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DETERMINING THE RESISTANCE OF ORGANIC POLLUTANTS TO BIODEGRADATION IN WATER AND WASTEWATER

The resistance of organic pollutants to biochemical degradation in water or wastewater can be described in terms of the dichromate COD to permanganate COD ratio (COD_d/COD_p). The value of this ratio depends on two major parameters influencing the kinetics of the biodegradation process, i.e., temperature and coefficient of oxygen uptake rate K included in the Streeter–Phelps equation. The COD_d/COD_p value describes, furthermore, the concentrations of biodegradable organics, refractory substances, and nitrogen compounds. Mathematical relations between the concentrations of these pollutants and the COD_d/COD_p values describe the pollution levels in a river or in wastewater and determine the biodegradability of organic pollutants.

1. INTRODUCTION

The resistance of organic pollutants to biochemical degradation (RBD) is an important factor affecting the kinetics of biochemical processes that occur in water or wastewater. The resistance to biochemical degradation (RBD) is of prime significance to wastewater treatment as well as to self-purification of surface water. Knowledge of RBD should be a prerequisite to enable a reliable design of wastewater-treatment plants or to determine the treatment efficiency desired. In the direct method of determination of the RBD value the factor K included in the Streeter–Phelps equation is used [1].

The objective of this study is to present a novel method of determination of RBD. The method proposed is simple and convenient because it uses the values of the following ratios: dichromate COD to permanganate COD, dichromate COD to BOD_5, or dichromate COD to TOC. For convenience, the dichromate COD and permanganate COD will be referred to in this paper as COD_d and COD_p, respectively.

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Some authors indicate that, as the degree of treatment efficiency of wastewater increases, the ratios of COD_d/TOC and BOD_5/TOC decrease [2].

In the course of the biodegradation process the amount of biodegradable organics decreases, and the values of the dichromate COD/permanganate COD and dichromate COD/BOD_5 ratios increase. The value of the dichromate COD/TOC ratio is an indicator of the oxygen amount required to the oxidation of organics in relation to organic carbon contained in the structure of the compound. As carbon dioxide is one of the final products of organic-matter oxidation under aerobic conditions, the reference value of the COD/TOC ratio is 2.66 of the oxygen/carbon weight ratio in the carbon dioxide particle. In engineering practice it is useful to determine the values of the COD_d/COD_p and COD_d/BOD_5 ratios. When the water under treatment contains toxic or inhibiting substances, the value of the COD_d/BOD_5 ratio does not describe the degree of biochemical degradation. Thus, the degree of biodegradation calculated from the COD_d/COD_p value is much more universal.

In this paper there are presented the relationships between the COD_d/COD_p value, BOD_5, ammonia nitrogen concentration, nitrate nitrogen content, and coefficient K of the Streeter–Phelps equation. These relations were studied in model experiments under static conditions on water samples collected from the Odra river and on samples taken from a number of wastewater-treatment plants.

2. METHODS

River water samples were aerated in 10 dm^3 glass vessels. The experimental series involved three samples. Two of them were mixed with raw wastewater at a proportion of 1:11 and 1:22, respectively. To avoid a complete mix, the samples were aerated in such a way that the aerating air be distributed in the form of single bubbles in order to cause a near-bottom sedimentation zone and a turbulence in the supernatant. Samples were collected for the analyses twice a week after a complete mix had been achieved.

Determinations were carried out both in filtered and unfiltered samples for BOD, COD_d, COD_p, pH, coloured matter, humic substances, ammonia nitrogen and nitrate nitrogen. The results were plotted and interpreted mathematically. Significance levels varied from 0.1 to 0.001.

3. RESULTS

The experiments consisted of four series of a duration time ranging between 38 and 52 days. The biodegradation that occurred in the course of the aeration process proceeded in two stages. In the first stage, there was a decrease of COD_d, COD_p, humic substance content, ammonia nitrogen and organic nitrogen concentrations.

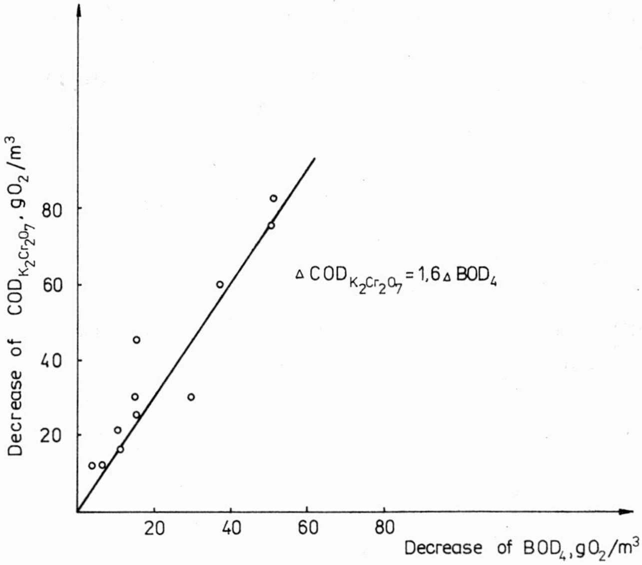

Fig. 1. COD_d versus BOD_4 during aeration of the Odra river water samples collected downstream of the Oława tributary

This stage lasted for 16 to 20 days. The aeration temperature was about 298 K. The second stage was characterized by an increase of COD_d, COD_p, humic substance content, nitrate and organic nitrogen concentrations. No variations were measured for BOD because of the photosynthesis and algae growth. The samples contained a great number of *Diatomae* and a certain number of *Chlorophyta.*

Analysis of BOD_4 reduction as well as of accompanying decrease of COD_d and COD_p observed in the first stage of the aeration process indicate that these relations are linear in nature, and may be described as follows:

$$\Delta COD_d = 1.6 \Delta BOD_4, \tag{1}$$

$$\Delta COD_p = 0.275 \Delta BOD_4 - 2.75. \tag{2}$$

These relations are plotted in fig. 1. They enable the calculation of biodegradable substances in terms of COD_d or COD_p.

4. DETERMINATION OF THE RELATIONSHIPS BETWEEN WATER COMPOSITION, THE COURSE OF THE BIODEGRADATION PROCESS DURING AERATION, AND THE COD_d/COD_p VALUE

As it has already been mentioned, biochemical processes consist of a number of stages which involve oxidation characterized by the decrease of BOD and organic nitrogen and nitrification characterized by the decrease of ammonia nitrogen as well as by the increase of nitrites and nitrates. Each of the stages is described by the relationships that occur between COD_d/COD_p, BOD_4, ammonia nitrogen and nitrate nitrogen concentrations. The relationship between BOD_4 and COD_d/COD_p in the aeration stage is expressed by the following formula

$$COD_p,\ BOD_4 = \frac{a}{(COD_d/COD_p)^b}, \tag{3}$$

a, *b* — constants.

As shown by eq. 3, BOD_4 decreases in the course of the biochemical oxidation as a result of organic matter degradation which is in agreement with the behaviour of BOD_4 during aeration.

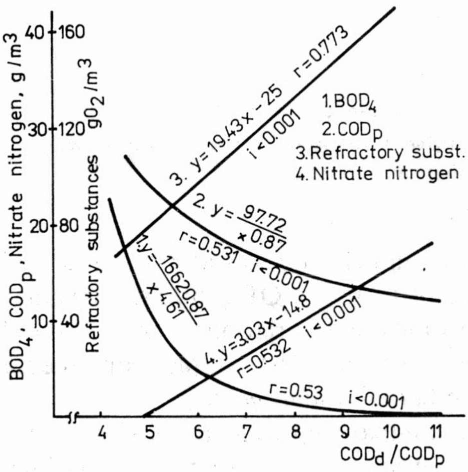

Fig. 2. BOD_4, COD_p, content of refractory substances and nitrate concentration versus COD_d/COD_p in aerated water samples

The relationship between BOD_4, COD_p, refractory substance content, and nitrate concentration versus COD_d/COD_p in aerated water samples is presented in fig. 2. Nitrate nitrogen content increases linearly with the increasing COD_d/COD_p value (fig. 2). This is in agreement with the data given in section 3. The concentration of nitrate nitrogen as related to the COD_d/COD_p ratio is

$$N_{NO_3^-} = a'(COD_d/COD_p) - b', \tag{4}$$

a', *b'* — constants.

The analysis of the organic nitrogen behaviour is much more complicated because the second stage of the biochemical oxidation (section 3) creates favourable conditions for algae growth. Depending on whether the increment of organic nitrogen concentration associated with algae growth was greater or smaller than its drop associated with biochemical oxidation, the concentration of this compound associated with a degree of biochemical degradation either increased or decreased. The concentration of N_{org} may be calculated from the formula

$$N_{org} = \frac{[(COD_d/COD_p)-6]^{1.96}}{1.08}+0.7. \tag{5}$$

Equation 5 shows that the organic nitrogen content decreases in the first stage as a result of biochemical oxidation and then increases as a result of algae growth. No relation was found between ammonia nitrogen concentration and the COD_d/COD_p value because the nitrification proceeded too rapidly as compared with the variations occurring in the organics concentration.

5. DETERMINATION OF THE RELATIONSHIP BETWEEN ORGANIC MATTER CONCENTRATION, NITROGEN COMPOUND CONTENT, AND COD_d/COD_p VALUE FOR THE ODRA RIVER WATER

As a result of biochemical oxidation, some compounds persist in the water under treatment, while others are products of biochemical transformations. Both kinds are highly resistant to oxidation. Such compounds are generally referred to in the literature as refractory substances. The results of investigations make it possible to determine their content. Using equation (1), it is possible to calculate the concentration of biodegradable substances in terms of COD_d, and from the difference between COD_d and the COD_d the refractory substance content results. Humic substances are resistant to biochemical degradation but they can be easily removed by coagulation. Therefore the approximate value of COD_d, which results from coloured matter content, has to be subtracted from the calculated refractory substances content. The relationship between COD_d and colour was established, using alkaline solutions of humic substances. The calculated values are approximated only because the humic matter of interest originated in soil.

The relations presented in fig. 2 show that when the degree of biochemical degradation (i.e., the COD_d/COD_p value) increases, so does during aeration the refractory substances' content in terms of COD_d, but BOD_4 decreases. The increase in the concentration of refractory substances is greater than it may be expected from the decrease of BOD_4 or from it initial value. This phenomenon is associated with algae growth; their biomass as a whole has been incorporated in the calculated COD_d value. But this does not hold for BOD_4 calculations which include only some part of the biomass.

The content of refractory substances RS during aeration can be calculated as follows:

$$RS = A(COD_d/COD_p)+B, \tag{6}$$

A, *B* – constants.

6. DETERMINATION OF THE RELATIONSHIP BETWEEN ORGANIC MATTER CONCENTRATION, NITROGEN COMPOUND CONTENT, AND THE COD_d/COD_p RATIO IN ODRA RIVER WATER

The relations were determined on the basis of physical-chemical analyses carried out in the Laboratory of the Environmental Monitoring Centre as well as on the basis of the author's own study. These relations were found to be similar to those established in the earlier study of water aeration. The equation for the BOD_5 versus COD_d/COD_p curve takes the same form as that for the aerated samples. Thus,

$$COD_p, BOD_5 = \frac{a}{(COD_d/COD_p)^b}. \tag{7}$$

There is only a slight difference in the values of a and b between the two equations (fig. 3).

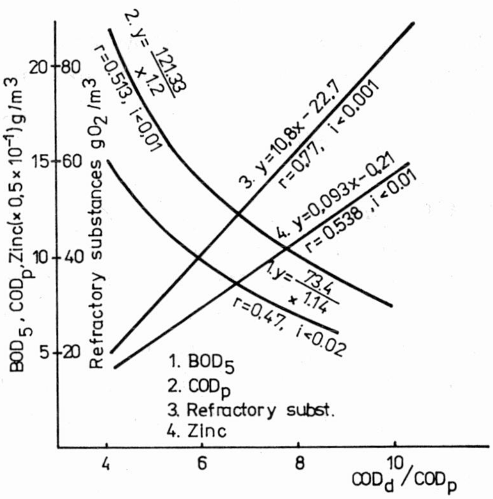

Fig. 3. BOD_5, COD_p, content of refractory substances and zinc concentration versus COD_d/COD_p in the Odra river water samples collected downstream of the Oława tributary

Refractory substances' content increases with the increasing degree of biodegradation and is described by the following formula

$$RS = C(COD_d/COD_p) - D, \tag{8}$$

C, D – constants.

Figure 3 presents the relationship between refractory substances' content in the Odra river water samples expressed in terms of COD_d and COD_d/COD_p. As shown in this figure, the concentration of refractory substances varies from 0 to 70 g O_2/m^3 in terms of COD_d, which accounts for 0 to 99% of total COD_d. In secondary effluents the concentration of substances highly resistant to biodegradation (tannins, lignin, anionic detergents, ether extraction solvents, humic substances) ranges from 68 to 77% [3].

The decrease of BOD_5 in the river water with the increasing COD_d/COD_p value is influenced by the kinetics of biochemical degradation which, in turn, is temperature-dependent. The COD_d/COD_p ratio increases linearly with the increase of temperature; this can be described by the following equation

$$COD_d/COD_p = 5.05\,t + 255.74 \tag{9}$$

where t denotes temperature in K.

When temperature increases, so does the degree of degradation, i.e., the concentration of organics of low resistance to biodegradation continues to decrease, whereas the amount of oxidizable products of biodegradation increases. This process is expressed by the relation of K-coefficient (included in the Streeter–Phelps equation) with the value of the COD_d/COD_p ratio (fig. 4), which depends primarily on the RBD. Hence,

$$K = \frac{0.918}{(COD_d/COD_p)^{0.84}}. \tag{10}$$

As shown in fig. 4, the value of K decreases with the increasing COD_d/COD_p ratio. This phenomenon is associated with the removal of biodegradable pollutants in the course of the degradation process.

The relationship between ammonia nitrogen concentration and degree of biochemical degradation is described by the equation similar to that for BOD_5:

$$N_{NH_4} = \frac{31.18}{(COD_d/COD_p)^{2.06}}. \tag{11}$$

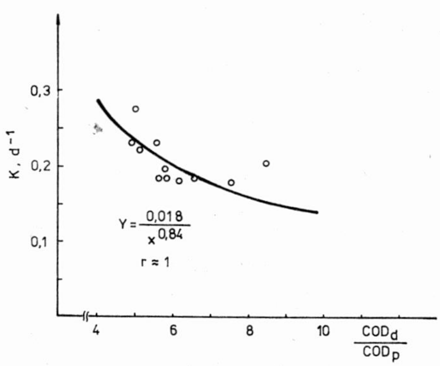

Fig. 4. Constant K versus COD_d/COD_p in the Odra river water samples collected downstream of Oława tributary

The decrease of ammonia nitrogen concentration with the increasing COD_d/COD_p value is influenced by the nitrification processes in which the increasing nitrate concentration acts as an indicator. However, there is no relation between organic nitrogen concentration and the COD_d/COD_p ratio in the water samples collected from the Odra river. This should be attributed to seasonal algae growth.

The concentrations of some heavy metals (zinc and lead) are also influenced by the COD_d/COD_p ratio (fig. 3). This relation is associated with the occurrence of metal-organic complex in the river water primarily suspensions [4]. Heavy metals are precipitated from the solution in the course of biochemical oxidation.

7. DETERMINATION OF THE RELATIONSHIP BETWEEN ORGANIC MATTER CONCENTRATION AND THE COD_d/COD_p RATIO IN WASTEWATERS

While determining this relationship, the author availed himself of the results obtained from the aeration of three types of samples containing raw wastewater as well as wastewater after primary and secondary treatments, respectively. The treatment procedure also involved sapromate [5]. The samples were aerated for 120 h. Every 24 h, BOD_5, COD_p, COD_d, and TOC were determined. On the basis of these data, the decrease of BOD_5 during aeration was related to the decrease of COD_d. In order to describe the relation of interest, the following equations were derived:

municipal sewage in the city of Wrocław

$$\Delta\, COD_d = 0.88\, \Delta\, BOD_5 + 12.6, \tag{12}$$

municipal sewage in Racibórz

$$\Delta\, COD_d = 0.855\, \Delta\, BOD_5 + 100, \tag{13}$$

municipal sewage in Opole (in 1982)

$$\Delta\, COD_d = 2.05\, \Delta\, BOD_5, \tag{14}$$

municipal sewage in Opole (in 1983)

$$\Delta\, COD_d = 1.79\, \Delta\, BOD_5 - 0.95. \tag{15}$$

Making use of relations (12)–(15), concentrations of refraction substances were calculated according to the method described in section 5. Figure 5 gives the plots of BOD_5, COD_p and concentration of refractory substances versus COD_d/COD_p. These relations differ from those obtained for the Odra river water samples. In the sewage samples from Opole and Wrocław (fig. 5, curves *1*, *2* and *1'*, *2'*) the concentrations of biodegradable compounds and refractory substances (RS) increase

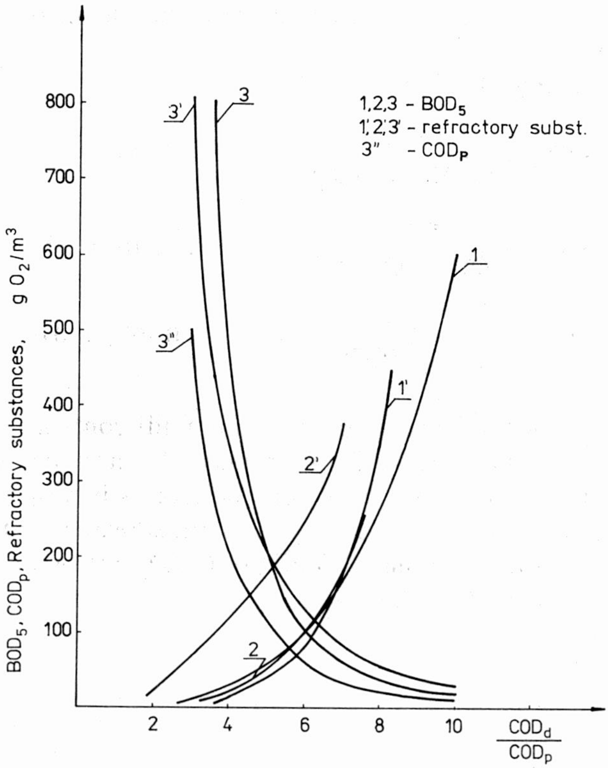

Fig. 5. Organic matter concentration versus COD_d/COD_p in wastewaters

with the increasing COD_d/COD_p ratio. The relation may be written as follows:

sewage samples from Opole

$$BOD_5 = \frac{(COD_d/COD_p)^{5.2}}{144.54}, \qquad r = 0.837,\ i < 0.001, \tag{16}$$

$$RS = \frac{(COD_d/COD_p)^{3.5}}{5.33}, \qquad r = 0.488,\ i < 0.01, \tag{17}$$

sewage samples from Wrocław

$$BOD_5 = \frac{(COD_d/COD_p)^{4.17}}{15.84}, \qquad r = 0.43,\ i < 0.05, \tag{18}$$

$$RS = 4.51\,(COD_d/COD_p)^{2.2}, \qquad r = 0.73,\ i < 0.001. \tag{19}$$

In sewage samples from Racibórz, both biodegradable compounds and concentrations of refractory substances decrease with the increasing COD_d/COD_p ratio (fig. 5, curves *3* and *3'*).

The relation acquires the form

$$BOD_5 = \frac{160324.56}{(COD_d/COD_p)^{4.2}}, \quad r = 0.235,\ i < 0.1, \tag{20}$$

$$RS = \frac{19054.6}{(COD_d/COD_p)^{2.9}}, \quad r = 0.76,\ i < 0.001, \tag{21}$$

$$COD_p = \frac{20892}{(COD_d/COD_p)^{3.33}}, \quad r = 0.49,\ i < 0.001. \tag{22}$$

The relationship between biodegradable compound content, concentration of refractory substances, and COD_d/COD_p is strongly influenced by the composition of the wastewater and the occurrence of organic pollutants in suspended or colloidal form. When the concentration of refractory substances related to the COD_d/COD_p ratio behaves in a way similar to that of BOD_5 or COD_p, the organics to be removed are highly resistant to biodegradation.

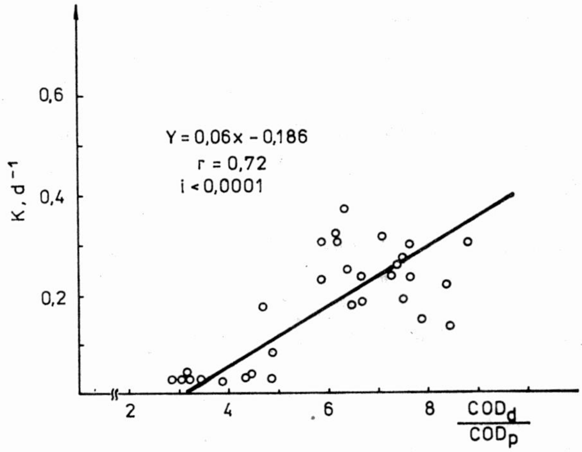

Fig. 6. Constant K versus COD_d/COD_p in the wastewater of Opole

The value of the K coefficient included in the Streeter–Phelps equation was also found to depend in the COD_d/COD_p ratio (fig. 6). As shown by the plots in fig. 6, the K constant for the wastewater samples from Opole increases with the increasing COD_d/COD_p ratio. This relation should be attributed to the removal of biodegradable pollutants in the course of the treatment process.

8. SUMMARY

The results of investigations show that the value of the COD_d/COD_p ratio describes the biodegradability of organic pollutants in water and wastewater. The value of the ratio depends on two major parameters characterizing the kinetics of the biodegradation process, temperature and coefficient of the oxygen uptake rate, K. Incorporated in the Streeter–Phelps equation, K is also an indicator of resistance to biodegradation (RBD). Making use of the relation between constant K and COD_d/COD_p, it is possible to determine the most probable RBD in water or wastewater. It is also easy to determine the water or wastewater resistance to biodegradation (RBD) depending on the physicochemical composition. The value of the COD_d/COD_p ratio is, furthermore, an indicator of the concentrations of biodegradable compounds, refractory substances, nitrogen compounds and some heavy metals. The mathematical relations between the pollutants mentioned and the COD_d/COD_p ratio describe the pollution levels in rivers or wastewaters and characterize the degree of biochemical degradation [6].

REFERENCES

[1] STOJDA A., GANTZ, E., *Metody obliczania współczynników kinetycznych w procesach biochemicznego zużywania tlenu*, Nowa Technika w Inżynierii Sanitarnej. Wodociągi i Kanalizacja, No. 11, Arkady, 1980.

[2] ECKENFELDER W. W. et al., *Physical, Chemical and Biological Processes*, Austin 1967.

[3] MANKA J. et al., *Characterization of organics in secondary effluents. Environmental Science and Technology*, [in:] *Handbook of Advanced Wastewater Treatment*, ed. by Von Nostrand Reinhold Company, New York 1974, p. 1017.

[4] *Micropollutants in river sediments*, Euro Reports and Studies, No. 61, Report on a WHO Group, Regional Office for Europe WHO, Copenhagen 1982, ICP/PCE.

[5] ROGOZIŃSKA D., *Ustalenie współczynnika charakteryzującego stopień biodegradacji związków organicznych dla ścieków miejskich Raciborza, Opola i Wrocławia*, Institute of Meteorology and Water Management, Wrocław 1982.

[6] KOWALSKI T., *Wpływ procesów biochemicznych na skład wód powierzchniowych. Ochrona Środowiska*, Informator Dolnośląskiego Oddziału PZTIS, Wrocław, No. 463(4C26), 1985.

OKREŚLENIE PODATNOŚCI ZANIECZYSZCZEŃ ORGANICZNYCH W WODACH I ŚCIEKACH NA ROZKŁAD BIOCHEMICZNY

Wykazano, że podatność zanieczyszczeń organicznych zawartych w wodach i ściekach na rozkład biochemiczny można określić podając wartość ChZT/utl. Wartość ta zależy od podstawowych parametrów kinetycznych procesu biochemicznego rozkładu, tj. temperatury i stałej szybkości poboru tlenu z równania Streetera–Phelpsa. Stosunek ChZT/utl. charakteryzuje stężenie zarówno zanieczyszczeń podatnych na rozkład biochemiczny, jak i refrakcyjnych, a także związków azotowych. Matematyczne zależności między stężeniem zanieczyszczeń a wartością stosunku ChZT/utl. opisują stopień zanieczyszczenia wód i ścieków oraz określają ich podatność na rozkład biochemiczny.

ОПРЕДЕЛЕНИЕ ПОДАТЛИВОСТИ ОРГАНИЧЕСКИХ ЗАГРЯЗНЕНИЙ В ВОДАХ И СТОЧНЫХ ВОДАХ К БИОЛОГИЧЕСКОМУ РАЗЛОЖЕНИЮ

Обнаружили, что податливость органических загрязнений, содержимых в водах и сточных водах, к биологическому разложению можно определить дая значение Химического Потребления Кислорода ХПК/окисляемость. Это значение зависит от основных кинетических параметров процесса биохимического разложения, т.е. температуры и постоянной скорости разбора кислорода и уравнения Стритера–Фельпса. Соотношение ХПК/окисляемость характеризует концентрацию как загрязнений податливых к биохимическому разложению, так и рефракционных, а также азотных соединений. Математические зависимости между концентрацией загрязнений и значением ХПК/окисляемость описывают степень заграснения вод и сточных вод, а также определяют их податливость к биологическому разложению.