINETIK DER AEROBEN, THERMOPHILEN STABILISIERUNG VON KONZENTRIERTEN ORGANISCHEN ABWÄSSERN

Eine Analyse der Kinetik der aeroben, thermophilen Stabilisierung hochkonzentrierter Abwässer hat erwiesen, daß verschiedene Phasen dieses Verfahrens mit den Gleichungen der Reaktionen nullter, erster und zweiter Ordnung in dem Maße beschrieben werden können, wie die verschiedenen Bestandteile des Substrats abgebaut werden. Im technischen Maßstab wäre eine Aufrechterhaltung der ersten Prozeßphase anstrebbar. Sie entspricht nämlich der Reaktion nullter Ordnung und somit ist der Wert der Reaktionskonstante *k* am größten. Diese Bedingungen kann man in Durchflußreaktor einhalten.

КИНЕТИКА ПРОЦЕССА АЭРОБНОЙ, ТЕРМОФИЛЬНОЙ СТАБИЛИЗАЦИИ КОНЦЕНТРИРОВАННЫХ ОРГАНИЧЕСКИХ СТОЧНЫХ ВОД

Анализ кинетики процесса аэробной, термофильной стабилизации концентриированных сточных вод показал, что различные фазы этого процесса могут описываться реакциями нулевого, первого и второго порядков по мере того, как происходит превращение различных компонентов субстрата. В промышленном масштабе было бы желательным поддерживание первой фазы процесса, соответствующей реакции нулевого порядка, для которой постоянная скорость k приобретает наибольшие значения. Эти условия могут быть удовлетворены в проточной системе.