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# FORMATION OF ORGANIC NITROGEN COMPOUNDS DURING CHLORINATION OF WATER AND WASTEWATER

Basing on the investigations performed, it has been shown that chlorination of water and wastewater yields not only organic halogen derivatives but also organic nitrogen compounds. The latter are formed in reaction of ammonia with organic halogen derivatives and the products of chlorine oxidation of organic compounds. The amounts of the produced organic halogen derivatives and organic nitrogen compounds depend on the concentrations of organic compounds in water and wastewater.

## 1. INTRODUCTION

Chlorination of water and wastewater consists, among others, of chlorination and oxidation of organic compounds, as well as some secondary processes, such as reactions of ammonia with organic halogen derivatives, oxidation products etc. [6]. Chlorination of organic compounds proceeds in two phases.

During the first phase of the process the amount of organic halogens increases with the dosage of chlorine until the maximum concentration is attained (chlorination phase), thereupon with a continuously increasing chlorine dosage it decreases (second phase — oxidation phase). If ammonium nitrogen is present, the two phases occur in the region of chloramine formation, the latter being also a chlorination factor. At the break point of the curve for chlorine demand and beyond this point (within the region of free chlorine) the oxidation of organic halogens is still continued.

Chlorination process is also influenced by the concentration of organic pollutants [7]. In polluted waters the amounts of organic halogens are decreasing, since chlorine is reduced due to the oxidation of organic compounds readily oxidized.

Chlorination of organic compounds in water and wastewater is chiefly an ionic process; chlorination according to radical mechanisms will not take place, since dissolved oxygen inhibits this process. Hence only some groups of organic compounds, such as olefins, aromatic compounds, aldehydes, ketons, organic nitrogen compounds (protein, amino acids) will undergo chlorination.

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Other processes taking place during chlorination are the reactions of ammonia with organic halogen derivatives [1, 8], e.g. substitution chlorine in alkyl chlorides results in hydrochlorides in primary, secondary and tertiary amines. Reaction of ammonia with halogen acids yields amino acids. Substitution of ammonia for chlorine in acid chlorides leads to formation of acid amides.

Ammonia reacts, moreover, with some chlorine-oxidation products, e.g. oxidation of phenol systems coming from lignin and reaction with ammonia [9] may lead to formation of carboxyl derivatives of pyridine; reaction with esters results in acid amides.

There is a number of organic compounds present in water and wastewater, the concentrations of which are not determined in terms of organic nitrogen by Kjeldhal method, e.g. azines, hydroazo compounds, nitriles, nitroso compounds, oxines and semicarbosones [2]. Some of these compounds can be transformed due to oxidation into other nitrogen compounds, e.g. nitriles undergo hydrolysis induced by hydrogen peroxide in weakly alkaline medium resulting in amides. Hence, the purpose of the present paper is to establish the course of chlorination process of organic compounds present in water and wastewater, the influence of chlorination on the formation of organic nitrogen compounds as well as the effect of the latter on the chlorination process. The influence of concentrations of organic compounds and ammonium nitrogen on the chlorination process and formation of organic nitrogen compounds will be additionally established.

## 2. METHODS

Water from the Odra river and wastewater after trickling filters and activated sludge treatment in Wałbrzych were chlorinated with varying dosages of chlorine, at the controlled pH value (pH 7-8). pH was adjusted by 0.1 M sodium hydroxide added to the sample. The concentrations of organic halogens were determined by mineralization of the sample at 1273 K in the presence of a catalyst [3]. Chlorine was determined iodinometrically at pH 6.5 in the presence of buffer [4, 5]. The above concentrations were determined after 6.5 and 24 h contacts with chlorine. In post-chlorination samples the concentrations of organic nitrogen have been also determined after chlorine was reduced with sodium thiosulphate.

## 3. RESULTS OF INVESTIGATIONS

During chlorination of samples with varying doses of chlorine it has been stated that the concentration of organic nitrogen increases with the chlorine dose (fig. 1), it reaches its maximum value and thereupon it decreases. At the same time the content of ammonium nitrogen decreases in the region of the increase of nitrogen (fig. 1). The maximum point of the increment of organic nitrogen occurs on the average at 0.65 chlorine dosage necessary to obtain the maximal point on the chlorination curve (tab. 1). At the break point the concentration of organic nitrogen decreased.

The increment of organic nitrogen during chlorination depends on the concentrations of organic pollutants, expressed by permanganate value and COD. At low concentrations of pollutants (for COD up to 70 g $O_2/m^3$ and permanganate value to about 15 g $O_2/m^3$) the increment of organic nitrogen is proportional to the values of the above indices (figs. 2

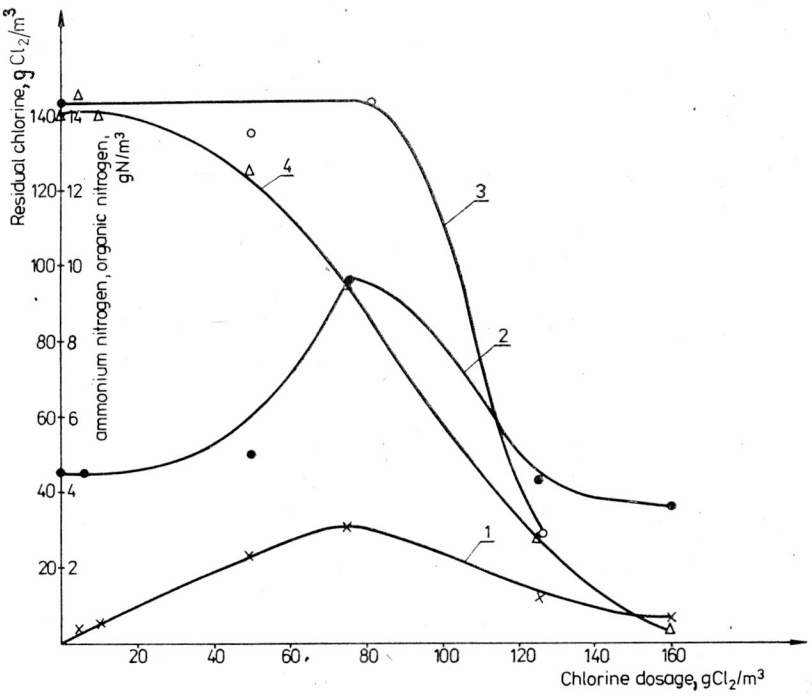


Fig. 1. Changes in the concentrations of organic and ammonium nitrogen during chlorination of biologically treated wastewater with varying doses of chlorine

1 — residual chlorine, 2 — organic nitrogen, 3 — total concentration of the particular forms of nitrogen, 4 — total contents of ammonium and chloramine nitrogen

Rys. 1. Przebieg zmian zawartości azotu organicznego i amonowego podczas chlorowania zmiennymi dawkami chloru ścieków biologicznie oczyszczonych

1 — chlor pozostały, 2 — azot organiczny, 3 — sumaryczna zawartość poszczególnych form azotu, 4 — suma zawartości azotu amonowego i chloraminowego

and 3). After the maximum is attained the increment of organic nitrogen decreases reaching zero values for water for which COD equals about 120 g $O_2/m^3$ and permanganate value ranges from 20 to 30 g $O_2/m^3$.

The value of the organic nitrogen increment depends also on the initial concentration of ammonium nitrogen. For a low concentration of organic compounds (permanganate value 4-9 g $O_2/m^3$) it depends weakly on the concentration of ammonium nitrogen, for higher concentrations of organic compounds this effect is observed for the concentration of ammonium nitrogen exceeding 14 g/$m^3$ (fig. 4). The COD/permanganate value ratio

Table 1

Results of water and wastewater chlorination
Wyniki chlorowania wód i ścieków

| Kind of water | PV* g $O_2/m^3$ | COD g $O_2/m^3$ | $N_{NH_4^+}$ g $N/m^3$ | Increment of organic nitrogen g $N/m^3$ after 0.5 h | Increment of organic nitrogen g $N/m^3$ after 24 h | $\frac{COD}{PV^*}$ | $Cl_2/N_{NH_4^+}$ ratio for the max. increment of organic nitrogen ($x_1$) on the average | $Cl_2/N_{NH_4^+}$ ratio for the max. appearing on the curve of chlorine demand ($x_2$) on the average | $\frac{x_1}{x_2}$ |
|---|---|---|---|---|---|---|---|---|---|
| Odra river | 16.5 | — | 2.40 | 6.0 | 4.0 | — | 4.15 | 12.4 | 0.335 |
| Biologically treated wastewater | 8.8 | 46.0 | 5.50 | 2.5 | — | 5.20 | 3.63 | 5.45 | 0.66 |
| | 17.6 | — | 17.5 | 0 | — | — | — | 5.10 | — |
| | 28.2 | — | 25.0 | 1.0 | — | — | 1.2 | 10.1 | 0.12 |
| | 18.0 | 120 | 22.5 | 2.0 | — | 6.66 | 1.34 | 10.20 | 0.13 |
| | 20.3 | 126 | 20.0 | 0.0 | — | 6.22 | — | 5.0 | — |
| | 17.0 | 91.0 | 25.0 | 0.5 | — | 5.34 | 10 | 10 | 1.0 |
| | 12.8 | 112.0 | 15.0 | 1.1 | — | 7.88 | 0.6 | 7.3 | 0.08 |
| | 7.0 | 70.4 | 25.0 | 2.0 | — | 10.0 | — | — | — |
| | 3.6 | 11.8 | 15.0 | 2.0 | — | 3.28 | 5.4 | 7.0 | 0.77 |
| | 16.4 | 126.0 | 9.0 | 0.5 | — | 7.90 | 0.55 | 8.0 | 0.07 |
| | 21.2 | — | 25.0 | 0 | — | — | — | 7.8 | — |
| | 20.7 | 32.7 | 27.0 | 2.0 | — | 1.63 | 1.3 | 6.1 | 0.21 |
| | 16.0 | 92.0 | 14.0 | 9.0 | — | 5.73 | 4.30 | 5.35 | 0.80 |
| | 6.0 | 33.6 | 20.0 | 3.0 | — | 5.57 | 4.5 | 6.5 | 0.75 |
| | 15.5 | 42.2 | 10.4 | 5.8 | — | 2.72 | 5.0 | 5.0 | 1.0 |
| | 11.7 | 75.0 | 15.5 | 7.0 | 5.5 | 6.4 | 6.40 | 5.0 | 1.28 |
| | 12.4 | 83.3 | 14.5 | — | 5.0 | 6.7 | 5.0 | 5.0 | 1.0 |
| Odra river | 5.4 | — | 10.0 | 2.0 | — | — | 3.75 | 5.0 | 0.75 |
| Biologically treated wastewater | 17.0 | 64.7 | 12.0 | 6.0 | 3.0 | 5.0 | 10.0 | 6.67 | 1.5 |
| | 13.0 | 53.5 | 7.0 | 4.2 | 3.0 | 4.22 | 5.72 | 9.0 | 0.635 |
| Odra river | 5.7 | — | traces | 3.0 | — | — | — | — | — |

* permanganate value.

at which the increment of organic nitrogen reaches its maximum amounts to about 4.66, the average COD/permanganate value ratio for the water examined being 5.6 (tab. 1).

Similar dependences have been obtained for chlorination of organic compounds. The increment of organic halogens for low values of permanganate value and COD is proportional to the concentrations of organic pollutants (figs. 3 and 5). The maximum increment of organic halogens occurred at the average value of COD equal to about

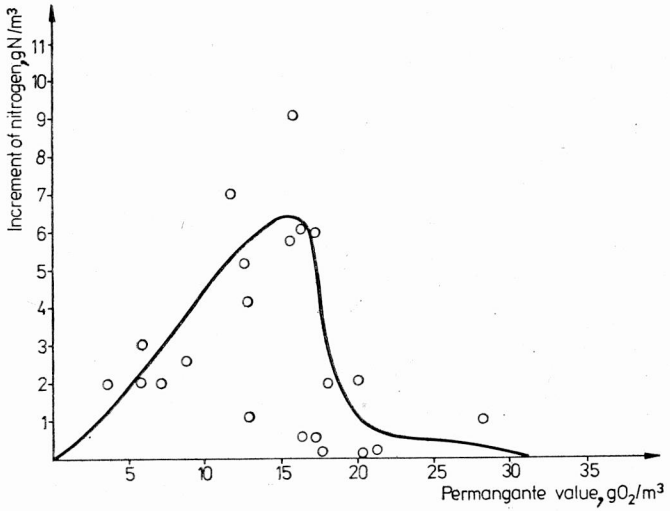


Fig. 2. Increment of the organic nitrogen concentration (at the points of maximum increment) during chlo rination vs. permanganate value

Rys. 2. Zależność przyrostu zawartości azotu organicznego (w punktach maksymalnego przyrostu) podczas chlorowania od utlenialności wód chlorowanych

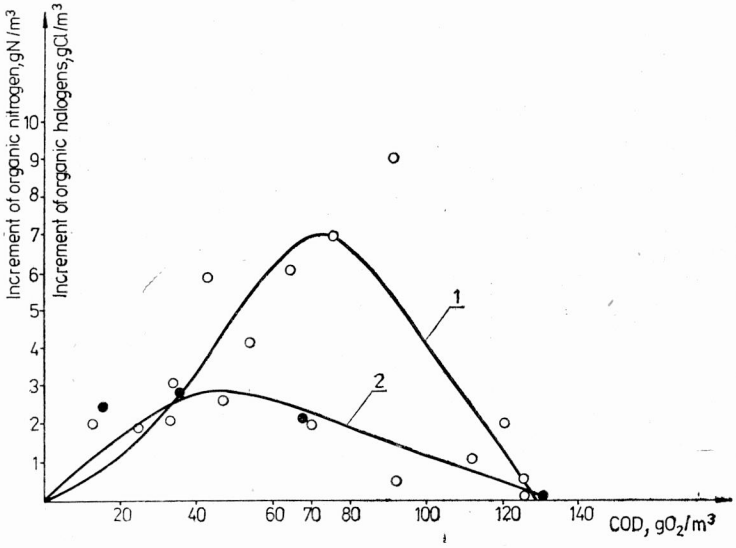


Fig. 3. Increment of the organic nitrogen and organic halogens concentrations (at the points of maximum increment) during chlorination vs. the COD value of chlorinated water

1 — organic nitrogen, 2 — organic halogens

Rys. 3. Zależność przyrostu azotu organicznego i chlorowców organicznych podczas chlorowania (w punktach maksymalnego przyrostu) od ChZT wód chlorowanych

1 — azot organiczny, 2 — chlorowce organiczne

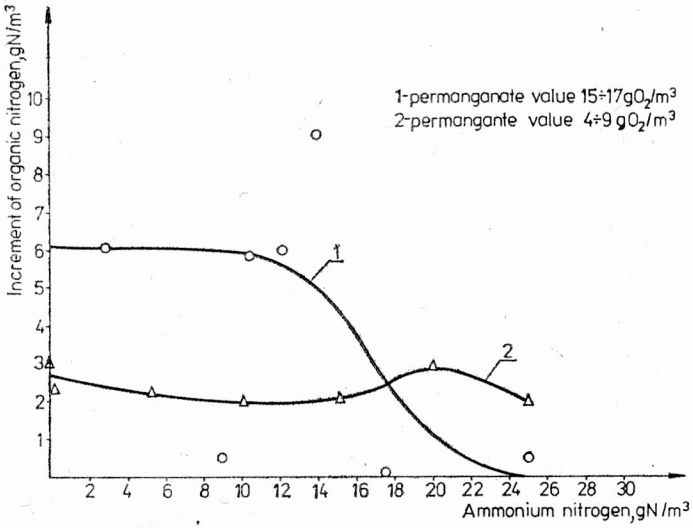


Fig. 4. Increment of organic nitrogen concentration (at the points of the maximum increment) during chlorination vs. permanganate value and the initial concentration of ammonium nitrate

Rys. 4. Zależność przyrostu zawartości azotu organicznego (w punktach maksymalnego przyrostu) podczas chlorowania od utlenialności i początkowej zawartości azotu amonowego

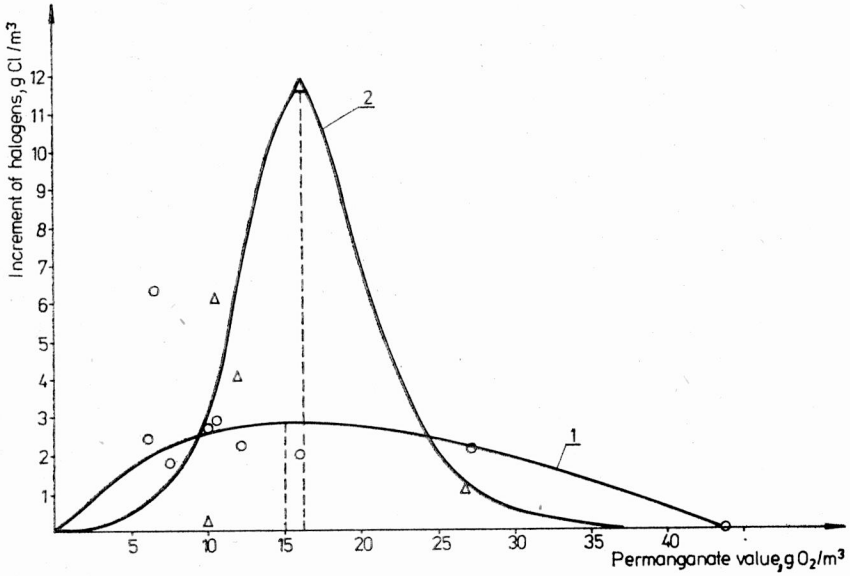


Fig. 5. Increment of organic halogens concentration (at the points of the maximum increment) during chlorination vs. permanganate value and time of contact with chlorine

1 — after 0.5 h contact with chlorine, 2 — after 24 h contact with chlorine

Rys. 5. Zależność przyrostu zawartości chlorowców organicznych (w punktach maksymalnego przyrostu) podczas chlorowania od utlenialności i czasu kontaktu z chlorem

1 — po 0,5 h kontaktu z chlorem, 2 — po 24 h kontaktu z chlorem

53 g $O_2/m^3$ and permanganate value of about 15 g $O_2/m^3$. With the increasing concentrations of organic compounds the increment in the contents of halogens dropped to zero (COD about 130 g $O_2/m^3$ and permanganate value about 40 g $O_2/m^3$). The maximum increment of organic halogens takes place at the same chlorine to ammonium nitrogen weight ratio. The required dose of chlorine amounts to 0.66 of the dose required to obtain the maximal point on the curve of chlorine demand. The COD/permanganate value ratio at the point of maximal increment of organic halogens amounts to 3.3, and for chlorinated water — 3.1 (tab. 2).

Table 2

Results of water and wastewater chlorination
Wyniki chlorowania wód i ścieków

| Kind of water | PV* g $O_2/m^3$ | COD g $O_2/m^3$ | $\frac{COD}{PV^*}$ | $N_{NH_4^+}$ g $N/m^3$ | Increment of organic halogens g $Cl/m^3$ | | $Cl_2/N_{NH_4^+}$ ratio at which the concentration of organic halogen is maximal ($x_1$) | | $Cl_2/N_{NH_4^+}$ ratio for the maximum appearing on chlorination curve ($x_2$) | $\frac{x_1}{x_2}$ on the average |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | after 0.5 h | after 24 h | after 0.5 h | after 24 h | | |
| Odra river | 7.5 | 24.7 | 3.3 | 20.3 | 1.8 | — | 2.5 | — | 7.5 | 0.33 |
| Odra river | 10.5 | 34.7 | 3.3 | 4.0 | 2.8 | 6.2 | 6.15 | 5.42 | 5 | 1.16 |
| Biologically treated wastewater | 16.0 | 68.6 | 4.3 | 14.0 | 2.0 | 11.7 | 2.5 | 3.2 | 5 | 0.55 |
| Biologically treated wastewater on trickling filters | 12.0 | — | — | 21.0 | 2.25 | 4.0 | 1.5 | 2.5 | 5.0 | 0.5 |
| | 10.0 | — | — | 4.0 | 2.6 | 0.2 | 7.5 | 5.0 | 10.0 | 0.62 |
| | 27.0 | — | — | 2.2 | 2.1 | 1.09 | 6.8 | 9.1 | 13.7 | 0.58 |
| Biologically treated wastewater with activated sludge process | 44.0 | 130.5 | 2.95 | 6.0 | 0 | — | — | — | 5.0 | — |
| | 6.6 | 15.3 | 2.30 | 6.0 | 6.5 | — | 5.0 | — | 5.0 | 1.0 |
| | 6.0 | 15.0 | 2.5 | 6.0 | 2.5 | — | 2.68 | — | 5.0 | 0.53 |

* permanganate value.

The differences in the increment of organic halogens are observed after a longer contact time with chlorine (after 24 h), (fig. 5). The increment of organic halogens after 24 h amounted to about 12 g $Cl/m^3$, and after 0.5 h it amounted scarcely to 3 g $Cl/m^3$. Concentration of organic nitrogen remained unchanged or only slightly decreased (tab. 1).

## 4. DISCUSSION OF RESULTS

From the above data it follows that both the chlorination of organic compounds and formation of organic nitrogen compounds are closely interrelated. During the first chlorination phase organic halogen derivatives are formed with chlorine mainly substituted at carbon atom, and organic compounds being the product of chlorine oxidation. Then, reaction of ammonia with the above compounds yields organic nitrogen compounds. From the analysis of quantitative decrement of ammonium nitrogen and increment of organic nitrogen, it follows that in some cases the increment of organic nitrogen exceeds the ammonia decrement. This is probably due to chlorination-induced transformations of nitrogen organic compounds. During the next chlorination phase organic nitrogen compounds become chlorinated by chloramines, since one observed the increment of the concentration of organic halogens and decrement of residual chlorine, and the amount of organic nitrogen remains unchanged or decreases.

The fact that there are close interrelations between the formation of organic halogens and organic nitrogen compounds indicates that the chlorination process follows the course described above. The point of the maximum increment of organic halogens and organic nitrogen takes place at the same chlorine to ammonium nitrogen ratio. The maximum increments of organic halogens and organic nitrogen have been obtained for almost the same values of COD and permanganate value.

## 5. CONCLUSIONS

Chlorination of water and wastewater gives rise not only to organic halogen derivatives but also to organic nitrogen compounds. The latter are formed in reaction of ammonia with organic halogen derivatives and with the product of chlorine oxidation of organic compounds. They are much susceptible to chlorination being chlorinated even by chloramines. Like organic halogen derivatives they are formed in the region of chloramine formation. The point of their maximum concentration expressed by the concentration of organic nitrogen occurs at 0.65 dose of chlorine necessary to obtain the maximum point on the curve of chlorine demand. The amounts of the produced organic halogen derivatives and organic nitrogen compounds depend on the concentrations of pollutants in water and wastewater. In chlorinated water and wastewater with COD = 50-70 g $O_2/m^3$ and permanganate value = 15 g $O_2/m^3$, their concentrations are proportional to the concentration of organic compounds. In water and wastewater with a higher concentrations of organic pollutants a drop in the increment of both organic halogen derivatives and organic nitrogen compounds has been observed.

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## POWSTAWANIE ORGANICZNYCH ZWIĄZKÓW AZOTOWYCH PODCZAS CHLOROWANIA WÓD I ŚCIEKÓW

Na podstawie badań wykazano, że w procesie chlorowania wód i ścieków obok chlorowcopochodnych organicznych powstają organiczne związki azotowe. Wytwarzają się one w wyniku reakcji amoniaku z chlorowcopochodnymi organicznymi i produktami utleniania związków organicznych chlorem. Ilość wytwarzanych chlorowcopochodnych organicznych i organicznych związków azotowych zależy od zawartości związków organicznych w wodach i ściekach.

## DIE BILDUNG VON ORGANISCHEN STICKSTOFFVERBINDUNGEN WÄHREND DER WASSER- UND ABWASSERCHLORUNG

Anhand von Untersuchungen ist bestätigt worden, daß während der Wasser- und Abwasserchlorung neben organischen Chlorderivaten auch organische Stickstoffverbindungen entstehen. Sie entstehen als Reaktionsprodukte des Ammoniaks, der organischen Chlorderivate und der Oxydationsprodukte von organischen Verbindugen mit Chlor. Die Menge der entstehenden organischen Chlorderivate und Stickstoffverbindungen hängt von der Gesamtmenge der organischen Stoffe im Wasser und Abwasser ab.

## ОБРАЗОВАНИЕ ОРГАНИЧЕСКИХ АЗОТНЫХ СОЕДИНЕНИЙ ВО ВРЕМЯ ХЛОРИРОВАНИЯ ВОД И СТОЧНЫХ ВОД

На основе исследований доказано, что в процессе хлорирования вод и сточных вод наряду с галоидноироизводными органическими соединениями образуются органические азотные соединения. Они образуются в результате реакции аммиака с галоидноироизводными органическими продуктами окисления органических соединений хлором. Количество образующихся галоидноироизводных органических соединений и органических азотных соединений зависит от содержания органических соединений в водах и сточных водах.