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EFFECT OF CAVITATION ON DISPOSAL OF LIQUID WASTES FROM OLEFINS PRODUCTION

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It was found that effective neutralization of liquid waste production of olefins, that contain compounds of mainly arene and diene rows, is possible by processing in cavitation fields. Usages of sodium hypochlorite solutions, which are the wastes of related production, as reagents allow intensify the oxidation of organic substances. The optimum ratio between liquid waste production of olefins and sodium hypochlorite was determined according to the change of the redox potential of the reaction system. It is shown that the oxidation of organic compounds occurs through stages of their cavitation and oxidation destruction.

Key words: olefins production, liquid waste, cleaning, cavitation, sodium hypochlorite.

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ДОСЛІДЖЕННЯ КАВІТАЦІЙНОГО ЗНЕШКОДЖЕННЯ РІДКИХ ВІДХОДІВ ВИРОБНИЦТВА ОЛЕФІНІВ

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Встановлено, що ефективно знешкодити рідкі відходи виробництва олефінів, які містять сполуки головно аренового та дієнового рядів, можна, обробляючи їх у кавітаційних полях. Використання як реагенту розчинів натрію гіпохлориту, які є відходами суміжного виробництва, дає змогу інтенсифікувати окиснення органічних сполук. Оптимальне співвідношення між рідкими відходами виробництва олефінів та натрію гіпохлоритом було визначено залежно від зміни величини редокс-потенціалу реакційної системи. Показано, що окиснення органічних сполук відбувається через стадії їх кавітаційної та окисної деструкції.

Ключові слова: виробництво олефінів, рідкі відходи, очищення, кавітація, натрію гіпохлорит.

Introduction. Chemical plants are belong to one of the most powerful sources of environment pollution, including the hydrosphere. This is caused by several factors, among which the most important are the output of large volumes of liquid wastes or wastewaters in chemical-engineering processes; high

concentrations of pollutants in these environments; formation of compounds, preferably organic, which are not produced in natural conditions. The situation determines impossibility of these compounds biological dehydration in natural ecosystems or biological treatment plants with the formation of harmless products. Harmful substances can be accumulated by different kinds of aquatic organisms and transferred by trophic chains. This leads to serious degradation of aquatic ecosystems and to growing demand for implementation of complex and energy intensive treatment processes in industrial or municipal sewerage and water supply systems.

Therefore it is important the deep disposal of liquid wastes or waste waters before moving them into natural lakes and rivers or biological treatment facilities. This problem can be solved on basis of new technologies developments, such as: using of actual wastes as neutralizing reagents for other water contaminants with antagonistic properties; the implementation of innovative processes that provide concentrated energy impacts on waste waters systems.

Formulation of the problem. Liquid wastes containing high concentration of organic compounds with high chemical oxygen demand (COD) – about 12000 mg O₂/dm³ and less concentrated waste waters are forming in the production of olefinic compounds.

However, the main problem of such environments for aquatic ecosystems is low biological oxygen demand (BOD), not exceeding 50 % of COD. Thus, the biological treatment of olefin production wastewaters is inefficient. Microflora deactivation in bioengineering water treatment facilities is also possible in this case. One of possible reason for the low efficiency of the biological treatment of organics-containing waste waters is theirs multicomponent composition due to gradual transformation of diesel fuel into olefins at chemical production plant. Until now the composition of liquid waste and waste waters generated in olefins technology was not determined properly.

Sorption methods [1], chemical treatment with application of oxidising compounds [2] and electrochemical anodic oxidation of organic substances [3] have been traditionally used for disposal of organic components of waste waters.

Non-standard solutions of sodium or calcium hypochlorite with oxidative properties are formed in Kalush Magnesium Plant of LLC Magnesium. Therefore it is a great interest for of the possibility study of their use for destruction of organic containing liquid wastes and effluents, which run out from technological facilities of LLC Karpatnaphthokhim. One of the methods to generate a strong oxidizer – atomic oxygen is a cavitation treatment of the reaction environment [4–7]. Destruction of organic compounds during the treatment is also possible, which could additionally facilitate the liquid wastes disposal.

The purpose. The purpose of the work was to establish the composition and characteristics of olefins production liquid wastes and identification of main methods of their disposal.

Experimental part. An UV-VIS spectrometer *Specord M40* with quartz cuvettes of 10 mm thickness in the wavelength range of 200...400 nm and a photometer KFK-3 with cuvettes of 30 mm thickness in the wavelength range of 335...405 nm were used to determine the qualitative composition of liquid olefin wastes and for analysis of reaction mediums during the study. The value of COD of olefine wastes and reaction mediums were determined due to ISO 6060:2003. Redox potential values of water solutions were determined by EV-74 ionomer with platinum EPL-01 measuring and saturated EVL-1 silver/silver chloride reference electrodes.

The study of the disposal of liquid wastes of olefins production was carried out using a laboratory setup that included: a thermostatted reaction flask with ports for potentiometric electrodes, fixed on a magnetic mixer, an ionomer EV-74, an ultra thermostat UV-8 with a remote thermostatic bath; *UD-20* ultrasonic transducer of magnetostriction type.

Waste waters from the olefinic production with COD value of 260 mg O₂/dm³ and sodium hypochlorite solution with a concentration of 47 g/m³ were used in the study.

A cavitation effect on the transformation of organic compounds and their interaction with sodium hypochlorite was investigated in a ultrasonic generator power range of 8.0–12.5 W.

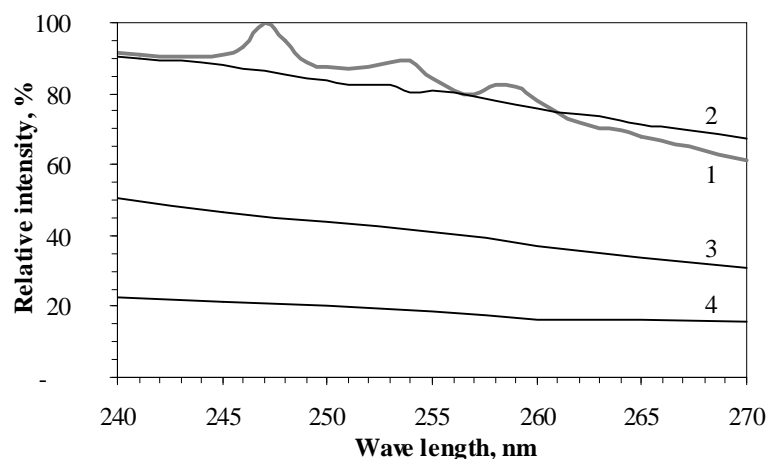
Results and discussion. It was established by UV/Viz-spectroscopy that industrial wastes of olefins production contain compounds with benzene structure and alkenes. The presence of benzene structures is confirmed by the band in the 230–269 nm range (Fig. 1, spectrum 1). It has well defined fluctuating structure, resulting in a peak splitting into three components, well known as B-band of benzene absorption [8]. Some difference in intensities ratio of the peak components in the spectra of studied wastes and pure benzene is likely to be caused by the presence of benzene homologues.

Absorption area without distinct peaks in the spectrum range of 310–390 nm indicates the presence in the wastes of linear compounds with double bonds. Multichrome displacement of absorption range to 360 nm most probably means availability of polyenes with number of conjugated double bonds from 3 to 4 [9].

Interaction of organic wastes with sodium hypochlorite was investigated by batch addition of oxidant. Stoichiometric concentration of sodium hypochlorite was calculated due to the reaction equation



The liquid wastes contain organic compounds of different classes such as arenes and alkenes. Therefore, the total content of these compounds ($C_{C_nH_{2n}}$) is equivalent to the value of chemical oxygen demand (COD). The sodium hypochlorite concentration was expressed by the molarity (mol/dm³) of oxygen, formed during the decomposition of NaClO in an alkaline environment. The approach was used for convenience of analysis of sodium hypochlorite effect on organic compounds oxidation.



*Fig.1. UV/Viz spectra of olefin production wastes:
1 – initial; 2 – after cavitation treatment; 3 – after addition of NaClO;
4 – after addition of NaClO and cavitation treatment*

It was found that oxidation of aromatic and diene structures occurs at their stoichiometric ratio with sodium hypochlorite. Accordingly, characteristic peak splitting of benzene rings is not observed (Fig. 1, spectrum 3), and the peak intensity, proportional to the concentration of aromatic compounds, is reduced by about 55 %. Spectrum character in the range of 310–390 nm changes with batch addition of sodium hypochlorite. Two peaks appear after an addition of NaClO in the amount of 20 % of the stoichiometric value: a pronounced first with a maximum at 354 nm and less intense and more blurred second with the maximum at 365 nm (Fig. 2, spectrum 1).

It is caused most probably by oxidative destruction of benzene structures as a result of their interaction with NaClO and linear polyenes formation. An intensity of the first peak rises simultaneously with its hypsochromic shift (about 3–4 nm), and an intensity of the second one decreases with an increase of sodium hypochlorite dosage (Fig. 2, spectrum 2). This is caused by the partial oxidation of polyenes with a decrease in the number of multiple double bonds. This conclusion is confirmed by the shape of the spectrum 3 (Fig. 2) obtained after further increasing of sodium hypochlorite concentration. The intensity of spectrum at 350 nm decreases and the peak at 365 nm disappears. The gradual increase of NaClO content

causes a reduction of intensity of the peak and its hypsochromic shift. This means an increase of relative quantity of compounds with low double bonds content with simultaneous decrease of their concentration in the environment (Fig. 2, spectra 4, 5). Thus, gradual oxidation of the organic compounds occurs in the environment. It is confirmed by a redox potential growth of the system, which depends on activities ratio between oxidants and reducers compounds.

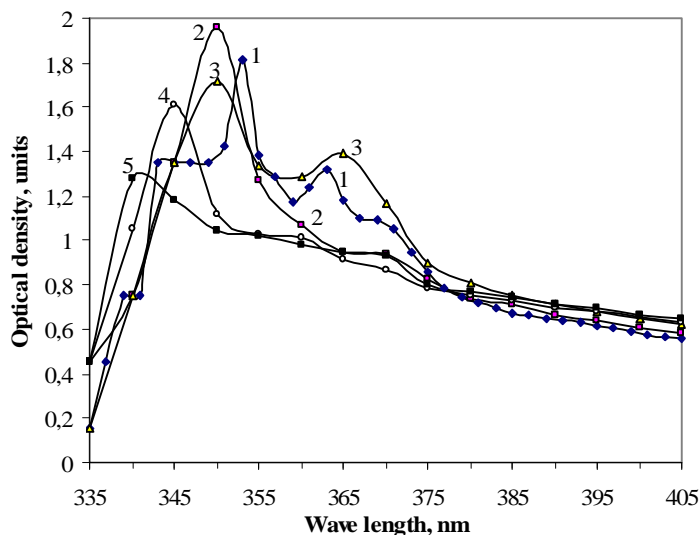


Fig. 2. Viz-spectra of reaction composition “olefin production wastes – NaClO” at NaClO concentration (in % from stoichiometric):
1 – 20; 2 – 30; 3 – 40; 4 – 50; 5 – 75

Overall, the dependence of end value of redox potential of the reaction system from stoichiometric rate of sodium hypochlorite has a typical shape of redox titration curve (Fig. 3). Apparently, the equivalence point is reached at 25 ± 2 % excess of sodium hypochlorite.

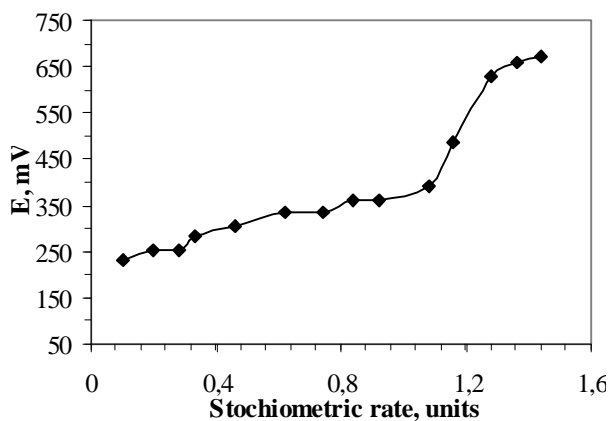


Fig. 3. Dependence of system redox potential from stoichiometric rate of NaClO

The redox potential value for the system exceeds 500 mV at stoichiometric rate of sodium hypochlorite above 1.25, which corresponds to an excess of the oxidant compound in the reaction system over 25 %. It means that oxidative conditions arised in the environment with an excess of the oxidant. The COD value for the stoichiometric rate was equal to $40 \text{ mg O}_2/\text{dm}^3$, the integral degree of organic compounds oxidation of amounted to 85 %. Incomplete oxidation of organic compounds can be explained by a presence in the system of relatively stable compounds with low molar mass. The oxidation of organic

compounds practically stops at NaClO excess over 40 % from stoichiometric ratio and value of the redox potential becomes higher than 600 mV.

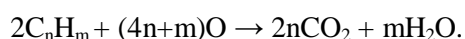
COD residual value of organic liquid wastes is close to 40 mg O₂/dm³ after almost complete stopping of organic compounds oxidation. Water solutions with the COD value may be discharged into natural environment or biological treatment facilities in accordance with current regulations. However the neutralized wastes contains residues of sodium hypochlorite, which acts as a reagent for disinfecting microorganisms of any ecosystem. Therefore, in this case, the discharge of the treated waste waters in ecosystems of rivers and lakes or in biological treatment facilities is unacceptable .

A control of the real ratio between organic compounds in olefin production wastes and sodium hypochlorite in order to achieve a permissible COD value and the absence of NaClO is technologically difficult. This is caused by different temperature of both media and possible qualitative and quantitative fluctuations in content of olefin production wastes and hypochlorite waste water. The factors can affect process durability. Apparently, the process durability will be biggest for the ratio between organic compounds and NaClO at which point of equivalence is achieved, because of both reagents concentration and reaction rate respectively will decrease with time.

Liquid wastes of olefins production were treated in cavitation field formed by ultrasound emitter for intensifying the process of cleaning. It was established that cavitation processing of the wastes leads to a degradation of benzene structures – characteristic splitting peak in the range of 230–269 nm is not observed – the signal not exceeds noise level (Fig. 1, spectrum 2). Only 13–15 % intensity decrease of absorption spectrum in the range of 246 nm and the increase of absorption intensity over 260 nm after waste water cavitation treatment confirms that there is a destruction of benzene and formation of diene linear structures. There is no absorption in the range of 310–390 nm. It may be caused by a number of series-parallel processes in cavitation fields. First of all, sonolysis of water with a formation of active reaction products with oxidizing properties occurs during the cavitation [10, 11]



Organic compounds present in the environment are destructed as a result of cavitation and interaction with oxidants from water sonolysis products (cavitation and oxidative degradation occurs). Part of organic compounds is oxidized to stable end products due to the gross equation



Reduction of COD value on 15–20 % indicates oxidation to stable products. Organic compounds defragmentation occurs in case of their destruction, and COD value, which depends on the total content of carbon and hydrogen, would not be changed. Simultaneously, the value of environment redox potential for ultrasonically treated wastes practically did not change and amounted about 200 mV. Compounds with reduction properties dominated in the system, while oxidizing water sonolysis products were almost completely utilized.

Intensity of absorption in the range of 246–248 nm decreased compared to initial more than in 4 times (Figure 1, range 4) in the case of treatment of organic waste by sodium hypochlorite under ultrasonic radiation field. More complete destruction of organic compounds is probably caused by an increase of oxidants concentration in the environment. Intensive decomposition of sodium hypochlorite in a cavitation field promotes that [6]. Herewith, the intensity of the absorption spectrum in the range of 310–390 nm is 15–20 % higher in comparison with pure water. Consequently, there is a deep oxidation of organic compounds, which integral content corresponds to COD value of 60±10 mg O₂/dm³.

Analysis of spectra of reaction medium in the presence of sodium hypochlorite in them indicates that formation of chloro-substituted organic compounds does not occur. This is probably due to the fact that the reaction medium is alkaline. In these circumstances, NaClO is decomposed due to oxygen mechanism – with the formation of atomic oxygen, while chlorine is present in the environment as anion. Therefore, there are no conditions for the formation of chlorine derivatives.

Conclusions. Destruction of organic compounds primarily of benzene structure present in liquid wastes of olefins production occurs under the influence of ultrasonic cavitation. The use of sodium hypochlorite solutions causes extensive destruction of organic compounds. Deep transformations of organic compounds due to cavitation-oxidative mechanism take place in case of initiation of cavitation in the reaction medium containing NaClO with formation stable end-products – carbon (IV) oxide and water.

Further work will be devoted for study of the transformation in the cavitation fields of individual organic compounds that are components of liquid olefins wastes, particularly in case of addition of compounds with oxidising properties.

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