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THE MECHANISM OF THE APPARENT BOD REDUCTION DUE TO CHLORINATION

An attempt to present the mechanism of the apparent BOD reduction due to chlorination has been made. Chemistry of chlorine reactions with various types of compounds have also been discussed. The results obtained indicate that there is no real reduction in the BOD reduction due to chlorination and, moreover, the process leads to the formation of trihalomethanes.

1. BACKGROUND

The use of chlorine as a disinfectant had its earliest beginnings in Vienna in 1848 when Ignaz Semmelweis suggested that physicians wash their hands in dilute calcium hypochlorite solution between operations. Prior to his suggestion, the death rate after surgery to correct a malady was many times greater than the death rate due to the malady alone. Initially, his suggestion was not very well received, but it did mark the first instance of the positive effects of chlorine disinfection.

Sixty years later, in 1909, the Jersey City, New Jersey, water facility began hypochlorite treatment of its public water supply. It was only through the intervention of a sanguine magistrate who upheld the right of the city to chlorinate the water supply in the best interests of public health that the practice was allowed to continue. Since then, chlorination of public water supplies has spread so that any public water not subject to chlorination is an extremely rare eventuality.

With the increased use of chlorine for disinfection purposes, there has been a remarkable decrease in the incidence of waterborne diseases such as typhoid, paratyphoid, and cholera. Chlorination, along with the pasteurization of milk, is responsible for the dramatic decline in the death rate shown in fig. 1.

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Chlorine is applied to sewage treatment plant effluents, industrial wastes, and to drinking water prior to discharge to the public. Current common practice is to chlorinate so that there is a certain chlorine level, referred to as chlorine residual, remaining after discharge to ensure protection from any unforeseen

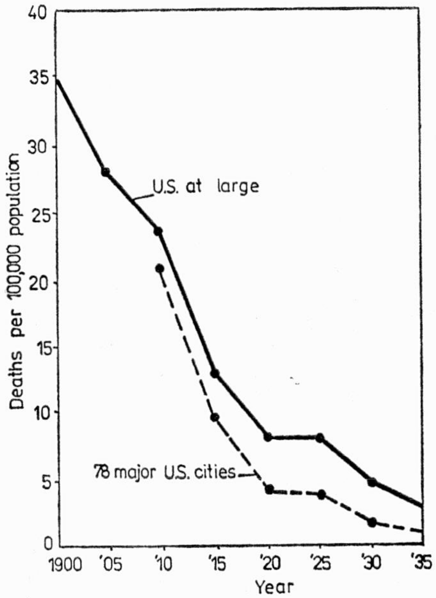
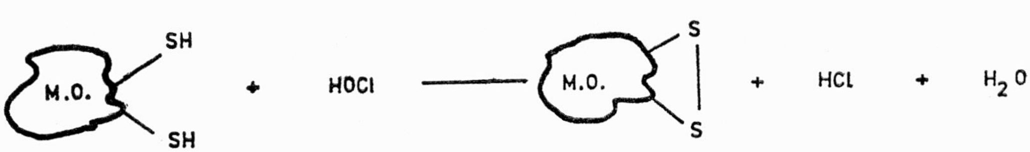


Fig. 1. Typhoid and para-typhoid death rate in the U.S. at large and in 78 major U.S. cities

Rys. 1. Zgony spowodowane tyfusem i paratyfusem w Stanach Zjednoczonych ogółem i 78 dużych miastach

contamination. Because the use of chlorine has become so widespread and commonplace, there is a tendency today to overchlorinate, which has led to serious environmental concerns.

The kill mechanism due to chlorine is rather simple and is primarily a chemical oxidation. For that reason, it is safe to assume that pathogenic microorganisms will not develop strains resistant to chlorine as certain other microorganisms have, as in the case of DDT. The chlorine is able to oxidize the sulfhydral group $(-SH)_2$ characteristic to microorganism enzymes to link the groups, and in doing so it inhibits enzyme activity. The inhibition mechanism is shown in reaction:



99 % organism kill can be accomplished in 1 mg/dm³ solution in as low as 15 min.

2. CHLORINE CHEMISTRY

Chlorine in significant concentrations is an oxidizing agent and is also very reactive as a substituting chemical. The following listing shows the reactions of chlorine with various types of compounds:

1) organic nitrogen,
2) inorganics, such as cyanides, lower valence stage metals, etc,
3) phenols,
4) ammonia,
5) organic oxidation,
6) trihalomethane formation.

The significant fact with chlorine oxidation of organics is that most reactions are very slow; there are few exceptions. The reaction with the most environmental concern is the reaction of certain acetyl group ($-\overset{O}{\overset{\|}{C}}-CH_3$) containing organics to trihalomethanes which are suspected carcinogens.

Another interesting reaction involving chlorine is its reaction with humic materials commonly found in wastewater. Humics are the end products of poorly biodegradable decomposition products, and they contain certain functional groups that form trihalomethanes rapidly. There have been suggestions to limit or replace chlorination with such alternatives as ozonation, gamma radiation, and various physical–chemical treatment methods.

3. REPORTED BOD REDUCTION DUE TO CHLORINATION

During wastewater treatment, organic compounds are oxidized in the presence of microorganisms to carbon dioxide and water as shown in reaction (2):

$$CHO + O_2 \xrightarrow{\text{microorganisms}} CO_2 + H_2O \qquad (2)$$

where CHO represents organic compounds.

Without the microorganisms present, the oxidation is very slow, so it can be said that the microorganisms catalyze the oxidation. In the early stages, the oxidation is rapid because of the large food supply, but as the food diminishes and the microorganism concentration increases, the oxidation becomes retarded. After the organics are oxidized, the microorganism concentration falls prey to predators and decreasing food supply. Plots of microorganism concentration are shown in fig. 2, assuming that the growth and death phases are first order reactions.

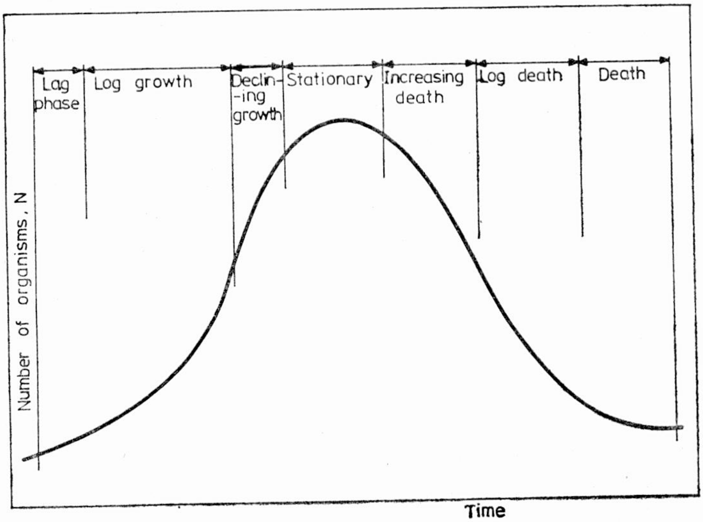


Fig. 2. Growth patterns for numbers of organisms
Rys. 2. Modele wzrostu dla danych ilości organizmów

Table 1

Investigator	Chlorine dose	Residual	BOD reduction	Sample	Comments
Barty, Bell [1]	10–15 ppm 10 min	0.2–0.5 ppm	42.7 %	Small town Imhoff Tank effluent	0.5 mg/dm³ No increase in BOD reduction
Bardy, Merrifield [2]			25–40 %		
Uzzle (1933)					
Griffin, Chamberlain [3]	6 ppm	0.2	75 %	A/S Effluent	The greater BOD the greater the removal by chlorination. No increase in BOD reduction after breakpoint
Keefer, Armeling [5]	3.69 ppm	1.0	35 %	Effluent	
Graft, Ridenour [4]				T/F Effluent Domestic sample	Chlorination at breakpoint did not result in increased BOD reduction
Zaloum [6]	3–13.7 ppm		0 %	Filtered samples	Used TOC

In biological wastewater treatment, either trickling filter or activated sludge, the effluent prior to discharge is chlorinated. The effluent will be characterized by a medium dissolved oxygen (DO) level, organics, and high microorganism concentration. Researchers have noted that if an effluent is sampled prior to and after chlorination, there is a reported BOD reduction. Table 1 summarizes these results. The explanation is that the reduction occurs because chlorine is an oxidizing agent and, therefore, any remaining organic compounds are simply oxidized. These findings are based on BOD_5 values taken for samples before and after chlorination. At that time, BOD_5 was the only accepted parameter used in water quality evaluation, and today many in the environment field subscribe to this reduction and incorporate it in their sewage treatment design. Unfortunately, BOD_5 is a misnomer and not a true reflection of the potential biochemical demand that will be exerted on a receiving body of water.

The methodology of the BOD test involved preparing triplicate samples of several dilutions of wastewater, incubating them, and then determining the DO of the samples and comparing the DO depletion due to oxidation to a control sample containing no wastes. Ideally, the test should be conducted

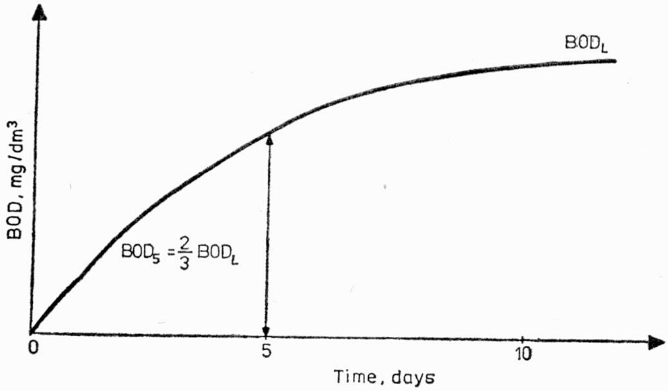


Fig. 3. Typical BOD curve
Rys. 3. Typowa krzywa BZT

for a length of ten days with daily analysis, but the amount of BOD bottles, chemicals, and equipment would be unnecessarily large. A typical carboneous BOD curve has the form shown in fig. 3, with the BOD being fully exerted after about ten days. As a rule of thumb, BOD_5 is usually 70% of BOD_L (ultimate or 1st stage BOD), and this value has become the most accepted value used. Obviously, if only analyzing at day 5, the analyst has no indication of the BOD values at any time other than day 5. If it is accepted that there is a BOD reduction due to chlorination, then it would be assumed that the curves would have the shape shown in fig. 4, with the differences in BOD after day 5 being the observed reduction phenomenon. When BOD reductions due to chlorination were reported, there was never any mention made of any complete BOD analyses up to day 10, which leads to the speculation that the BOD curves may not be the idealized forms shown in the figures.

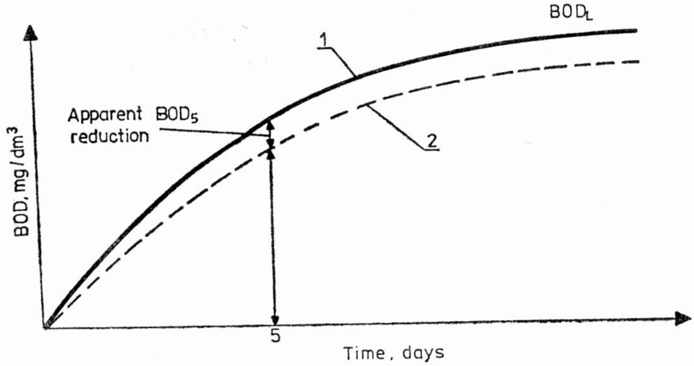


Fig. 4. BOD curves showing apparent BOD reduction as compared to a control

1 – normal BOD curve, *2* – chlorinated BOD curve

Rys. 4. Krzywe BZT przedstawiające przypuszczalną redukcję BZT w porównaniu z kontrolą

1 – krzywa normalna, *2* – krzywa doświadczalna

With the introduction of Dissolved Oxygen meters using sensitive oxygen reading probes, the task of simplifying BOD analyses has increased tremendously. Rather than preparing hundreds of bottles for the wet chemical analysis to be analyzed daily and then discarded, a small number of dilutions can be prepared and analyzed daily over and over again. The reproducibility and accuracy are greatly increased, and BOD analysts are doing more complete determinations rather than only the BOD$_5$ value. It is now easier to construct complete BOD curves and to observe demand trends for the entire time period.

4. AFTERGROWTH

An interesting phenomenon was observed when examining changes in microorganism concentrations resulting after wastewater samples had been chlorinated. If, in fact, wastewater effluents are chlorinated to 0.5 to 1.0 mg/dm^3 chlorine residual and then allowed to stand, a rapid *increase*, not a decrease, in microorganism concentration occurred. This phenomenon is known as aftergrowth. Defined, it can be stated as the rapid, accelerated growth of microorganisms as a result of an environmental stress. When chlorinated microorganism populations are monitored and compared with a control, the population changes which occur are shown in fig. 5.

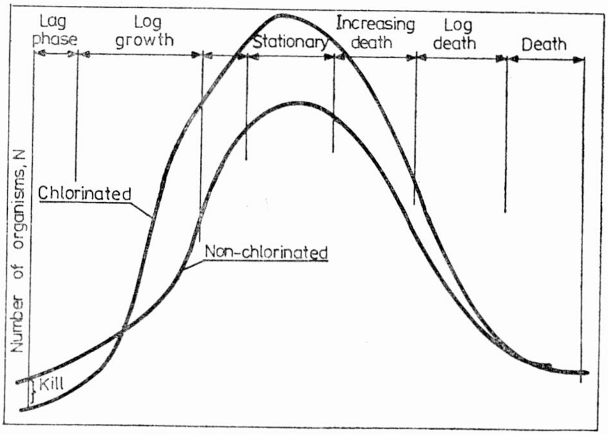


Fig. 5. Growth patterns for organisms and organisms subject to chlorination
Rys. 5. Modele wzrostu dla organizmów kontrolnych i tych poddanych chlorowaniu

The explanation is that chlorine kills both the single cell catalytic microorganisms and the organisms that prey on them. However, the generation time (time required to double the population) of the single cell organism is approximately 20 min, whereas for the predators it is 8 h. This means the single cell organisms will experience 24 (8 ×3) doublings of their population for only a single doubling of the predator organisms. If, in fact, 99% of the single cell organisms are killed by chlorine, any remainder which survive will then experience the rapid population increase because the food/organisms ratio is very high, and there is nothing for the organisms to do but to increase in population. In approximately four days, the single cell organisms will reach their maximum population, after which the food supply begins to diminish and the predators begin to assert their presence. The single cell organisms will suffer a population decline until equilibrium is again established and the normal prechlorination conditions again prevail. The important facts to remember from these observations are:

1. There is an unexpected increase in microorganism population.

2. Wastewater samples are chlorinated to 1 mg/dm^3 the same value as performed during effluent disinfection.

3. There is a decrease in organic concentration.

With these results in mind, it was then decided to investigate any correlation between the apparent BOD reduction previously reported and the aftergrowth results.

5. LABORATORY EXPERIMENTATION

The experimental portion was divided into two parts after the wastewater sample was filtered to remove solid particles and dosed with various amounts of chlorine. Only those samples exhibiting 0.3 to 0.8 mg/dm³ chlorine after one hour were retained for analysis. Chlorine concentrations were determined using the standard starch-iodide tritration method.

5.1. AFTERGROWTH

The organism selected for monitoring was total coliform because of the ease of analysis and the reproducibility of results. It is true that many other organisms are present in wastewater, but any changes in the coliform population would be representative of the entire microorganism population. The microorganisms were measured using Millipore equipment and media on series dilution samples. The results are shown in tab. 2 and fig. 6. The microorganism growth is expressed in logarithms to account better for the changes, and the slope of the curve is the growth rate constant.

Table 2

Microorganism data after chlorination
Mikroorganizmy po chlorowaniu

	Microorganism concentration			
	Residual chlorine			
days	control	0.3 mg/dm³	0.5 mg/dm³	0.7 mg/dm³
0	1×10^5	5×10^4	4×10^3	8×10^2
1	1×10^6	8×10^5	1×10^5	9×10^4
2	1×10^7	5×10^7	1×10^7	5×10^6
3	3×10^8	1×10^9	7×10^8	8×10^8
4	4×10^9	2×10^{10}	5×10^{10}	1×10^{11}
growth constant 1/day	1×10^8	5×10^9	1.3×10^{10}	2.5×10^{10}
kill %	–	50%	96%	99.2%

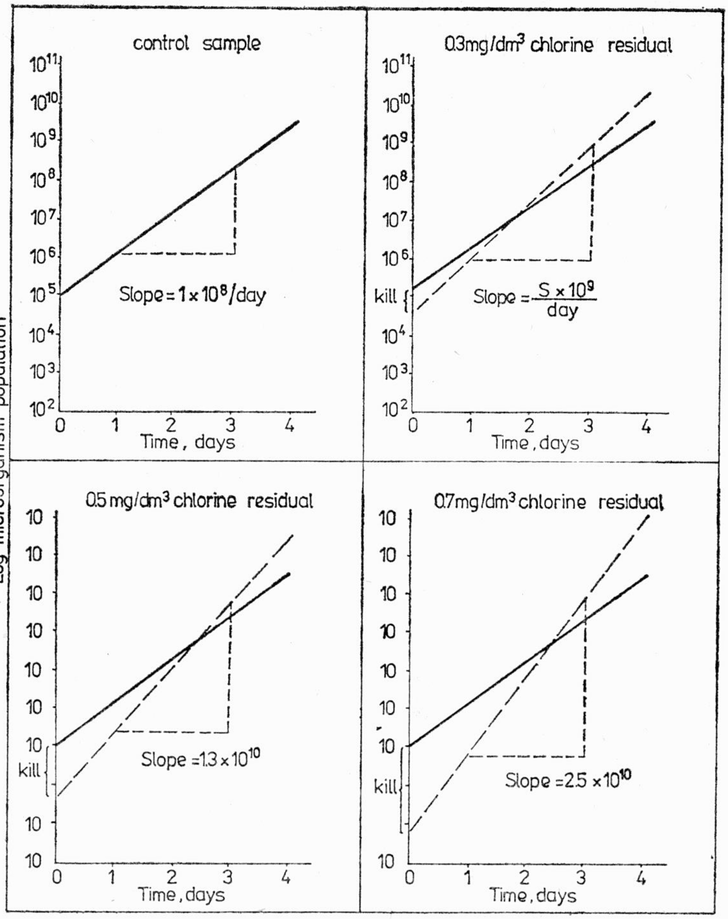


Fig. 6. Microorganisms growth curves
Rys. 6. Krzywe wzrostu mikroorganizmów

5.2. BIOCHEMICAL OXYGEN DEMAND

BOD samples were prepared by adding 5 to 15 cm^3 of chlorinated sample to BOD bottles and filling with seeded dilution water. Three trials were run: 0.3, 0.5, and 0.7 mg/dm^3 chlorine residual after one hour detention time. The bottles were incubated for a period of ten days at 20°C with DOs taken daily. A Weston and Stack DO meter was used, and these readings were converted to BOD values. The results are shown in tab. 3 and fig. 7.

The results can be explained as follows: For the chlorinated sample, there is a lag time necessary for the organisms to become acclimated to the stress. After this occurs, there is a rapid rise in oxidation until the material is finally

Data sheet key

Days	1	1	1	1	1
B1	2	2	2	2	2
B2	3	3	3	3	3
4	6 7	6 7	6 7	6 7	6 7
5	6 7	6 7	6 7	6 7	6 7
Ave.	8	8	8	8	8

1 – period of incubation, days.
2 – dissolved oxygen, blank No. 1, mg/dm^3, labelled DO_B.
3 – dissolved oxygen, blank No. 2, mg/dm^3, labelled DO_B.
4 – BOD sample volume, cm^3.
5 – another BOD sample volume, cm^3.
6 – dissolved oxygen (DO) of sample after indicated incubation time, mg/dm^3, labelled DO_S.
7 – calculated BOD, mg/dm^3,

$$\mathrm{BOD} = \frac{(DO_B - DO_S)(300)}{\text{sample vol., cm}^3}.$$

8 – average BOD for indicated incubation time, mg/dm^3.

Control sample

Days	1.3	2.0	3.1	4.0	5.0	6	7	8	10	
B1	8.6	8.5	8.5	8.4	8.3	8.2	8.1	8.1		
B2	8.6	8.4	8.3	8.3	8.2	8.2	8.0	8.0		
5 cm^3	7.0 96	6.3 129	5.4 180	5.2 189	4.6 219	4.4 228	4.0 243	4.0 243		
8 cm^3	6.0 98	5.0 130	3.8 172	3.3 190	2.5 215	2.1 228	1.6 241	1.4 250		
10 cm^3	5.4 100	4.1 130	2.8 168	2.0 190	X X	6 228	X X	X X		
15 cm^3	3.6 100	2.0 129	X X	X X	X X	X X	X X	X X		
Ave.	97	129	174	190	217	228	242	247		

oxidized. If only day 5 is examined, there appears to be a reduction in BOD, but this occurs as an aberration due to the displacement of the chlorinated BOD curve. If the lag time is displaced, the curves have the profile shown in fig. 8.

0.3 mg/dm³ residual chlorine

Days	1.3	2.0	3.1	4.0	5.0	6	7	8		10
B1	8.5	8.5	8.4	8.4	8.3	8.2	8.0	8.0		
B2	8.5	8.5	8.3	8.2	8.2	8.1	8.1	7.9		
5	7.8 42	7.2 78	5.9 147	5.3 180	4.7 213	4.5 219	4.1 237	4.0 237		
8	7.3 43	6.5 75	4.5 144	3.6 176	2.6 212	2.3 219	1.8 234	1.5 242		
10	7.0 45	6.0 75	3.6 142	2.3 180	1.25 210	8 220	X X	X X		
12	7.0 38	5.4 78	2.6 143	2.3 180	X X	X X	X X	X X		
Ave.	42	77	144	178	212	220	235	240		

0.5 mg/dm³ residual chlorine

Time	1.3	2.0	3.1	4.0	5.0	6	7	8	10	
B1	8.6	8.5	8.4	8.4	8.3	8.2	8.1	8.0		
B2	8.6	8.5	8.3	8.3	8.3	8.2	8.1	8.0		
5 cm³	8.3 18	7.9 36	6.7 99	6.0 141	5.4 174	4.7 210	4.2 234	3.9 246		
8 cm³	8.0 23	7.7 30	5.7 99	4.6 140	3.9 165	2.6 210	1.8 236	1.5 243		
10 cm³	7.9 21	7.3 36	5.1 100	3.7 139	2.6 171	1.7 210	X X	X X		
15	7.6 20	7.0 30	3.4 99	1.35 140	X X	X X	X X	X X		
Ave.	21	33	99	140	170	210	235	245		

0.7 mg/dm³ residual chlorine

Days	1.3	2.0	3.1	4.0	5.0	6	7	8	10	
B1	8.6	8.5	8.4	8.3	8.2	6.1	8.1	8.0 8.1		
B2	8.6	8.5	8.3	8.2	8.2	8.2	8.1			
5	8.4 12	8.2 18	7.4 57	6.6 99	5.7 150	4.8 201	4.3 228	4.0 243		
8	8.3 11	7.9 22	6.9 54	5.5 103	4.3 146	2.8 200	2.1 225	1.5 245		
10	8.2 12	7.6 27	6.5 55	4.9 100	3.5 141	1.6 196	8 219	X X		
12	8.2 10	7.5 25	6.0 59	4.2 104	2.5 142	X X	X X	X X		
Ave.	11	23	56	102	145	198	224	244		

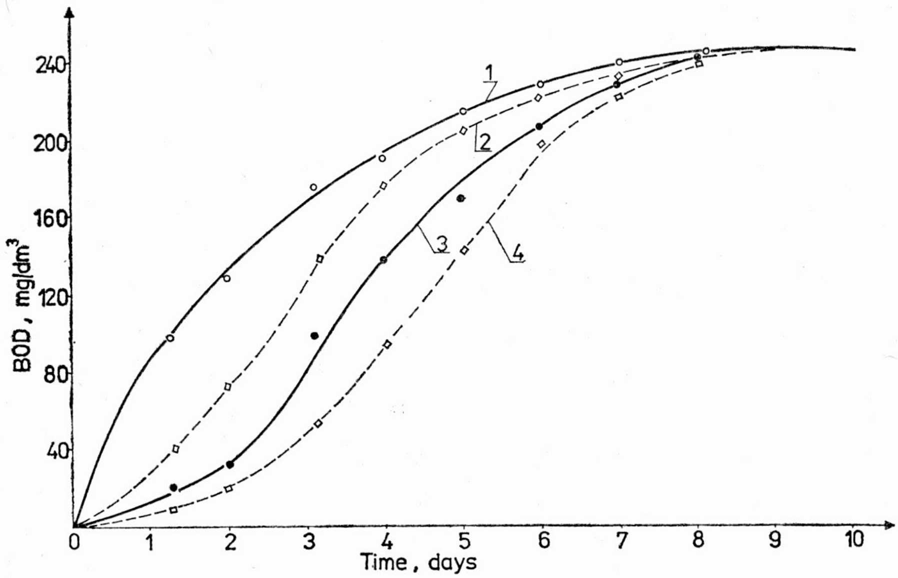


Fig. 7. Variation of BOD as a result of chlorine dosage

1 – control sample, *2* – 0.3 mg/dm³ chlorine dose, *3* – 0.5 mg/dm³chlorine dose, *4* – 0.7 mg/dm³ chlorine dose

Rys. 7. Zmiany BZT w zależności od dawki chloru

1 – próba kontrolna, *2* – 0,3 mg/dm³ chloru, *3* – 0,5 mg/dm³ chloru, *4* – 0,7 mg/dm³ chloru

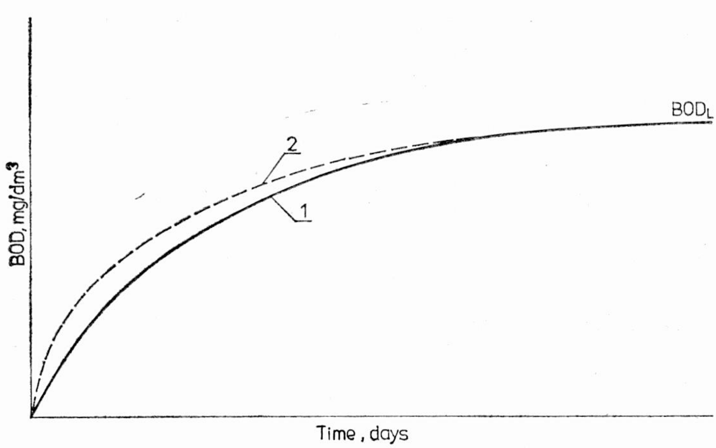


Fig. 8. Actual BOD curves for samples subjected to chlorination

1 – normal BOD curve, *2* – chlorinated BOD curve

Rys. 8. Aktualne krzywe BZT dla próbek poddanych chlorowaniu

1 – krzywa normalna, *2* – krzywa doświadczalna

The chlorinated sample displays a faster rate of reaction as a result of the increased microbial activity. There is no real reduction in the BOD because of these conditions — chlorine does not act as an oxidizing agent. The results of this investigation suggest that any changes in BOD due to chlorination were misunderstood from reading only BOD_5 values. If there is no BOD reduction due to chlorination, this may be another argument in favor of replacing chlorine as a disinfection process. Together with the formation of trihalomethanes, there is sufficient cause to seek alternative methods to disinfect effluent wastewater.

Table 3

BOD values (mg/dm^3) after chlorination
BZT (w mg/dm^3) po chlorowaniu

Days	Control	0.3 mg/dm^3	0.5 mg/dm^3	0.7 mg/dm^3
0	0	0	0	0
1.3	97	42	21	11
2.0	129	77	33	23
3.1	174	144	99	56
4.0	190	178	140	102
5.0	217	212	170	145
6.0	228	220	210	198
7.0	242	235	235	224
8.0	247	240	245	244

REFERENCES

[1] Baity H. G., Bell F. M., *Reduction of sewage by chlorination,* Sewage Works Journal, Vol. 1 (1929), p.279.

[2] Baity H. G. et al., Some effects of sewage chlorination upon the receiving streams, Sewage Works Journal, Vol. 5 (1933), p. 429.

[3] Griffin A. E., Chamberlain N. S., *Exploring the effect of heavy dosages of chlorine in sewage,* Sewage Works Journal, Vol. 17 (1945), p. 730.

[4] Graft G., Ridenour G. H., *Effects of breakpoint chlorination on the BOD of sewage,* Sewage Works Journal, Vol. 15 (1943), p. 847.

[5] Keefer, Armeling, *BOD of chlorinated sewage,* Journal of Sewage and Industrial Wastes, Vol. 24 (1952), p. 689.

[6] Zaloum R., Reduction of oxygen demand of treated wastewater by chlorination, Journal Water Pollution Control Federation, Vol. 46, 12, (Dec. 1974), p. 2770.

PRZYPUSZCZALNY MECHANIZM REDUKCJI BZT W PROCESIE CHLOROWANIA ŚCIEKÓW

Podjęto próbę przedstawienia przypuszczalnego mechanizmu redukcji BZT w procesie chlorowania ścieków. Przedstawiono i omówiono reakcje chemiczne chloru z różnymi związkami. Badania wykazały, że chlorowanie ścieków nie prowadzi do rzeczywistej redukcji BZT, lecz powoduje powstanie trójchlorowcometanów.

ÜBER DEN MECHANISMUS DER BSB-REDUKTION IM VERLAUF DES ABWASSERCHLORUNGSPROZESSES

Besprochen werden chemische Reaktionen, die zwischen dem Chlor und anderen Substanzen zustandekommen. Die Analyse der Untersuchungsergebnisse hat gezeigt, daß während des Abwasserchlorungsprozesses keine BSB-Reduktion erfolgt und nur Trihalogenmethane erzeugt werden.

ПРЕДПОЛАГАЕМЫЙ МЕХАНИЗМ ВОССТАНОВЛЕНИЯ БПК В ПРОЦЕССЕ ХЛОРИРОВАНИЯ СТОЧНЫХ ВОД

Предпринята попытка представления предполагаемого механизма восстановления БПК в процессе хлорирования сточных вод. Приведены и обсуждены химические реакции хлора с различными соединениями. Исследования показали, что хлорирование сточных вод не приводит к действительному восстановлению БПК, а вызывает образование трихлорнитрометанов.