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MODEL EXAMINING OF SURFACE WATER DISINFECTION BY OZONE

Bactericidal effectiveness of disinfection is described by Chick's law in accordance with the kinetics of 1st order reaction $N_t = N_0 e^{-kT}$. The dependence has been confirmed experimentally many times, but mainly for the cases of pure water disinfection by chlorine. Due to the increasing industrial pollution of natural waters as well as the application of other strong oxidizers, mainly ozone, disinfection conditions have undergone great changes. Disinfection in such waters is accompanied by oxidation reactions which result in the increase of ozone dose and change in the order of reaction. The applicability of n-order reaction to the quantitative characteristics of ozone disinfection is demonstrated empirically. The investigations were carried out on surface waters from the Odra, Oława and Kaczawa rivers and on infiltration water from the infiltration pond. The waters are characterized by the varying degree of physico-chemical and bacteriological pollution. Because of the laboratory scale of experiments the error was analysed and based on this analysis the method of measurements as well as main dimensions of the testing equipment were selected. Experimental results were approximated by the dependence $N_t = N_0 e^{(-kT)^n}$ with the application of the least squares method. The values of the constant n, except for waters from the Oława river, were different from 1. The disinfection time, ozone dose, and variations in physico-chemical composition of water were determined. Effects of disinfection were determined based on the number of meso- and psychophilic bacteria.

1. AIM AND RANGE OF INVESTIGATIONS

The investigations aimed at determining the influence of ozone on basic physico-chemical and bacteriological components of surface and infiltration waters. Surface waters were taken from the Odra, Oława and Kaczawa rivers [3]. Infiltration water came from the Kaczawa river and was taken from the infiltration pond and cumulative well.

2. SCALE OF INVESTIGATIONS AND TESTING EQUIPMENT

The investigations were conducted on a laboratory scale on the tubular ozonator presented in fig. 1. The air was supplied to the ozonator by a cased fan and autotransformer.

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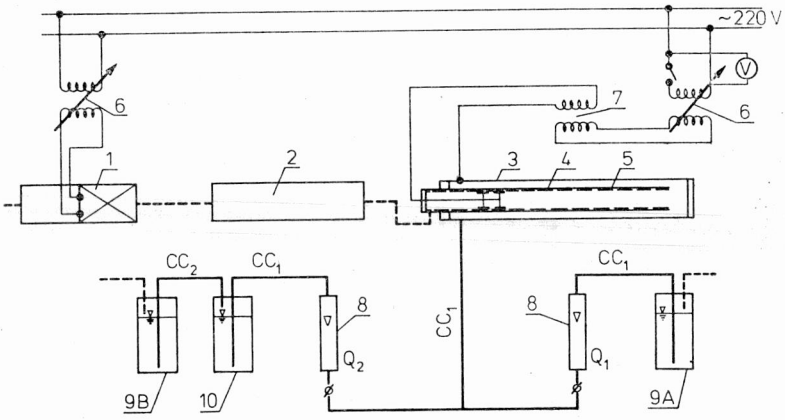

Fig. 1. Scheme of experimental apparatus

1 – fan, *2* – absorber, *3* – aluminium sleeve, *4* – glass pipe, *5* – silver plated mirror, *6* – autotransformer, *7* – high voltage transformer, *8* – rotameter, *9* – gas washer with 2% KJ, *10* – gas washer with sample – – – – – – air, ——— sample with ozone

Rys. 1. Schemat aparatury doświadczalnej

1 – wentylator, *2* – absorber, *3* – tuleja aluminiowa, *4* – rura szklana, *5* – lustro srebrzane, *6* – autotransformator, *7* – transformator wysokiego napięcia, *8* – rotametr, *9* – płuczka gazowa z 2% KJ, *10* – płuczka gazowa z próbką – – – – powietrza, ——— powietrza z ozonem

To decrease the content of air moisture a single-stage absorber in the form of a glass pipe 0.045 m in diameter and 1.1 m long filled with granulated silica gel was applied.

A prototypical testing ozonator generating ozone by means of silent electrical discharges in an electrode-dielectric-electrode system was applied to ozone production. One of the electrodes was an aluminium sleeve, and the other was the silver coating at the inner side of the glass pipe, functioning as the dielectric. The inside diameter of the aluminium sleeve was equal to 5.8×10^{-2} m and that of the glass pipe to 4.6×10^{-2} m. The active length of the ozonator was equal to 1.0 m.

The ozonator was supplied with electric energy by two transformers of low and high voltage.

Ozonated air was divided into two streams which were supplied through rotameters to appropriate gas washers (fig. 1).

3. PLANNING OF THE EXPERIMENT

3.1. METHODS OF INVESTIGATION AND CRITERIA OF SELECTING THE TESTING EQUIPMENT

The ozone dose was determined by balancing the ozone supplied to a water sample and the excess one present in the air at the outlet. The method of measurements is explained by fig. 1. The quantity of ozone supplied to water was measured in a 9*A* washer and that of excess ozone was determined in a 9*B* washer. The searched dose was determined from

the difference between the quantities of the supplied and excess ozone, corrected by the flow intensity. The choice of parameters and washers making up the testing equipment significantly affects, the accuracy of ozone dose measurement, what can be seen from the structural function given by

$$D = f(V_1; V_2, Q_1, Q_2, n, w, T). \tag{1}$$

The (after-mentioned) detailed form of the function was the criterion for selecting the testing equipment

$$D = \left(V_1 - V_2 \frac{Q_1}{Q_2}\right)_n 24 \frac{1000}{w}, \text{ mg } O_3/dm^3 \tag{2}$$

where D is the ozone dose (mg O_3/dm^3), V_1 is the volume of $Na_2S_2O_3$ used for titration of iodine educed by ozone in $9A$ washer (dm^3), V_2 is the volume of thiosulphate used for titration of iodine educed by the excess ozone in $9B$ washer (dm^3), Q_1 is the intensity of ozonated air flow through $9A$ washer (dm^3/h), w is the volume of the examined water sample (cm^3), 24 is the ozone molecular mass, and 1000 is the conversion factor of ozone consumption per dose.

The error at the dose measurement, as found from (2) is given by

$$\Delta D = \left(\Delta V_1 - \Delta V_2 \frac{Q_1}{Q_2} + V_2 \frac{\Delta Q_2 \cdot Q_1}{Q_2^2} - V_2 \frac{\Delta Q_1}{Q_2}\right) \cdot n \cdot 24 \frac{1000}{w} - \\ - \left(V_1 - V_2 \frac{Q_1}{Q_2}\right) \cdot n \cdot 24 \cdot \frac{1000 \Delta w}{w^2}. \tag{3}$$

The error resulting from the solution normality is neglected since this parameter is assumed to be of at least one order higher accuracy than the others. By assuming that

$$\Delta V_1 = \Delta V_2 = \Delta V \tag{4}$$

and

$$V_2 = cc_2 \cdot T \cdot Q_2 \tag{5}$$

we obtain

$$\Delta D = \left[\Delta V \left(1 + \frac{Q_1}{Q_2}\right) + \left(\Delta Q_1 + \frac{Q_1}{Q_2} \Delta Q_2\right) cc_2 T + \frac{1000 \Delta w}{w^2}\right] n \cdot 24. \tag{6}$$

It follows from eq. (6) that the error is directly proportional to the ratio Q_1/Q_2; Q_2; cc_2;T;w;Q_1; n; and inversely proportional to the examined sample volume raised to the second power (w^2).

The calculations account for the necessity of applying precise rotameters and burettes, as well as for the titration with the dilute solution of $Na_2S_2O_3$, application of the largest possible sample volume, and assuming of a small Q_1/Q_2 ratio and low ozone concentration (cc_2).

By applying rotameters of the same accuracy, i.e. $Q_1 = Q_2 = Q$, eq. (6) can be fur-

ther simplified and rewritten as

$$\Delta D = \left(2 \cdot \Delta V + 2\Delta Q \cdot cc_2 \cdot T + \frac{1000\Delta w}{w^2}\right) \cdot n \cdot 24. \tag{7}$$

The assumption $Q_1 = Q_2 = Q$ is justified and realized under experimental conditions by applying identical flow intensities in both rotameters. The parameters of the experimental installation were as follows:

$w = 1\ \mathrm{dm}^3$

$Q = \pm 0.5\ \mathrm{dm}^3/\mathrm{h}$

$w = \pm 4 \times 10^{-3}\ \mathrm{dm}^3$

$V = \pm 0.1 \times 10^{-3}\ \mathrm{dm}^3$

To the chemical analysis of ozone quantity 0.025 n solution of $Na_2S_2O_3$ was applied and the ozonization time was measured in minutes.

Taking account of these assumptions the error of the installation applied is given by

$$\Delta D = (0.2004 + 0.0167 cc_2 T)\ 0.6,\ \mathrm{mgO_3/Qm^3}. \tag{8}$$

Substitution of cc_2 in mg O_3/dm^3, and T in minutes in (8) yields the value of dose error in mg O_3/dm^3. In the investigations reported here the error was directly proportional to the excess ozone concentration. The concentration can be controlled by means of the voltage U applied to the ozonator electrodes. The relation between the concentration of the ozone produced and the voltage was determined experimentally. The results are given in table 1.

Since the concentration of ozone depends, apart from voltage, on weather conditions i.e. on the composition and temperature of the air, the above relation is valid for constant parameters of air.

Table 1

Ozone concentration vs. voltage

Zależność stężenia ozonu od napięcia

No.	u	T	O	cc_{O_3}
—	V	min	dm^3/h	mg O_3/dm^3
1	45	5	20	0.9
2	55	5	20	1.55
3	60	5	20	2.67
4	70	5	20	6.23
5	75	5	20	7.02
6	80	5	20	8.34
7	90	5	20	10.92
8	100	5	20	17.28

3.2. MATHEMATICAL INTERPRETATION OF RESULTS

The experimental data was interpreted on the basis of the analysis of the varying content of psycho- and mesophilic bacteria as a function of ozonization time. The changes were approximated by the dependence (9) describing the course of *n*-molecular reaction.

The destruction of microorganisms is defined by Chick's law which assumes that the reduction in the number of live microorganisms takes place in accordance with the kinetics of monomolecular reaction [1]. The law describes the action of chlorine with respect to microorganisms as well as that of other bactericides. However, the atrophy a of microorganism in the investigated waters under the influence of ozone was approximated by a more general dependence (9), which in the case of $n = 1$ is reduced to Chick's law. The experimental realization of the assumed mathematical model allows the determination of the value of n.

The values of the constants k, n were determined by considering the experimental data in a double logarithmic plot [2] according to eqs. (9)–(12)

$$\frac{N}{N_0} = e^{-(kT)^n} \tag{9}$$

where N is the number of bacteria after T time, N_0 is the initial number of bacteria, k is the constant of disinfection rate, n is the exponent indicating the order of reaction, and T is the time of water contact with ozone.

When subject to double logarithmization eq. (9) becomes

$$\ln N_0 - \ln N = (kT)^n, \tag{10}$$

$$\lg(\ln N_0 - \ln N) = n\lg k + n\lg T. \tag{11}$$

Eq. (11) may be given in the following form

$$y = ax + b \tag{12}$$

where:

$y = \lg(\ln N_0 - \ln N)$,

$a = n$

$x = \lg T$

$b = n\lg k$ hence $k = 10^{b/n}$.

4. RESULTS

The decrease of COD in ozonated waters depended on the initial permanganate value as well as on the dose and time of ozonization. In the case of high COD of raw water the decrease was quite significant, whereas at COD lower than 3 mg O_3/dm^3 no decrease was observed. The changes of COD falling to 1 mg O_3/dm^3 as a function of time are given in fig. 2.

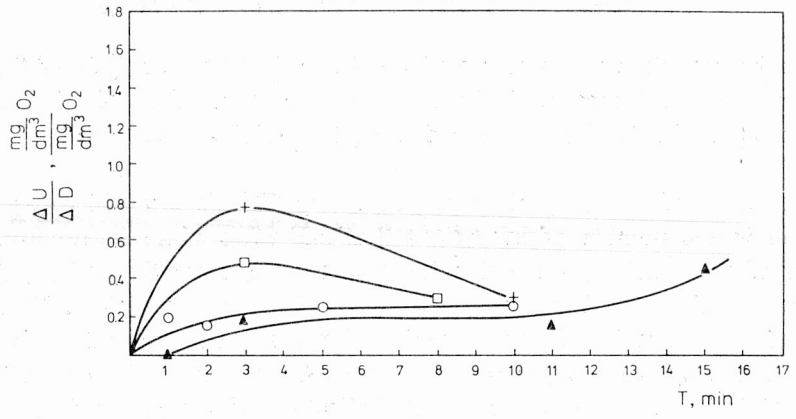

Fig. 2.

——▲——▲—— river Odra, —○—○— river Oława, ——□——□—— river Kaczawa, ——+——+ —— infiltration pond

Rys. 2.

—▲—▲— Odra, ——○——○—— Oława, ——□——□—— Kaczawa, ——+——+—— staw infiltracyjny

The content of nitrite nitrogen decreased rapidly with ozonization time what confirms high oxidability of NO_2 by ozone. The same dependence was observed in all the examined cases. The content of nitrite nitrogen remaining after the ozonization ranged within 0.06 mg/dm³ for water from the Odra river and within 0.02 mg/dm³ for water from the Kaczawa river.

The content of nitrate nitrogen increased with ozonization time due to the reaction $NO_2^- \xrightarrow{O_3} NO_3^-$ and the oxidation of organic nitrogen to nitrates.

Variation of colour of ozonated water, as well as that of permanganate value, depended on the colour of the initial ozone dose as well as ozonization time and the degree of water pollution.

The ozonization time and ozone dose were found to have no effect on the reaction and alkalinity. This may mean that organic compounds occurring in the examined waters were not oxidated to organic acids. Otherwise the decrease of alkalinity at the constant pH or the decrease of water pH would have been observed.

During investigations, besides the above-mentioned physico-chemical indicators of water, there were also determined

— ammonia nitrogen,
— solid residue,
— loss at roasting,
— chlorides,
— hardness.

These parameters, however, did not change with ozonization time in all the examined cases. Their initial values are given in table 2.

Table 2

Some physico-chemical parameters of the examined waters, not changing with ozonization time
Niektóre parametry fizyczno-chemiczne badanych wód, nie ulegające zmianie w czasie ozonowania

	Cl^- mg/dm³	s. poz. mg/dm³	s. p. p. mg/dm³	N_{NH} mg/dm³	Hardness °tw
The Odra river	168	549	133	0.05	8.3
The Oława river	52	462	153	0.1	8,7
The Kaczawa river	26	408	189	0	8.4
Infiltration pond	26	653	136	0	8.2

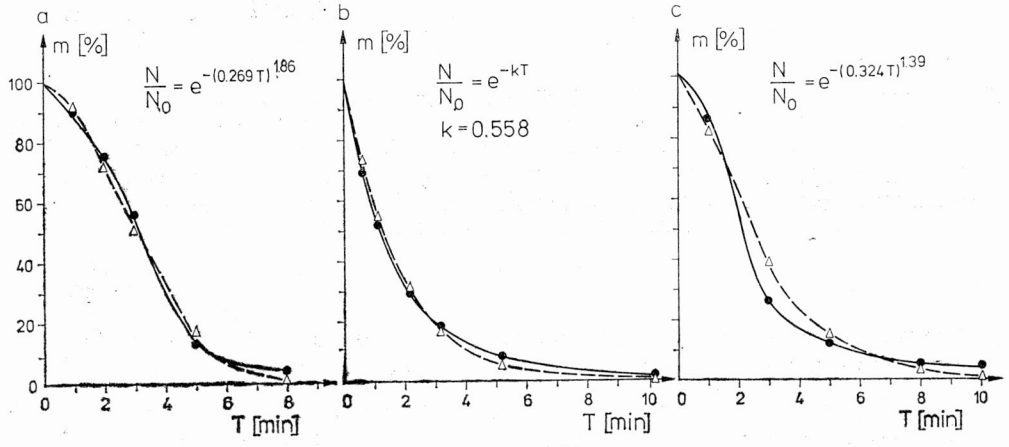

Fig. 3. Approximation of the bacteriocidal effects of ozone mesophilic bacteria
a — water of the river Kaczawa, *b* — water of the river Oława, *c* — water from the infiltration pond, *m* [%] — number of mesophilic bacteria, *T* — contact time in min

Rys. 3. Aproksymacja efektów niszczenia bakterii mezofilnych ozonem ($N/N_0 = e^{(-kT)n}$
a — wody rzeki Kaczawy, *b* — wody rzeki Oławy, *c* — wody ze stawu infiltracyjnego, *m* [%] — ilość bakterii mezofilnych *T* — czas kontaktu w minutach

Results of the destruction of meso- and psychophilic bacteria by ozone as well as the applicability of eq. (9) to their approximation are given in figs. 3 and 4. The obtained values of the constants are presented in table 3.

From the dependences obtained, it follows that Chick's law is insufficient for modelling the effects of water disinfection by ozone. Only in the case of the Oława river the kinetics of the bacteria destruction was properly described by the law.

With ozonization of waters from the Odra river the disinfection was still more complex. Some characteristic phases of the process are illustrated by the dependence given in fig. 5. At the initial stage of ozonization a phase of the growing of number of bacteria was observed; it was followed by the equilibrium phase and the third phase of bacteria destruction, proceeding in accordance with the character of water disinfection. Another

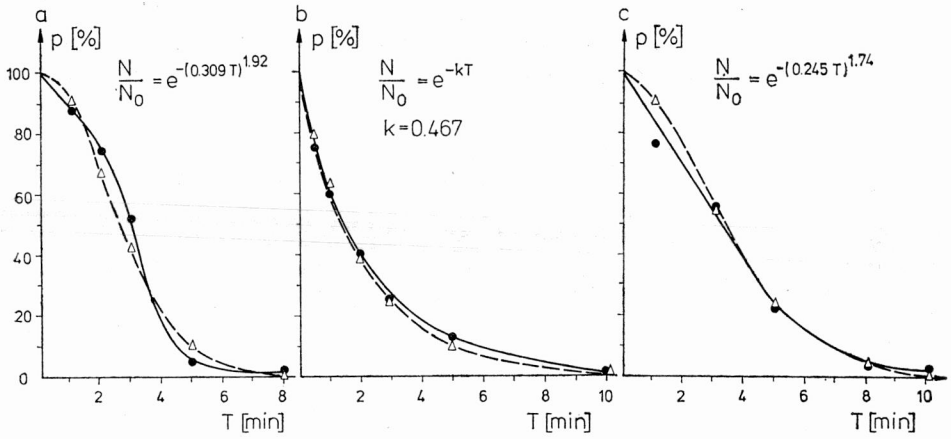

Fig. 4. Approximation of the bacteriocidal effects of ozone psychophilic bacteria $N/N_0 = e^{(-kT)^2}$
a — water from the river Kaczawa, *b* — water from the river Oława, *c* — water from the infiltration pond, *m* [%] — number of psychophilic bacteria in per cent, *T* — contact time, ●—— measurement △——— calculation

Rys. 4. Aproksymacja efektów niszczenia bakterii psychofilnych ozonem zależnością $N/N_0 = e^{(-kTn2}$
a — woda rzeki Kaczawy, *b* — woda rzeki Oławy, *c* — woda stawu infiltracyjnego, *p* [%] — ilość bakterii psychofilnych w procentach, *T* — czas kontaktu w minutach ●—— pomiar, △——— obliczenie

Table 3

The values of constants characterizing the effects of surface water disinfection by ozone
Wartości stałych charakteryzujących efekty dezynfekcji wód powierzchniowych ozonem

Type of bacteria	Mesophilic bacteria		Psychophilic bacteria	
Type of the examined water	*k*	*n*	*k*	*n*
The Oława river	0.558	1	0.477	1
The Kaczawa river	0.269	1.86	0.309	1.92
Infiltration pond	0.324	1.39	0.245	1.74

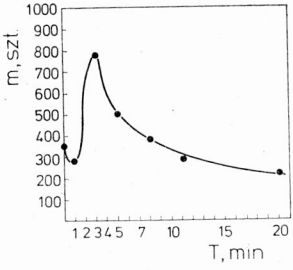

Fig. 5
Rys. 5

characteristic is a rather small difference between the numbers of bacteria at the 1st and 20th minute of ozonization. In light of these observations the pollution of waters from the Odra river with toxic substances seems quite possible. This supposition is also confirmed by a small initial number of bacteria i.e. 340 pieces/cm^3. Physico-chemical composition of the examined waters was found to affect significantly the ozone demand, e.g. during 10 min the ozone uptake by the water from the Oława river was equal to 5 mg/dm^3 whereas that by the water from the Kaczawa river only to 2 mgO_3/dm^3, although the number of bacteria in raw water and the disinfection effects being quite comparable. Such a big difference between the doses is due to various contents of oxidable substances. COD of waters from the Oława river was equal to 6 mg O_2/dm^3 and decreased with ozonization time to 4.7 mg O_2/dm^3 whereas COD of waters from the Kaczawa river was equal to 3.0 mg O_2/dm^3 and did not change with disinfection time. Similar effects were observed when comparing the ozonization processes of waters from the infiltration pond and the Kaczawa river; as well as, even more visibly, in the case of very pure infiltration water from the cumulative well (COD of raw water was equal to 1.3 mg O_2/dm^3), in which, after one minute of ozonization the number of bacteria decreased by 100% and the ozone dose was equal to only 0.3 mg O_3/dm^3.

5. CONCLUSIONS

During ozonization of the examined waters the decrease of COD and nitrites and increase of nitrates were observed. The variations of COD were rather small and did not exceed 20%, whereas the concentration of nitrites decreased by about 60% to 85%. The increase of the concentration of nitrates was, as a rule, conditioned by the decrease of the concentration of nitrites. The initial values of the indicators were found to affect significantly the variations observed.

The effects of disinfection, referring to meso- and psychophilic bacteria as well as *coli* bacteria were markedly dependent upon the degree of the examined water purity.

River	Odra	Oława	Kaczawa	Water after infiltration
		Direction of the increase in water pollution ←		
Ozone dose necessary for disinfection mg/dm$_3$/O_3	5.0	5.0	1–2.5	0.3
Ozonization time min	20	10	10–5	1

From the above statement it follows that, in view of the disinfection effects and the water conditioning costs, it is both advisable and necessary to treat water before the disinfection. The rate of bacteria removal during ozonization increases with the decre-

asing degree of water purity. In waters being polluted to the same degree the disinfection effects depend on the initial content of bacteria. An increase in the content of bacteria results in the increase of the ozonization dose and time. The obtained equation characterizing the disinfection effectiveness is in the form

$$\frac{N}{N_0} = e^{-(kT)^n}.$$

The equation describes the rate of n-order reaction. By means of the commonly applied equation

$$\frac{N}{N_0} = e^{-kT}$$

only the results of examining the waters from the Oława river could be approximated with sufficient accuracy. Hence the equation proposed may be acknowleged to be more general than the commonly applied one.

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DEZYNFEKCJA WÓD POWIERZCHNIOWYCH OZONEM W UJĘCIU BADAŃ MODELOWYCH

Skuteczność bakteriobójczą dezynfekcji określa prawo Chicka, zgodnie z kinetyką reakcji I rzędu: $N_t = N_0 e^{-kT}$. Zależność ta była wielokrotnie potwierdzona doświadczalnie, głównie dla przypadków dezynfekcji wód czystych chlorem. Wzrost zanieczyszczenia wód naturalnych związkami pochodzenia przemysłowego oraz stosowanie innych silnych utleniaczy, przede wszystkim ozonu, doprowadziło do znacznej zmiany warunków dezynfekcji. W wodach takich obok dezynfekcji przebiegają także reakcje utleniania, które prowadzą do zwiększenia dawki ozonu i zmiany rzędu reakcji. W pracy wykazano na drodze empirycznej, przydatność reakcji n-tego rzędu dla ilościowej charakterystyki dezynfekcji ozonem. Badania przeprowadzono na wodach powierzchniowych z rzeki Odry, Oławy, Kaczawy, ze stawu filtracyjnego i wody infiltracyjnej. Wody te charakteryzują się różnym stopniem zanieczyszczenia fizyko-chemicznego i bakteriologicznego. Laboratoryjna skala eksperymentu była przyczyną wykonanej analizy błędu oraz doboru, na tej podstawie, techniki pomiaru i podstawowych wymiarów aparatury. Wyniki badań aproksymowano zależnością $N_t = N_0 e^{(-kT)^n}$, stosując metodę najmniejszych kwadratów. Wartość stałej n, z wyjątkiem wód rzeki Oławy, były różne od jedności. Określono czas dezynfekcji, dawkę ozonu, oraz zmiany w składzie fizycznochemicznym wody. Efekty dezynfekcji określono na podstawie ilości bakterii mezofilnych i psychofilnych.

DESINFEKTION VON OBERFLÄCHENWASSER IN MODELLUNTERSUCHUNGEN

Die Keimabtötung im Desinfektionsverfahren vollzieht sich nach einer Reaktion erster Ordnung $N_t = N_0 e^{-kT}$ und ist als Chick'sches Gesetz in der Mikrobiologie bekannt. Diese Formel wurde vielmals empirisch bestätigt, vor allen bei der Desinfektion von Reinwasser mittels Chlor. Der Anstieg der Verschmutzung im Oberflächenwasser, die Anreicherung mit (Schmutz) Stoffen industrieller Herkunft und die Anwendung anderer starker Oxydationsmittel wie z. B. von Ozon, führen zur Änderung der Desinfektionsbedingungen. Im verschmutzten Wasser laufen auch Redox-Reaktionen ab, was eine Änderung der Reaktionsordnung zu Folge hat und zur Erhöhung der O_3-Dosis führt.

Der Ozonierung wurde empirisch die Reaktion *n*-ter Ordnung angepasst. Untersucht wurden die Flußwässer der Oława, Odra und Kaczawa, das Wasser aus einem Speiseteich und ein künstlich infiltriertes Grundwasser. Alle Wässer waren in verschiedenem Maß verschmutzt. Das Labormaßstab diente zur Fehleranalyse und zur Anpassung der entsprechenden Meßtechnik. Die Ergebnisse approximierte man gemäß der Formel $N_t = N_0 e^{(-kT)n}$ unter Bezugnahme der Methode der kleinsten Quadrate. Die Konstante *n* war nur für das Oława-Wasser gleich 1. Bestimmt wurde die Kontaktzeit, die Ozondosis und Änderungen der Wasserbeschaffenheit. Die Abtötungsrate wurde an den meso- und psychrophilen Keimen nachgewiesen.

ДЕЗИНФЕКЦИЯ ПОВЕРХНОСТНЫХ ВОД ОЗОНОМ ПРИ ПОДХОДЕ МОДЕЛЬНЫХ ИССЛЕДОВАНИЙ

Бактерицидная эффективность дезинфекции определяет закон Чика (Chicka) соответственно с кинетикой реакции I порядка: $N_t = N_0 e^{-kT}$, эта зависимость была многократно подтверждена опытным путём, главным образом для случаев дезинфекции чистых вод хлором. Увеличение загрязнения природных вод соединениями промышленного происхождения, а также применение других сильных раскислителей, главным образом озона, что привело к значительному изменению условий дезинфекции. В таких водах, наряду с дезинфекцией, происходят также реакции окисления, которые приводят к увеличению дозы озона и изменению порядка реакции. В работе эмпирическим путём доказана пригодность реакции *n*-ого порядка для количественной характеристики дезинфекции озоном. Исследования проведены на поверхностных водах из рек Одра, Олава, Качава, из фильтрационного пруда и инфильтрационной воды. Эти воды характеризуются различной степенью физико-химического и бактериологического загрязнений. Лабораторный масштаб эксперимента был причиной выполненного анализа ошибки, а также подбора на этой основе техники измерения и основных размеров аппаратуры. Результаты исследований аппроксимированы зависимостью $N_t = N_0 e^{(-kT)n}$, применяя метод наименьших квадратов. Значения постоянной *n*, за исключением вод реки Олавы, были отличны от единицы. Определены время дезинфекции, доза озона, а также изменения в физикохимическом составе воды. Эффекты дезинфекции определены на основе количества мезофильных и психофильных бактерий.