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ДОСЛІДЖЕННЯ КАВІТАЦІЙНОГО РОЗКЛАДУ НАТРІЮ ГІПОХЛОРИТУ В ІЗОТЕРМІЧНИХ УМОВАХ

Досліджено кавітаційний розклад натрію гіпохлориту, що міститься у стічних водах цеху каустичної соди і хлору, за ізотермічних умов. Встановлено залежність тривалості та кінетичних параметрів процесу від температури та потужності УЗ-випромінювання. Встановлено, що ефективність розкладу натрію гіпохлориту за дії акустичних коливань УЗ-діапазону є істотно вищою, ніж під час його термічної каталітичної деструкції як промислового процесу.

Ключові слова: стічні води, натрію гіпохлорит, очищення, кавітація.

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INVESTIGATION OF CAVITATIONAL EXPANSION OF SODIUM HYPOCHLORITE UNDER ISOTHERMAL CONDITIONS

The study of cavitational decomposition of sodium hypochlorite contained in wastewaters from the production of caustic soda and chlorine under isothermal conditions was carried out. The dependence of the duration and kinetic parameters of the process on the temperature and power of ultrasound radiation is established. It is established that the efficiency of the decomposition of sodium hypochlorite under the action of acoustic oscillations of the ultrasound band is significantly higher than during its thermal catalytic degradation as an industrial process.

Key words: wastewaters, sodium hypochlorite, purification, cavitation.

Introduction. Liquid waste and wastewater, one of the components of which is sodium hypochlorite or calcium hypochlorite, are formed during the production of chlorine and caustic soda; electrolytic production of magnesium and chlorine; in the processes of whitening of wood in the production of pulp and paper products; in the technology of hydrazine and other processes of organic synthesis; at hydrometallurgical reception of precious and non-ferrous metals; After disinfection of production equipment and facilities of enterprises on processing agricultural products. The highest content of hypochlorite characterized by wastewater from the production of chlorine and caustic soda, which are formed in particular KARPATNAFTOCHIM LTD, and wastewater from the production of magnesium and chlorine – it reaches 40 g/dm^3. Such waste waters belong to non-standard ones, and therefore they are not used again in the corresponding technological processes [1].

Hypochlorites belong to strong oxidants, which is characterized by a very pronounced antibacterial action [2, 3]. Thus, in an acidic medium, the value of the redox potential of ClO^-/Cl_2 and ClO^-/Cl^- systems is 1.63 and 1.58 V, respectively, and in the alkaline medium for the ClO^-/Cl^- system it is 0.89 V. Therefore, the discharge of wastewaters into treatment biological structures or in natural reservoirs without their prior treatment is not allowed. It can cause significant damage to the ecosystems of the specified biocenoses or even cause their profound degradation. In addition, hypochlorite solutions have a pronounced corrosion activity, even at their low concentrations. The rate of corrosion of the most common grades of steel reaches 10 mm per year. Consequently, hypochlorite wastewaters must be disposed of at

local treatment facilities, which should be located as close as possible to the place of their formation, in accordance with the current normative documents.

Problem statement and review of literature. A number of methods, which differ by physico-chemical principles, are proposed for neutralization of hypochlorites. These include thermal non-catalytic, photochemical, ultraviolet (UV) radiation [4], catalytic [5, 6], reagent using inorganic and organic compounds [7, 8].

At present, liquid waste and wastewaters containing hypochlorites on an industrial scale, as a rule, neutralize the catalytic decomposition at a temperature of 5080 °C in the presence of nickel sulfate and copper sulfate. However, due to high alkalinity of wastewaters (pH 11–12), Nickel and Copper ions are mostly converted into insoluble hydroxides, which, together with wastewater, are discharged into the sludge drain. To reduce the losses of the catalyst, not salts are used, but practically insoluble oxides of the above metals, from which form catalyst particles that are located in the reactor in the form of a filtering layer, which increases the hydraulic resistance in the apparatus. The duration of the decomposition of hypochlorites is 32 hours, which requires very high energy consumption.

The photochemical decomposition of sodium hypochlorite is limited by the depth of penetration of UV rays into the thickness of wastewaters. It occurs only in a thin layer of liquid, which due to the presence in the wastewaters of dispersed particles does not exceed several centimeters. Therefore, the process performance is low and the energy intensity is high. In addition, it is necessary to periodically treatment of the sources of UV radiation, which complicates the technological process.

Reactive methods require significant expenditures of substances that have inherent restorative properties, such as sodium sulphite, sulphide, thiosulphate [7], carbamide, and the like. They are a commodity product that require additional costs for their purchase, and also requires precise dosage. Therefore, reactive methods are used only in the case of low concentrations of hypochlorites or for the treatment of wastewaters.

The above disadvantages of existing methods of wastewater treatment make it necessary to search for technologically, energetically and economically efficient methods of degradation hypochlorites. Based on the results of previous studies performed by us [9], it can be argued that the cavitation method has considerable practical interest in wastewater treatment from hypochlorites.

The purpose of the work: the study of destruction of sodium hypochlorite under the action of cavitation, excited by acoustic radiation of the ultrasound range.

Experimental part. The research was carried out on a laboratory installation consisting of an ultrasonic emitter of the magnetostrictive type "Ultrasonic Disintegrator UD-20" (22 kHz radiation frequency), a reaction flask with electrodes for potentiometric studies, which was located in a thermostat-bath, a pH meter, magnetic stirrer, which placed the thermostat-bath. The power of the ultrasonic transducer was changed discretely in the range of 8.0 to 12.5 Watts. The research was carried out under isothermal conditions at a temperature of 293, 303 and 313 K. The research was carried out using industrial wastewater with a NaClO concentration of 0.503 mol/dm^3 (37 g/dm^3); the volume of the solution used in the studies was 1 dm^3. For comparison, a control experiment was carried out on the thermal decomposition of NaClO using both $NiSO_4$ and $CuSO_4$ catalysts, which concentration in the reaction medium was 0.057 and 0.053 g/dm^3, respectively.

Analysis of the reaction medium on the NaClO content was carried out using the spectrometric method (Specord M40 spectrometer) in the range 200–400 nm and iodometric method according to the standard methodology.

Research results and their discussion. In the control experiment, the process of decomposition of NaClO was studied under conditions that correspond to the production conditions (Fig. 1a, curve 4). As can be seen, decomposition of NaClO preceded the induction period, which lasts about 15 minutes. Perhaps it is due to the fact that sewage waters have a pH of about 11.5, and as it is known, NaClO in the alkaline environment is much more stable than in neutral or acidic environments.
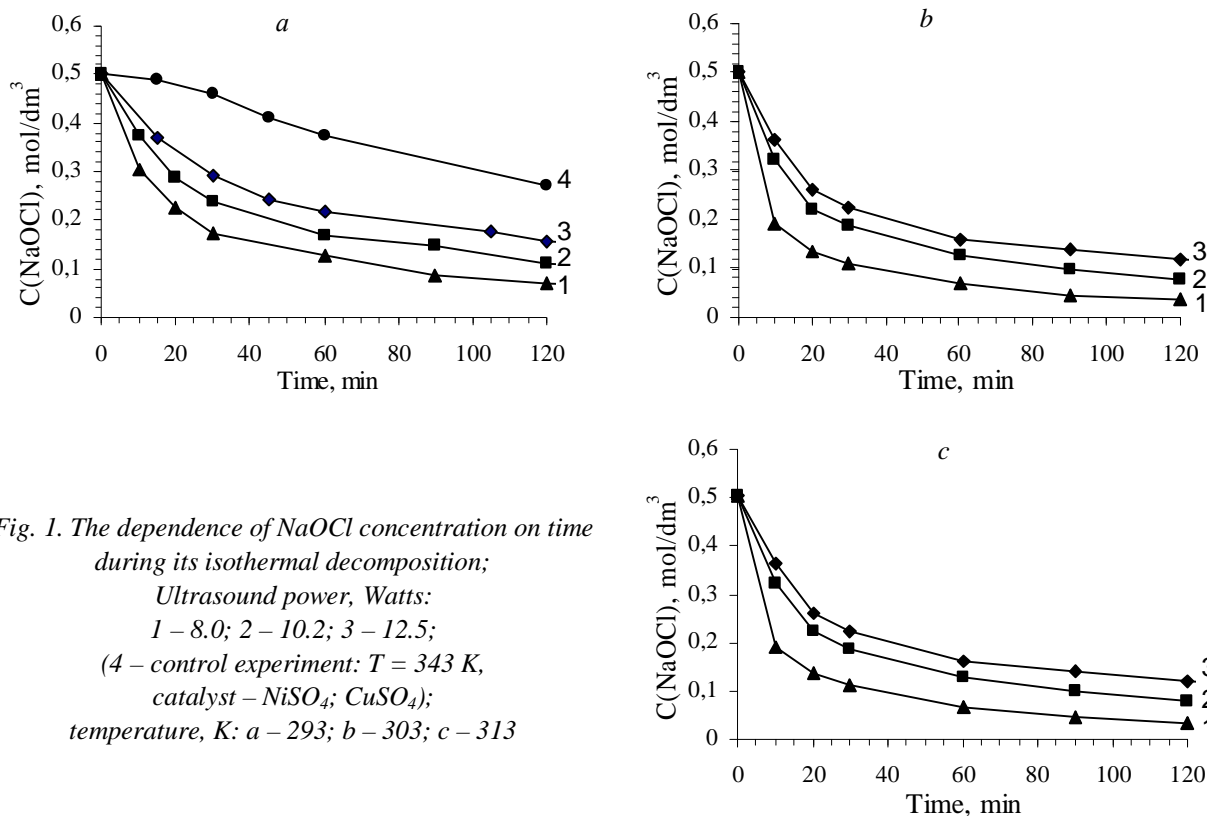
Fig. 1. The dependence of NaOCl concentration on time
during its isothermal decomposition;
Ultrasound power, Watts:
1 – 8.0; 2 – 10.2; 3 – 12.5;
(4 – control experiment: T = 343 K,
catalyst – NiSO₄; CuSO₄);
temperature, K: a – 293; b – 303; c – 313

In all cases when destruction of NaClO was carried out in the cavitation field, the intensity of its decomposition was significantly higher than the thermal decomposition (Fig. 1 a, b, c). The decomposition of NaClO begins almost immediately after excitation of cavitation. Probably this is due to the fact that the cavitation field is concentrated in a limited volume directly under the concentrator of the magnetostrictive (Fig. 2).
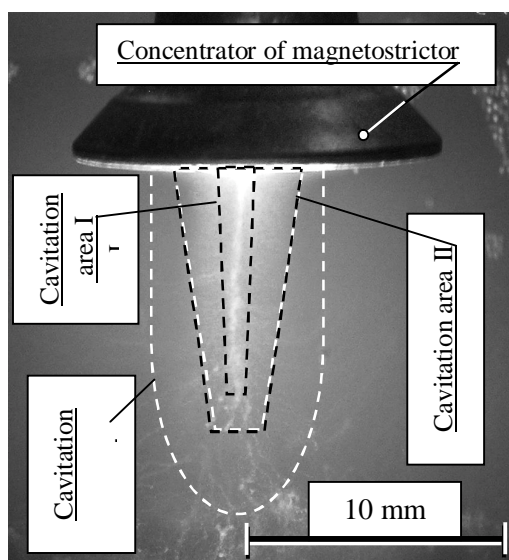

Fig. 2. Image of the cavitation area under the
concentrator of the magnetostrictor
on the power of ultrasound radiation 12.5 Watts
(photo taken using orange light filter)

Analyzing photographic images, in particular, shown in Fig. 2, it can be noted that the cavitational field is not homogeneous in space. It can distinguish at least three areas of cavitation. The first area is the most intense, the area of cavitation is concentrated practically along the vertical axis of the concentrator of magnetostrictor. It is characterized by the highest concentration of cavitation bubbles, as evidenced by the most intense scattering of light. This area is sharply defined. Accordingly, the intensity of the cavitation in

this area is greatest. In the second region, the intensity of the cavitation is less than in the first region, but its volume is much bigger. The boundary between the second and third regions is blurred – diffuse. If the first two areas can be observed even visually, then the third can be detected only by analyzing photos taken through a light filter, in particular, orange (absorption region 590–625 nm). In the second and third regions, there are chaotic formations, similar to the discharges. Most likely, they are due to fluctuations in the volume of the environment. They are due to the complicated hydrodynamic and thermal structure of the flows under the action of acoustic oscillations excited by oscillations of the magnetostrictive, oscillations and the gradient of temperatures caused by the cavitation bubbles splashing. The local temperature in the area of closure of cavitation bubbles is 1000K or more, which provides an intense decomposition of NaClO.

Due to the mixing of the NaClO solution with a magnetic stirrer, new portions of sodium hypochlorite are constantly fed into the cavitation field. This leads to a more intense, than under the thermal catalytic process, integral decomposition of NaClO.

The main kinetic parameters of the decomposition of NaClO were calculated by the method of graphic differentiation. Thus, the order of the reaction of the cavitation decomposition of sodium hypochlorite varies in the range of 0.73 to 1.03 in different conditions, which is generally approximates to unity. This order is characteristic for the reactions of decomposition and radical processes. Thus, the calculated order of the reaction of the thermal decomposition of NaClO is also about 1, namely – 0,93.

However, along with the decomposition of NaClO, the course of radical processes is possible. They are due to cavitational decomposition of NaClO and water sonolysis by the following reactions:

$$NaClO \rightarrow NaCl + O; \tag{1}$$
$$H_2O \rightarrow HO + O. \tag{2}$$
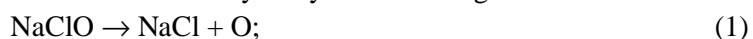
The atomic oxygen generated by the reactions (1,2) in the cavitation field can interact with water molecules with formation of the hydrogen peroxide

$$O + H_2O \rightarrow H_2O_2. \tag{3}$$

In the alkaline medium, the hydrogen peroxide has more pronounced restorative properties, as evidenced by the value of the redox potential

$$H_2O_2 - 2e + 2OH^- \rightarrow 2O + 2H_2O \rightarrow O_2 + 2H_2O \ (E = 0,076 \text{ V}). \tag{4}$$
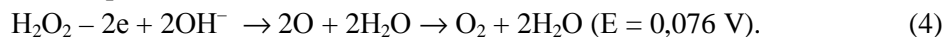
Therefore, formed hydrogen peroxide can interact with sodium hypochlorite as a reducing agent

$$H_2O_2 + NaClO \rightarrow H_2O + NaCl + 2O. \tag{5}$$

Atomic Oxygen can also cause the conversion of sodium hypochlorite

$$O + NaClO \rightarrow NaCl + 2O. \tag{6}$$

Consequently, given that the conversion of sodium hypochlorite occurs with the participation of atomic Oxygen, which has radical properties, it can be assumed that the process of decomposition of NaClO in the cavitation field takes place under a radical mechanism.

About the more intense decomposition of NaClO under the action of ultraviolet radiation that stimulates cavitation, as compared with the control study (thermal catalytic decomposition), are the values of the rate constants of this process. So, if the constant of the reaction rate in the control experiment was equal $0,47 \cdot 10^{-4}$ s^{-1}, then at a temperature of even 293 K it equaled $2,48 \cdot 10^{-4}$; $4,3 \cdot 10^{-4}$ та $6,84 \cdot 10^{-4}$ s^{-1} for the specific power of radiation 8,0; 10,2 i 12,5 J/s·dm^3 respectively.

It is established that the dependence of the rate constant of the decomposition of NaClO on the power of the ultrasound emitter in the range 8.0–12.5 W at a temperature of 293, 303 and 313 K is straightforward (Fig. 3).

Assuming that the power of an ultrasound emitter transmitted to the reaction system is equivalent to the thermal energy emitted during the operation of the conditional heating element, the process of decomposition of NaClO in the studied range of power of the ultrasound emitter occurs in the quasikinetic region. That is, the process is limited by the amount of energy brought to the system. This conclusion is confirmed by the fact that with increasing of temperature of NaClO solution, the value of the constants of the reaction rate for the same power of ultrasound radiation significantly increased. Thus, the temperature increase from 293 to 303 and 313 K leads to an increase in the value of the constant of the reaction rate, on average by 1.8 and 2.4 times, respectively.

$y_1 = 1{,}0039x - 5{,}9441$ $y_2 = 1{,}9291x - 11{,}312$
$R_1^2 = 0{,}9512$ $R_2^2 = 0{,}971$

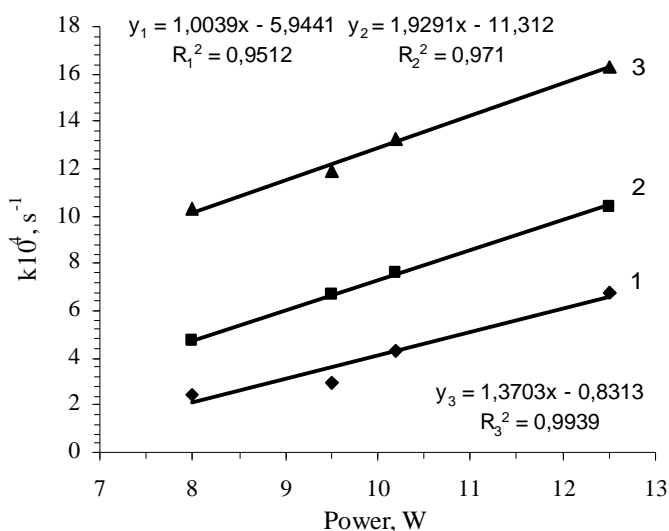$y_3 = 1{,}3703x - 0{,}8313$
$R_3^2 = 0{,}9939$

Fig. 3. Dependence of the rate constant of the decomposition of NaClO on the power of the ultrasound emitter; temperature, K: 1 – 293; 2 – 303; 3 – 313

A certain increase in the rate constant with an increase in the power of an ultrasound emitter indicates about an increase in the role of temperature as one of the types of energy introduced into the reaction system. Thus, at a temperature of 292,303 and 313 K, the growth rate of the constant of the reaction rate was 0,96; 1,27 and 1,35 ($s^{-1} \cdot W^{-1}$) respectively. However, if the growth rate of the reaction rate constant with increasing temperature from 293 to 303 K increased by 1,3 times, then with an increase in temperature from 303 to 313 K it grew by only 1.06 times. The decrease in the rate constant of a process with increasing temperature can be due to two factors. First, this may be due to an increase in the partial pressure of water vapor in cavitation bubbles as the temperature of the water medium rises. This leads to a decrease in the intensity of their splashing, since the water vapor inside the bubble can be considered as some elastic body, on compression of which is consumed part of the energy of the splashing. At the same time, the amount of energy released during the bubble splashing decreases. Secondly, the temperature in the 313K to flow process is characterized by the formation of cavitation bubbles of high – bubstons [10] which is characterized by high stability; they do not split or aggregate with the formation of larger sized bubbles. Accordingly, the intensity of energy release in the region of temperature 313K decreases.

Consequently, it can be argued that after reaching a certain temperature, with its further increase, the energy efficiency of the medium in the form of thermal energy decreases.

These conclusions are confirmed by calculations of the temperature coefficient of the decomposition of sodium hypochlorite. At the specific power of the ultrasound emitter 8.0 W/dm^3 with an increase in temperature from 293 to 303 and from 303 to 313K, the value of the temperature coefficient was 1.89 and 2.19. That is, these values are close to 2, which are characteristic for typical homogeneous processes, which can be considered a decomposition of NaClO in the aqueous medium by reaction (1). However, with the increase in the power of ultrasound, the value of the temperature coefficient, especially with increasing temperature, decreases. Thus, if the power density of 9,5 W/dm^3 temperature coefficient for these temperatures was almost the same (1.83 and 1.81), then the power density of 10.2 and 12,4 W/dm^3 value of this ratio (for temperatures 293/303 and 303 / 313K) were 1.73 and 1.65 and 1.48 and 1.32, respectively.

The values of the temperature coefficients of sodium hypochlorite decomposition, obtained in previous similar studies, were somewhat [11] higher, but the general trend of their change was the same. Previously, similar results were explained by the fact that the process takes place in a limited area of the region located under the magnetostrictor. Since there is a sufficiently blurred boundary between the area where the cavitational field is concentrated and the rest of the solution, it was believed that the process of cavitational decomposition of NaClO can be considered as heterogeneous [11], that is, quasi-heterogeneous. However, during these studies, it was clearly established that the intense mixing of the reaction medium creates turbulent conditions in which the ideal mixing mode in the reaction flask is realized [12]. Therefore, the concentration of all components of the reaction medium is almost

instantaneously aligned throughout the volume. Consequently, the conclusion in the previous paper on the quasi-heterogeneous process of the NaClO decomposition was incorrect.

The duration of the process to achieve the degree of NaClO conversion to 99.9 % was calculated by changing the concentration of sodium hypochlorite over time (Fig. 4).

Fig. 4. Dependence of the NaClO decomposition time (conversion rate 99.5 %) on the specific power of ultrasound radiation; temperature, K: 1 – 293; 3 – 303; 3 – 313
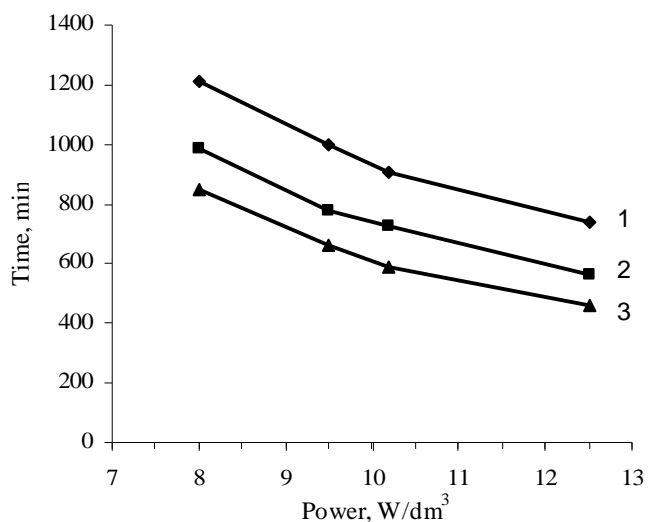
In the control experiment (according to the catalytic thermal decomposition), the estimated duration of the process was 1800–1900 minutes. As can be seen from Fig. 4, the use of ultrasound radiation allows to significantly, at least 1.5 times, reducing the duration of the process. At the same time it can be seen that with an increase in temperature from 293 to 303 K, for example, the specific power of ultrasound radiation of 12.5 W/dm^3, the process duration is reduced by 23.5 %, and with the temperature rise from 303 to 313 K – by 18.6.

At the same time, the duration of the cavitation process under different conditions, calculated from the characteristic equation for a perfect mixing reactor, in which the first-order reaction occurs, is much larger than that calculated by the kinetic curves (Fig. 1). For example, in order to achieve a degree of NaClO conversion of 99.5 % at a temperature of 293 K and a specific power of 8.0 W/dm^3, the process duration should be 13370 minutes, which is an order of magnitude more than determined by changing the concentration of NaClO for 120 minutes. (Fig.1). Such a significant difference in the time of decomposition of NaClO may be due to the peculiarities of this process in the cavitational field. With the decrease in the concentration of NaClO during its decomposition, water sonolysis with the formation of intermediate products for example, atomic Oxygen will increasingly prevail. Atomic Oxygen can participate in reactions (3, 6), which cause an additional disposition of sodium hypochlorite, which contributes to a significant reduction in the duration of the process.

Conclusions. The application of ultrasonic radiation that causes the cavitation phenomenon significantly reduces the decomposition time of sodium hypochlorite compared to the thermal catalytic decomposition.

The method of graphic differentiation has established that the cavitation decomposition of NaClO, as well as the thermal catalytic, is described by the first-order equation.

With the increase in the temperature of the cavitational decomposition of NaClO, which occurs in isothermal conditions, it contributes to an increase in the rate constant of the process. However, the growth of the rate constant with increasing temperature is smaller, which is probably due to an increase in the partial pressure of water vapor and the possibility of formation of relatively stable microbubbles – babustons at a temperature of about 313 K. The duration of this process varies according to the change in the value of the speed constant with the increase in the specific power of ultrasound radiation and temperature.

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The actual duration of the cavitational decomposition of NaClO is an order of magnitude smaller than that calculated for the characteristic equation for the ideal mixing reactors due to the participation in this process of products of water sonolysis, in particular atomic Oxygen.

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