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TREATMENT OF WASTEWATERS FROM PRODUCTION OF AMINOETHERS

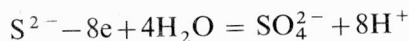
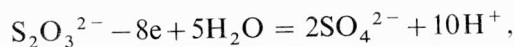
Wastewaters, which are the subject of our investigations, came from the production of aminoethers and were characterized by the following properties: pH = 12.2, COD = 358 kg O₂/m³, concentration of sulfide ions = 26 kg/m³, and concentration of thiosulfate ions = 271 kg/m³. The method of electrochemical oxidation combined with combustion was applied for treatment of the wastes. Investigations of electrochemical oxidation were carried out by periodic method. Platinum and oxide-titanium-ruthenium electrodes were used. During this process, after complete oxidation of sulfide ions, separation of the wastes took place. The upper layer was burnt. Toxicity of wastewaters treated in such a way decreased 37 times for *Lebistes reticulatus* and 2.5 times for *Daphnia magna*. Chemical oxygen demand (COD) of wastes decreased by 87%. Elementary consumption of electric energy varied, depending on the conditions of the process, from 10 to 20 kWh on kg of the oxidized sulfur. As a result of the application of this method, 90% of thiosulfate ions, over 99% of organic substances and all the sulfide ions were removed from the wastewaters.

1. INTRODUCTION

Production of aminoethers is accompanied by the formation of wastewaters which can pose a great threat to the natural environment. Wastewaters formed in this way contained slight quantities of organic substrate compounds, final products or by-products. Moreover, they characterized by the following properties: dark brown colour, pH = 12.2, COD = 358 kg O₂/m³, concentration of sulfide ions = 26 kg/m³, and concentration of thiosulfate ions = 271 kg/m³. Acute toxicity to fish (*Lebistes reticulatus*) was $R_{50} = 1 + 2261$ while to crustaceans (*Daphnia magna*), $R_{50} = 1 + 85719$. Thus, these wastewaters need to be treated before being introduced into receiving bodies of water. None of the methods of treating wastewaters containing sulfide and thiosulfate ions suggested in the literature [1], [2] was satisfactory as regards the wastewaters study [3]. Of the treatment methods comprising evaporation, crystallization, chemical and electro-chemical oxidation, and high-temperature combustion, the best results (over 90% purification) were

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obtained when the electro-chemical method was combined with high-temperature combustion. The essence of this method consists in electro-chemical oxidation of sulfide and thiosulfate ions according to the reactions:



and evolution of organic compounds in the form of a separate phase. The layer evolved, containing organic compounds, is then subjected to high-temperature combustion.

2. EXPERIMENTAL

The investigations were carried out on a laboratory scale. A non-diaphragm cell of 2 dm³, and platinum, platinized, and ruthenium-titanium oxide electrodes were used. The electrode surface area was changed from 2 to 180 cm². The current density ranged from 0.05 to 5 A/cm². The concentrations of the sulfide ions and thiosulfate ions were determined throughout the electrolysis process. The combustion of organic compounds was carried out in the tube reactor of diameter of 1.0 cm, without packing, heated electrically. Apart from the mixture of organic compounds, air was let into the reactor. The temperature of the process ranged from 660 to 1160°C. Air excess coefficient was 1.5. The reactants stayed in the zone of high temperatures for 1.5 s. Combustion gases leaving the reactor were cooled and the condensate was sampled for the analysis. The contents of nitric oxides and sulfur dioxide in the combustion gases after the separation of the condensate were also determined.

The results obtained have been presented in figs. 1–3 and tabs. 1, 2. The results obtained for platinum and platinized electrodes were better than those for ruthenium-titanium ones. Figure 1 presents the change in oxidation degree of sulfide

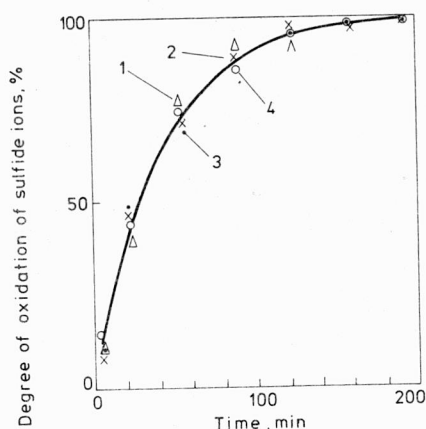


Fig. 1. Changes in the degree of oxidation of sulfide ions according to the duration of the electrolysis process for different current densities 1 – 0.055 A/cm², 2 – 1.0 A/cm², 3 – 3.0 A/cm², 4 – 5.0 A/cm², *I* – 10 A and temperature of process 40 C

ions on the platinum electrodes during the electrolysis for different current densities. It has been found out that during the electrolysis the oxidation degree of sulfide ions increases until they are entirely oxidized.

The data given in fig. 2 show that oxidation degree of thiosulfate ions increases to about 90% with an increase in the duration of electrolysis with the application of platinum electrodes.

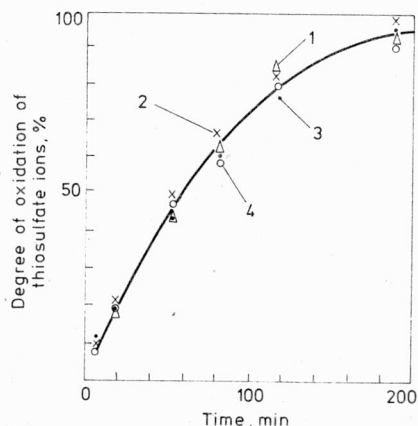


Fig. 2. Changes in the degree of oxidation of thiosulfate ions according to the duration of the electrolysis process for different current densities

1 - 0.055 A/cm², 2 - 1.0 A/cm², 3 - 3.0 A/cm², 4 - 5.0 A/cm²,
 $I = 10$ A and temperature of process 40°C

The results presented in figs. 1 and 2 show that current density has no effect on the yield of oxidation of sulfide and thiosulfate ions. On the other hand, the magnitude of electric charge has a decisive effect upon the oxidation degree reached. It has been found out that the charge needed to obtain the maximum yield of oxidation of sulfide and thiosulfate ions, in terms of the sulfur mass, amounts to 420 Ah/1 kg of sulfur. The average electric energy consumption during the electrolysis was relatively small and ranged from 10 to 20 kWh/1 kg of the oxidized sulfur depending on the condition. After the delamination of wastewaters during the electrolysis and evolution of the organic phase from them, the remaining water layer was light brown, and COD of this layer was 45 kg O₂/m³. It was reduced by about 87% in relation to COD of wastewaters before the electrolysis. The upper layer containing organic compounds was dark brown and constituted about 15% of the entire volume of wastewaters. COD of this layer was 2176 kg O₂/m³. It contained compounds like RCH₂NH₂, Ar-O-R, Ar-R, ArNO₂, ArNHR (where R = -C_nH_{2n+2}, Ar = -C₆H₅). The elementary composition of this layer has been given in tab. 1. In order to treat toxic compounds, the organic layer was subjected to combustion. The results of the elementary analysis of the condensate obtained during the combustion process are given in tab. 1. Having taken into consideration the mass of condensate and the mass of the organic phase being burnt, the decrement of carbon, nitrogen and sulfur in the condensate was determined in relation to the contents of these elements in the wastewaters subjected to combus-

Table 1

Elementary composition of the organic layer evolved from wastewaters and condensate after combustion in the temperature range from 660 to 1160°C

| Element | Composition in the organic layer | Composition of the condensate at the temperature | | |
|---------|-------------------------------------|---|-------|--------|
| | | 660°C | 820°C | 1160°C |
| | % | % | % | % |
| C | 68.32 | 4.42 | 0.65 | 0.32 |
| H | 7.64 | 9.37 | 11.20 | 10.67 |
| N | 11.22 | 3.21 | 0.98 | 1.30 |
| S | 0.62 | 0.80 | 0.35 | 0.41 |

tion. This decrement, expressed in weight %, is presented in tab. 2. The values given in the table, proving the high yield of organic substance combustion, increase for all the elements given with temperature growing from 660 to 820°C. A further increase in the temperature does not essentially affect the condensate composition.

Table 2

Degree of mass conversion of C, N, S as a result of combustion of evolved organic part of wastewaters in the temperature range from 660 to 1160°C

| Degree of conversion of element | Degree of conversion at the temperature | | |
|------------------------------------|--|-------|--------|
| | 660°C | 820°C | 1160°C |
| α_C | 95.5 | 99.35 | 99.68 |
| α_N | 80.0 | 94.0 | 92.0 |
| α_S | 10.0 | 61.4 | 52.4 |

The degree of oxidation of organic substances, assumed on the grounds of the decrement of carbon mass, exceeds 99% if the combustion takes place at the temperature higher than 800°C. After the combustion of the organic layer at 820°C, several percent of initial nitrogen quantity remains in the condensate. Sulfur, that was present in the organic phase in low concentration, remained in the condensate in 50%.

Figure 3 presents the dependence of condensate's COD on the combustion process temperature. An increase of the temperature from 660 to 1160°C corresponds to

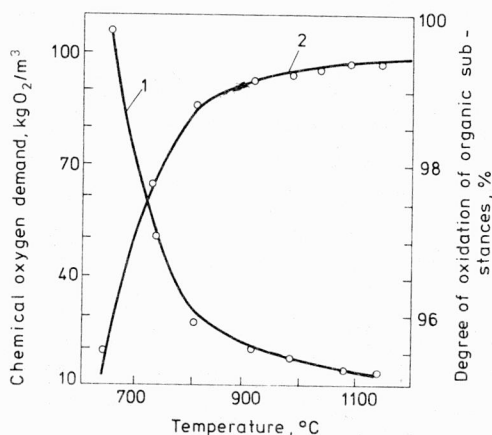


Fig. 3. Dependence of the chemical oxygen demand (COD) of the condensate after combustion (curve 1) and the degree of oxidation of organic substances (curve 2) on temperature

COD decrease from 105 kg O₂/m³ to 14.0 kg O₂/m³. The yield of the combustion process of organic substances, calculated on the grounds of the COD values given, increases from 95.2 to 99.3%. The presence of nitrogen and sulfur in the substrate subjected to combustion makes it necessary to control the concentration of toxic NO_x and SO₂ in the combustion gases released into the atmosphere. The concentration of NO_x increases from 0.044 g NO₂/m³ at 660°C to 0.057 g NO₂/m³ at 820°C and 1160°C. The content of SO₂ increases from 0.0026 g/m³ at 660°C to 0.0045 g/m³ at 820°C and 1160°C.

3. DISCUSSION

The results presented refer to the variant of wastewater treatment that has been considered to be the optimum one. We have also found out that it is possible to regain thiosulfate present in wastewaters. In this case, the process of electro-chemical oxidation should be finished at the moment when complete oxidation of sulfide ions and separation of phases take place. The degree of oxidation of thiosulfate ions is then small and ranges from 20 to 30%. About 60% of thiosulfate is regained by crystallization from the water layer evolved. Its repeated crystallization from ethanol in the presence of active carbon ensures the product obtained to be pure and free from the odour characteristic of organic compounds occurring in wastewaters. Absorption spectrum in infrared radiation of the crystals obtained showed the presence of bands characteristic for vibrations of the bonds occurring in thiosulfate, while there were no bands confirming the presence of contamination in the form of organic compounds in it. Another method of thiosulfate regeneration, consisting in its direct evolution from crude sewage by their concentration and crystallization, is

ineffective since, as the investigations have shown, the yield of pure thiosulfate is small, about 30%. This necessitates carrying out repeated crystallization. The relatively low price of thiosulfate can make its recovery unprofitable.

As can be seen from the results presented (fig. 2), electro-chemical oxidation of thiosulfate ions up to 90% proceeds fairly fast. A further increase, above 90%, in the degree of oxidation is accompanied by a considerable increase in the time of electrolysis, hence by an increase in the unitary consumption of energy. The investigations carried out have not dealt with the minimization of energy consumption.

Constructional changes of the electrolyser might possibly reduce energy consumption below 10 kWh/kg S. Total energy consumption in the treatment is also connected with the organic substances combustion. This combustion proceeds with very high efficiency amounting to 99.3% at 820°C. Due to considerable calorific value of the organic phase one can expect an auto-thermal course of the combustion process. The appearance of NO_x and SO₂ in the exhaust gases after combustion can bear some anxiety. It is, of course, possible to remove these components from the combustion gases. The exceeding of permissible concentrations of nitrogen and sulfur oxides, however, can take place only in the case if treating a very large quantity of wastewaters.

4. CONCLUSIONS

The applied method of treating wastewaters from the production of aminoethers enables complete oxidation of sulfides, about 90% removal of thiosulfate ions and over 99% removal of organic compounds, thus making wastewaters free from one of the most dangerous components. At the same time, the value of COD is reduced by about 87% and toxicity decreases 37 times in relation to *Lebistes reticulatus* and 2.5 times to *Daphnia magna*. This ensures correct and failure-free operation of the biological treatment plant.

REFERENCES

- [1] KELLER J. A., POLLAKOWSKI C., Ger. (East) 147/092/Cl CO2 F1/58 18.03.1981., Ref. Z. Chem., 21 B 1079 (1983).
- [2] CHIU G., MEEHEN E. J., Journal of Colloidal Interface Science, 62 (1977), 1.
- [3] GORZKA Z., JÓZWIAK A., *Sprawozdanie ICHO*, Politechnika Łódzka, (1984), p. 46.

UNIESZKODLIWIANIE ŚCIEKÓW Z PRODUKCJI AMINOETERÓW

Zaproponowano metodę unieszkodliwiania ścieków pochodzących z produkcji aminoeterów i charakteryzujących się następującymi własnościami: pH = 12,2, ChZT = 358 kg O₂/m³, stężenie jonów siarczkowych 26 kg/m³, stężenie jonów tiosiarczanowych 271 kg/m³. Metoda polega na połączeniu

elektrochemicznego i termicznego utleniania związków zawartych w ściekach. Badania procesu elektrochemicznego utleniania wykonano metodą okresową, stosując elektrody platynowe i tlenkowe tytano-rutenowe. Podczas tego procesu, po całkowitym utlenieniu jonów siarczkowych, nastąpiło rozdzielanie ścieków na dwie warstwy. Górna warstwa była spalana. W ten sposób uzyskano 37-krotne zmniejszenie toksyczności ścieków dla ryb (*Lebistes reticulatus*) i 2,5-krotne dla skorupiaków (*Daphnia magna*). ChZT ścieków zmniejszyło się o 87%. Zużycie energii wynosiło od 10 do 20 kWh/kg utlenionej siarki w zależności od zastosowanych warunków procesu. W wyniku zastosowania opisanej metody usunięto ze ścieków 90% jonów tiosiarczanowych, ponad 99% substancji organicznych i całkowicie usunięto jony siarczkowe.

ОБЕЗВРЕЖИВАНИЕ СТОЧНЫХ ВОД, ПРОИСХОДЯЩИХ ИЗ ПРОИЗВОДСТВА АМИНОЭФИРОВ

Предложен новый метод обезвреживания сточных вод, происходящих из производства аминокэфиров и характеризующихся следующими свойствами: $\text{pH} = 12,2$, ХПК = 358 кг $\text{O}_2/\text{м}^2$, концентрация сульфидных ионов 26 кг/ м^3 , концентрация тиосульфатных ионов 271 кг/ м^3 . Метод состоит в соединении электрохимического и термического окисления соединений, содержащихся в сточных водах. Исследования электрохимического процесса окисления были выполнены периодическим методом с применением платиновых и окисных титано-рутениевых электродов. Во время этого процесса, после полного окисления сульфидных ионов, наступало разделение сточных вод на два слоя. Верхний слой был сожжен. Таким образом получили 37-кратное понижение токсичности сточных вод для рыб (*Lebistes reticulatus*) и 2,5-кратное — для ракообразных (*Daphnia magna*). ХПК сточных вод понизилось на 87%. Потребление энергии составляло от 10 до 20 кВт/кг окисленной серы в зависимости от примененных условий процесса. В результате применения описанного метода удалили из сточных вод 90% тиосульфатных ионов, свыше 99% органических веществ и наступило полное удаление сульфидных ионов.