NANOSIZED Co-OXIDE SYSTEM AS EFFICIENT HETEROGENEOUS CATALYST FOR LOW-TEMPERATURE COMPLETE OXIDATION OF FORMALDEHYDE IN AQUEOUS SOLUTIONS

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Abstract

Formaldehyde is considered a carcinogen compound because causes DNA damage, mutations in microorganisms and mammalian cells. Therefore, treatment of effluents containing HCHO prior disposal into waterways is an important target from the environmental point of view. In the present study liquid-phase catalytic oxidation of 50 mg dm^{-3} HCHO with NaOCl at mild conditions was studied using nanosized Co-oxide system as catalyst. CoO$_x$ was synthesized by non-conventional ultrasound assisted precipitation-oxidation method with reverse order of precipitation. The synthesis' conditions favour the formation of catalytic systems with desired structure, morphology and surface properties typical of environmental catalysts. The catalyst was characterized by XRD, FT-IR spectroscopy, thermal and chemical analyses. The catalytic activity of CoO$_x$ was evaluated through both the rate constant (k, min^{-1}) and the overall degree of HCHO conversion (α, %). The effect of main operational parameters influencing HCHO degradation efficiency such as catalyst loading, temperature, and oxidant concentration was investigated. The method of the planned experiment has been applied for determination of the optimal technological parameters of the process. Results obtained show that the optimal conditions for achieving complete conversion of HCHO are temperature 30°C, catalyst loading 1.5 g dm^{-3}, and NaOCl concentration 15 ml dm^{-3}.

Key words: *CoO$_x$ catalyst, HCHO complete oxidation, NaOCl, wastewater treatment*

1. INTRODUCTION

Water resources are determinative factor for the existence of the natural ecosystems and of man but they have become more and more confined due to the increase of the population, strengthening urbanization, and the climatic changes. Because of that, the preservation and the rational utilization of waters have got social, economic, and ecological significance. These problems stand with particular acuteness for this country which has got at its disposal limited water resources. That's why *the removal of the pollution risk for the natural environment still in the very production process* pertains to the basic trends of ecology. It is related to the development of effective technologies for treatment of wastewaters of the industrial productions and their introduction into the purification installations of all enterprises. *The priority compounds subjected to binding control and purification as well as their limiting admissible concentrations (LAC) for all categories of water receptacles* have been specified in the normative documents of the Ministry of environment and water of R. of Bulgaria. Aldehydes, and formaldehyde in particular, phenols and alcohols belong to the priority organic pollutants. The considerable increase of the requirements, the strict control and the restrictive measures towards chemical productions related to the preservation of the environment, and the implementation of the European standards in the ecological legislation have set new tasks to be solved in front of the formalin production as well.

Wastewaters of a series of productions – production of formalin, carbamide- and phenolformaldehyde resins, plastics, gums for the furniture industry, organic synthesis, pharmaceutical industry, etc – contain formaldehyde – an object of the present study. Studies about the influence of HCHO on the human organism have pointed out that, depending on the concentration, it exerts cancerogenic, asthmatic, and irritating action on vision and skin. Organic substances of various composition, stability and toxic effect, including formaldehyde, that have been emitted out of control in water basins not

only have been deposited and cumulated in various components of the vital environment, but through migration can get into the food chains. The latter creates a potential risk for the health of the humans as a final link of the food chain. The presence of these pollutants in water basins has resulted in an increase of the values of the indices chemical oxygen demand (COD) and biological oxygen demand (BOD) beyond the *LAC*, decreasing the concentration of oxygen dissolved in them. This fact, in turn, has hindered the photosynthetic activity of the water fauna which inevitably has negatively affected the growth of water organisms as well.

It follows from the above-mentioned facts that in the industrial productions related to the derivation of formaldehyde as well as utilizing HCHO as precursor for the production of a series of materials and compounds, it is binding to propose effective methods for its neutralization, and, on that base, to develop technologies for wastewaters treatment with these productions in which the concentration of HCHO exceeds LAC.

The biological methods are among the methods most often applied to the practice for purification of polluted waters because of their ecological conformity, effectiveness and economic cost price (Moussavi et al. 2009). These methods are based on the natural self-purification of waters which proceeds under the exerted influence of microorganisms, most frequently bacteria and fungi, under aerobic or anaerobic conditions. The biological purification has been applied when the ratio BNO/CNO is higher than 0.5. The anaerobic methods have been used as a first stage of purification of heavily polluted industrial wastewaters with the aid of anaerobic bacteria. The aerobic processes have been applied as a second stage of purification and have proceeded with the participation of active precipitate representing a population of microorganisms. The literature data, however, have indicated that the effectiveness of degradation of organic pollutants by means of active precipitate of bacteria has been unsatisfactory because of the excretion of secondary pollutants and intermediates (Prieto et al. 2012). For example, with the biological purification of industrial wastewaters, containing formaldehyde with concentrations from 31.5 to 300 mg/l, partial (with the lower concentrations) and complete (with the higher ones) inhibition of microbial cultures has been observed (Lotfy and Rashed 2002). The low rate of this process can be indicated as a disadvantage of the biopurification. It has created conditions for poisoning the biomass as the larger part of the microorganisms has been poisoned with high concentrations of toxic compounds (Liotta et al. 2009). Besides, many organic compounds containing aromatic or condensed nuclei have been bioundegradable and thus, the biological purification in a series of cases has been found as ineffective or poorly effective.

The physical methods are alternative to the conventional biological methods for purification of wastewaters. Most often, adsorption of toxic compounds has been applied on appropriate adsorbents (Salman et al. 2012). The physical adsorption has been an undestructive, effective, and easy to adapt to a specific system method employing cheap, accessible, and harmless adsorbents (Yousef et al. 2011). The most thoroughly studied adsorbents in the scientific literature have been activated charcoal, clay minerals, zeolites, various polymers, biosorbents, etc. A comparative analysis of the adsorption of formaldehyde on bentonite and kaolin has ascertained that bentonite has been assessed with a higher adsorption capacity. The determined maximum adsorption capacity has revealed that 1 g of kaolin has adsorbed 3.41 mg formaldehyde whereas the maximum quantity adsorbed formaldehyde on bentonite has been 5.03 mg (Yousef et al. 2011). Natural and synthetic zeolites have also represented interest and have been intensively studied aimed at their application as adsorbents because of their highly developed surface. A distinctive feature of the zeolites is that they can be regenerated preserving their initial composition. Authors, by studying the adsorption of formaldehyde in water phase on natural zeolite have found that the highest degree of adsorption extraction has been achieved in 8 hours contact time between the adsorbent and the adsorbate with concentration of the formaldehyde 2 mg/l (Kulikauskaite and Paliulis 2015). It has been proven that pH of the solution has not affected the adsorption capacity of the zeolite.

The thermal decomposition (pyrolysis) is another implemented technology for making harmless toxic organic pollutants in waters. Temperatures of 1800ºC and pressure of 15 barr have been required with the application of pyrolysis for purging formaldehyde from water solution; with it, complete destruction has been achieved only in solutions of relatively low concentration of formaldehyde – 7

ppm (Friedrichs et al. 2006).

The oxidizing methods also belong to the conventional methods for purification of wastewaters containing aldehydes. The chemical oxidation has been one of the simplest destructive technologies based on degradation of the pollutants contained in wastewaters to harmless products under the effect of strong oxidizers, such as ozone (O_3), hydrogen peroxide (H_2O_2), sodium hypochlorite (NaOCl) (Melero et al. 2009). Studies have shown that the use of pure oxygen for oxidizing degradation of formaldehyde in water solutions has been ineffective. Low degree of conversion of formaldehyde has been achieved – 38% for 180 min at temperature of 200°C and pressure up to 35 bar (Silva et al. 2003).

The search for innovative approaches for the overcome of the disadvantages of the conventional methods for purification of wastewaters has led to the elaboration of a wide range of oxidizing processes known as *advanced oxidation processes (AOP's)*. These have been based on the formation, under the effect of UV radiation, ultrasound or suitable catalysts, of strongly reactive radicals ($^\bullet$OH hydroxyl, $O_2^{\bullet-}$ peroxide, $SO_4^{\bullet-}$ sulfate) which easily attack and destruct organic molecules to harmless products (CO_2 and H_2O). *"Wet air oxidation"* (*WAO*) (Pintar et al. 2004, Zou et al. 2007) and "supercritical water oxidation" (*SCWO*) (Raumchat et al. 2006) have been pertained to *AOP's*. The practical utilization of *WAO* and *SCWO* in detoxifying wastewaters from harmful compounds, however, is limited because of the high energy consumption, complex and expensive apparatuses, requiring high pressures and temperatures. That's why the processes of low-temperature liquid-phase catalytic oxidation are perspective alternative for purification of wastewaters. Their basic advantages to *SCWO* and *WAO* are: they proceed with considerably milder conditions (room temperature and atmospheric pressure); with a selection of suitable catalytic systems and conditions, the process flows selectively to products of complete oxidation; simplified apparatuses. Depending on the nature and the concentration of toxic substances in wastewaters, these processes can be applied either only for the reduction of the concentration of the pollutants with subsequent biotreatment or to their complete oxidation into harmless products.

It has been found that effective catalysts for complete oxidation of formaldehyde can be synthesized on the basis of noble metals (Huang and Leung 2011, Zhang et al. 2009, Peng and Wang 2007). Complete oxidation of formaldehyde in water solutions at room temperature has been achieved with participation of a reduced with $NaBH_4$ Pd/TiO_2 catalyst (Huang and Leung 2011). It has been suggested that role of active centers play Pd- nanoparticles possessing high potential for activation of surface oxygen. The catalytic activity of a series of noble metals (Rh, Pt, Pd) deposited on TiO_2 has been studied for complete oxidation of HCHO in gas phase at low temperatures (Peng and Wang 2007). It has been ascertained that Pt/TiO_2 with surface concentration of Pt of 0.6 mass % has revealed the highest activity. The influence of the nature of the carrier on the effectiveness of the oxidation process has been also studied; the activity of the deposited catalysts for oxidation of HCHO changes in the following order:

$$TiO_2 > SiO_2 > Ce_{0.8}Zr_{0.2}O_2 > Ce_{0.2}Zr_{0.8}O_2.$$

The different degree of dispersed platinum nanoparticles on the surface of the carrier and the various interactions active phase – carrier have been pointed out as a main reason for different catalytic activity of the mentioned catalysts.

Although noble metals have revealed excellent catalytic properties, their high price has got a negative effect on the economic expedience of the process. As alternative, catalysts based on transition metals and their oxides, deposited on appropriate substrates, have been proposed. Many researchers have studied catalysts in which the transition metals or their oxides (Ni, Fe, Cr, Mn, Co) have been deposited on different substrates: MnO_x (Sidheswaran et al. 2011), MnO_x – CeO_2 (Tang et al. 2006), CuO – ZnO/Al_2O_3 (Silva et al. 2003), etc. It has been reported that with the use of MnO_x – CeO_2 for the complete oxidation of HCHO particularly important role has played the higher oxidation state of the Mn – ion and the larger amount of mobile oxygen at the surface for the effective activation of the molecular oxygen as a result of the mechanisms of oxygen transfer (Tang et al. 2006). Christoskova and Stoyanova (2002) have studied the catalytic degradation of formaldehyde in water phase at room

temperature and atmospheric pressure. The synthesized after an unconventional method nonstoichiometric NiO_x has been discerned with high effectiveness and selectivity in the complete oxidation of formaldehyde in water solutions under "mild conditions". The method of synthesis with reverse order of precipitation, proposed by the authors, has resulted in preparation of a non-stoichiometric nickel oxide characterized with high content of overstoichiometric active oxygen; the latter has been a basic requirement for the catalysts with complete oxidation to harmless products CO_2 and H_2O. 90% degree of conversion of formaldehyde has been achieved for 150 min at temperature of $25^{\circ}C$ and concentration of the catalyst 2 g dm^{-3}. The synthesized catalyst has been tested under industrial conditions.

The aim of the present study is to examine the possibility for complete catalytic oxidation of HCHO with NaOCl in water solutions with participation of nanosized CoO_x at room temperature and atmospheric pressure as well as to determine the optimal technological parameters of the process by applying the method of the planned experiment.

2. EXPERIMENTAL PART

2.1. Catalyst preparation and characterization

The CoO_x catalyst was synthesized by using the precipitation-oxidation method with reverse order of precipitation in combination with ultrasound stimulation realized by ultrasound homogenizer UP100H. 0.4 M solution of $Co(NO_3)_2 \cdot 6H_2O$, 4M solution of NaOH and 1M solution of NaOCl have been used for the synthesis of the catalyst. The applied inverse order of feeding the precipitator to the system ($Me^{2+} \rightarrow OH^- + OCl^-$) favours the formation of hydrophilic residue. The OH groups, included in the oxide system and thus increasing its activity in oxidation processes, take part in the oxidation mechanism. On the other hand, the Co(II) ions act as a catalyst in the decomposition of NaOCl producing highly reactive nascent oxygen (Bielanski and Haber 1991). The latter increases the oxidation state of the cobalt ions in the oxide system and ensures a high concentration of ionic oxygen species (O^-, O_2^-) on its surface and play a main role in the oxidation catalysis The stimulation of the synthesis by ultrasound cavitation provides, from the one hand, conditions for more efficient homogenization of the reaction mixture, and from the other, is a prerequisite for the preparation of highly dispersive and nano-sized systems with higher specific surface. The latter contributes to increasing the number of accessible catalytic centres for substrate adsorption and catalyst activation, which in its turn favors the reaction kinetics. The synthesis has been carried out at room temperature upon continuous stirring. The black precipitate formed was allowed to age in the mother solution for 24 hours, followed by filtration, washing with distilled water to a negative reaction towards Cl^- ions and neutral pH. The precipitate was dried at $105^{\circ}C$ in air overnight to constant mass (the sample was marked as CoO_x). For comparison, Co_3O_4 was also prepared by calcination of part of CoO_x at $300^{\circ}C$.

2.2. Characterization of catalysts

In order to determine the phase composition of the samples, the content of active oxygen, the strength of the M-O bond and the coordination of the metal cation, the synthesized CoOx system was characterized by means of X-ray diffraction, chemical and thermal analyses and FTIR spectroscopy. Data obtained were compared with those of a reference Co_3O_4 sample.

The chemical analysis of the synthesized CoO_x and Co_3O_4 has included determination of the active oxygen content – total (O*) and surface (O_S*) – expressed in % and $mol.g^{-1}$, the amount of cobalt in gram sample, as well as determination of the solubility of the samples at different pH values of the medium.

Active oxygen is the amount of over-stoichiometrical oxygen in the oxide above that corresponding to the lowest stable oxidation state. The total active oxygen content was determined by a direct iodine method (Nakagava et al., 1962). The sample (0.1g) was dissolved in dilute (1:10) sulphuric acid containing 2g of potassium iodide. The solution was magnetically stirred and after a complete decomposition the liberated iodine was titrated with standardised 0.1 N sodium thiosulphate using starch as indicator. The relative standard deviation of the method is 4.71%.

The total active oxygen content in g-at.g^{-1} and % was determined according to the equations:

$$O* = \frac{N \times V \times mgE_{O_2}}{m \times 16}, g-at/g \qquad\qquad O* = \frac{N \times V \times mgE_{O_2}}{m} \times 100, \%$$

where: N – normality of the titrant; V – volume of the consumed titrant solution, cm^3; m- catalyst amount, g; $mgE_{O_2} = 0.008$, miligram equivalent O$_2$.

The amount of surface active oxygen was measured by the hydrazine method (Ushijima et al., 1967). A measured amount of 0.1 N hydrazine sulphate solution is allowed to react with a known weight of catalyst sample for about 20 min in a closed vessel. The residual hydrazine after filtration was titrated against 0.1 iodine solution at pH = 7.2. The relative standard deviation of the method is 5.02%.

Total cobalt content was determined by atomic absorption measurement carried out with a Spectro-Flama IOP-OES spectrometer at the corresponding resonance wavelength.

XRD was performed using a X-ray diffractometer TUR-MA 62, operating at U = 37kV, Cu Kα radiation (λ = 1.5406 Å) and I = 20mA. The diffractometer was supplied with a computer-contolled goniometer (HZG -3), scanning step of the spectrum of 0.04^0 and collection time of impulses - 1.2 s. The samples were scanned in 2θ range within 10 - 80^0. The FTIR spectra were monitored on a 1750 Perkin Elmer spectrophotometer, with 2 cm^{-1} resolution, in KBr tabletes (1 mg of the corresponding sample in 100 mg KBr). The differential thermogravimetry (DTG), differential thermal analysis (DTA) and thermogravimetry (TG) curves were taken with a Derivatograph Q in air under the following conditions: mass of the sample 0.1 g, sensitivity 0.5 mV for DTA, 1.8 mV for DTG and 0.1 mV for TG; temperature range 20 - 1000°C; heating rate 10°C min^{-1}.

2.3. Experimental procedure

The catalytic oxidation of HCHO was carried out in a 400 mL thermostated reactor at batch mode with constant stirring throughout the reaction at around 400 rpm to ensure continuous contact between the solution and catalyst. In a typical run, 200 ml 50 mg/L HCHO aqueous solution was saturated with oxygen by bubbling air under atmospheric pressure for 30 minutes. Then a predefined volume of 10% aqueous solution of NaOCl was added into the solution. The experiment was initiated by the addition of a fixed amount of catalyst. At specific time intervals, samples of 5 ml were withdrawn from the suspension and were centrifuged at 4000 rpm for 1 min to remove the catalyst. The concentration of HCHO in the filtrate was monitored spectrophotometrically (λ$_{max}$=565 nm) using Spectroquant® Formaldehyde test (Merck), compatible with the spectrophotometer NOVA 400 (Merck). The UV–Vis spectra as well as their first derivatives (D1) were recorded by two-beam scanning UV-Vis spectrophotometer (Cintra 101) in the range of 400-700 nm. Depletive oxidation experiments (without adding of NaOCl) were also performed in order to clarify the reaction mechanism.

The efficiency of the process of heterogenous catalytic oxidation of formaldehyde over CoO$_x$ was assessed by the degree of HCHO conversion at a given moment during the course of the reaction (α, %), calculated using following equation:

$$\alpha = \frac{C^o - C}{C^o} \cdot 100 \quad,$$

and by the rate constant (*k*, min^{-1}), determined by the kinetic equation of a first-order reaction:

$$k = \frac{1}{t} \ln \frac{C^o}{C}$$

where C^o and C are the initial and the HCHO concentration at time t (mol dm^{-3}), respectively.

All experiments have been repeated three times and the reproducibility was confirmed.

3. RESULTS AND DISCUSSION

3.1. *Characterizing the Co-oxide catalytic system*

Chemical analysis

The data of the chemical analysis of the CoO_x and Co_3O_4, including determination of the concentration of active oxygen, Co content and the solubility of the samples at different pHs'are presented in Table 1 and Fig.1.

Table 1. The content of active oxygen and cobalt in the as-prepared catalysts

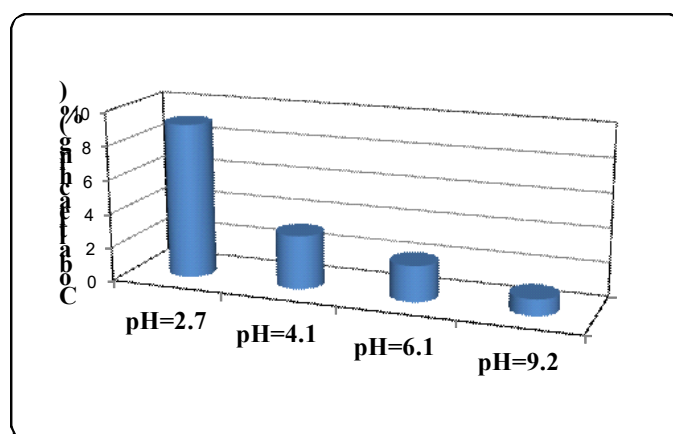| *Catalyst*	*Active oxygen content*				*Cobalt content*
	total (O*)		surface (O_s*)		
	g-at.g^{-1} .10^3	%	g-at.g^{-1} .10^3	%	g-at.g^{-1} .10^3
CoO_x	4.64	7.42	1.19	2.97	5.52
Co_3O_4	0.64	1.03	0.13	0.21	12.46

Fig. 1. Influence of pH on the solubility of CoO_x and Co_3O_4

It is seen from Table 1 that the applied method for synthesis favors the formation of oxide catalytic system characterized by high content of active oxygen which is highly reactive and causes heterogeneous oxidation of the substrate even at room temperature. It is worth noting that large portion of O* has been concentrated on the CoO_x surface (O_S* is $\approx$ 40% of the total active oxygen). The quantity of O* in the sample thermally treated at 200°C has remained unchanged and has sharply decreased under heating at temperatures above 300°C ($\approx$ 1%) due to phase conversion into Co_3O_4.

The results illustrated in Fig.1 have shown very low solubility of CoO_x in neutral and alkaline media (under 5%) which has been an indication for its high stability under the effect of the reactive medium and, respectively, preserving the initial activity with multiple participation in the catalytic reaction.

Powder X-ray diffraction (XRD)

The results of XRD analysis have revealed that an amorphous Co-oxide system has been obtained after the proposed synthesis. The amorphous nature of the fresh sample has presumed structural and chemical isotropy of the active sites of the catalyst that is a prerequisite for high selectivity in oxidation reactions. The fresh sample, thermally treated at 300°C, undergoes changes in its composition and structure and turns into a Co_3O_4 with a spinel structure.

Infrared spectral analysis (FT-IR)

The FT-IR spectra of CoO_x and of Co_3O_4 are presented in Fig.2. A characteristic feature of the CoO_x spectrum is the presence of a broad and intensive absorption band at 586 cm^{-1}. The indicated band has been observed at frequencies higher than those due to vibrations of the Co–O bond in the corresponding hydroxide – 460 cm^{-1}. It has been determined by valence vibrations of the metal–oxygen bond on the surface of the sample and has accounted for the presence of active oxygen in it. The intensity of the band is proportional to the concentration of O* in the catalyst. It has been found that the thermal treatment of CoO_x at 200ºC has not caused changes as in the intensity and the position of the band at 586 cm^{-1} as well as in the concentration of active oxygen. A process of spinel formation has begun at higher temperatures confirmed by a completely identical IR-spectrum of CoO_x heated at 300ºC with that one of standard Co_3O_4 (Fig.2b). The change in the phase composition and the structure of the oxide system has also proposed a difference in the catalytic behavior that has been confirmed with a comparative study of the activity of CoO_x and Co_3O_4 in a reaction of liquid-phase oxidation of HCHO.
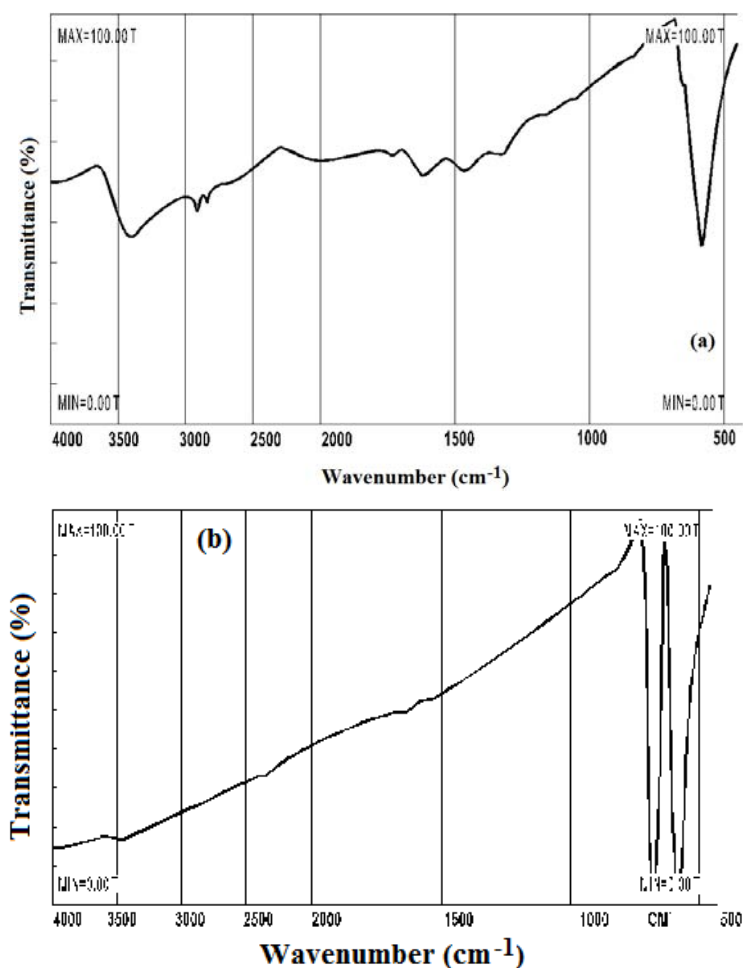

Fig. 2. FT-IR spectra of CoO_x (a) and Co_3O_4 (b)

X-ray photoelectron spectroscopy (XPS)

The oxidation state of Co in the synthesized catalytic system has been studied by means of X-ray photoelectron spectroscopy. O1s and Co2p$_{3/2}$ lines of CoO_x in the X-ray photoelectron spectra are presented in Fig.3.
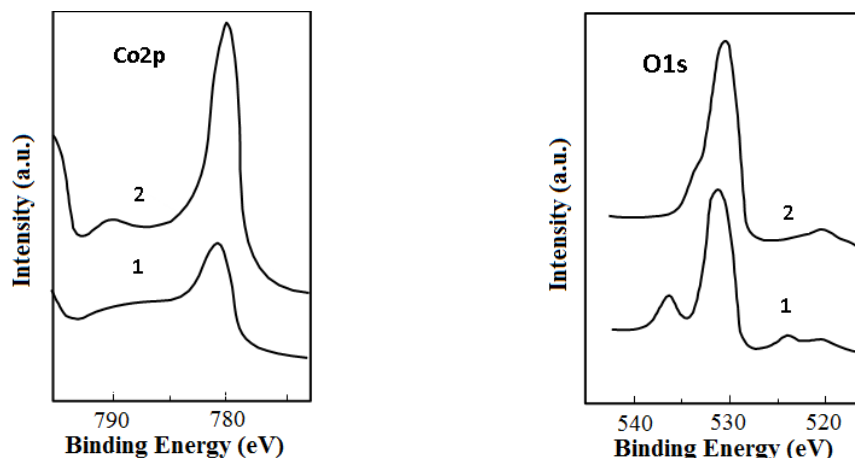
Fig. 3. $Co2p_{3/2}$ and O1s envelopes of CoO_x before (curve 1) and after depletive oxidation of HCHO (curve 2)

It is seen in the Co2p spectrum of CoO_x that the binding energies of $Co2p_{3/2}$ and $Co2p_{1/2}$ electrons are 780.9 eV and 795.7 eV, respectively. The spin-orbit component of $Co2p_{3/2}$ has got a weakly pronounced satellite peak located at 6 eV above the basic peak. The comparison of the Co2p spectrum of CoO_x with those of other cobalt oxides, e.g. with Co_3O_4 and CoO(OH), has shown difference. $Co2p_{3/2}$ spectrum of Co_3O_4 has contained basic peak at lower binding energy (779.9 eV). The spin-orbit splitting $2p_{3/2}$–$2p_{1/2}$ for CoO_x has been 14.8 eV against 15.1 eV for Co_3O_4. The discrepancy in the Co2p spectra of both samples, i.e. the observed difference in the binding energy of the $Co2p_{3/2}$ electrons and the difference in the values of spin-orbit splitting, has evidenced for a difference in the surface chemical composition of both oxides. It has given grounds to assume that in the synthesized by us oxide system the cobalt ions have been in a higher oxidation state compared to those in Co_3O_4, i.e. higher than (+3).

The maximum for the $Co2p_{3/2}$ electrons in the spectrum of the reduced after the depletive oxidation of HCHO catalyst (Fig.3, curve 2) has been shifted towards lower binding energy (780.2 eV) compared with the initial sample (780.9 eV) that probably is due to the change of the oxidation state of Co as a result of the oxidation of the substrate. The calculated value of spin-orbit splitting $2p_{3/2}$–$2p_{1/2}$ for the worked off sample (15.1 eV) has been higher for that of CoO_x (14.8 eV) that has also given grounds to assume that the reduced catalyst has contained Co ions in a lower oxidation state compared to the initial one.

Thermal analysis

The freshly obtained Co-oxide system has been an X-ray amorphous one but the thermal analysis has revealed clearly marked transformations (Fig.4).
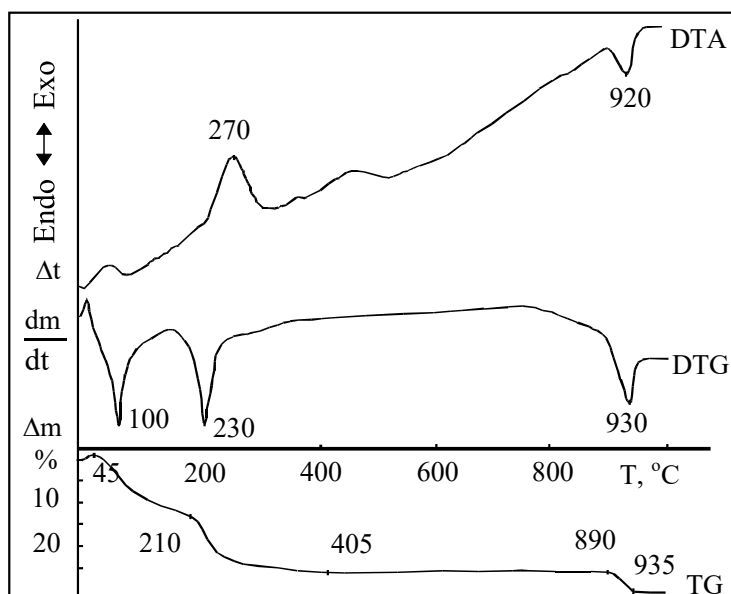
Fig. 4. DTA, DTG and DTG profiles of the as-prepared CoO_x

Three endo-effects have been registered in the DTA and DTG curves of CoO_x. The clearly marked endo-effect at temperatures 100-110°C has been due to release of physically adsorbed water. The loss of mass between 100°C and 210°C registered in the thermogravimetric curve has been basically due to release of chemically bound or compositional water. The endo-effect at 230°C has been probably due to release of active oxygen since a process of spinel formation has initiated simultaneously. The last endo-effect at 900-930°C has indicated that the spinel formed at temperature above 250°C has begun to decompose at ≈ 920°C after the process

$$Co_xO_{3-x}O_4 \rightarrow CoO + Co_yO_{3-y}O_4 + O_2$$
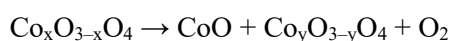
with formation of CoO and a spinel phase with composition close to that of Co_3O_4.

No effects have been observed in DTA and TG curves in the temperature range 300-900°C. Two exo-effects have been registered in the DTA-curve of CoO_x which are lacking in the derivatogram of Co_3O_4. The first, clearly marked exo-effect has been at 270°C while the second one has been at 450°C; both have been probably related to the formation of Co_3O_4 and its crystallization. This conclusion has been also confirmed by the data obtained by means of the XRD and the FT-IR spectral characterization of the samples. The results from the thermal analysis of the Co-oxide system have shown that the sample has remained unchanged up to 200°C, but after further heating, changes have occurred in its composition and structure revealed in:

– release of O* that has resulted to reduction of the active sites of the oxide and to formation of spinel structure;

– transition from X-ray amorphous into crystalline state;

– part of the octahedrally coordinated metal ions have passed into tetrahedral coordination.

It has been known that the mentioned effects lead to a decrease of the oxide activity in the oxidation processes.

3.2. Catalytic activity of CoO$_x$ in a reaction of complete oxidation of HCHO with NaOCl in water solutions under mild conditions – atmospheric pressure and room temperature

3.2.1. Chemical oxidation of HCHO

It has been pointed out here that formaldehyde pertains to the basic organic pollutants of the wastewaters and that its concentration in such waters is liable to binding sanitary control. It has been

prohibited by normative documents to release wastewaters containing formaldehyde above the *LAC* for all categories of water receptacles including urban purification stations. That's why the development of scientific fundamentals of innovative methods for purification of such wastewaters has been an immediate problem as from scientific viewpoint as well as from point of view of their implementation into practice.

In order to substantiate the expedience of bringing a catalyst into the system HCHO – oxidant, a control experiment has been carried out for evaluation of the possibility for chemical oxidation of formaldehyde to harmless products – CO_2 and H_2O. As oxidants, 30% solution of H_2O_2 and 10% solution of NaOCl have been used. The change of the concentration of HCHO has been monitored during the oxidation process spectrophotometrically, as well as by means of gas-chromatographic analysis. The results of the control experiments have shown that complete conversion of formaldehyde has not been achieved with stoichiometric and twofold amounts of H_2O_2. Under the studied conditions, 70% only of HCHO has been oxidized, however, to formic acid which has not undergone further oxidation even at complementary adding of H_2O_2 (Fig.5).
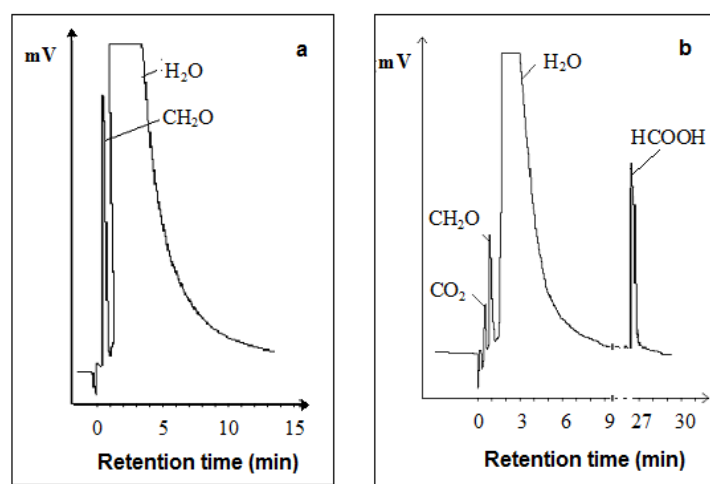

Fig. 5. GC analysis of reaction mixture during chemical oxidation of HCHO with H_2O_2: (a) 0 min; (b) 20 min

These preliminary studies have revealed that the development of a method based on chemical oxidation of HCHO with hydrogen peroxide is inexpedient for the following considerations:

– complete conversion of formaldehyde has not been attained. Its residual concentration has exceeded *LAC* (for third category of water receptacles);

– the product of oxidation of HCHO has been formic acid that has not been oxidized completely to harmless products (CO_2 and H_2O). It should be noted that formic acid has been added to the toxic organic substances and it has affected the index COD;

– the high price of the hydrogen peroxide and the necessity of a special equipment and conditions for its storage have restricted its application for solving ecological problems related to the purification of wastewaters from toxic organic compounds including HCHO.

Chemical oxidation of HCHO with 10% NaOCl has been carried out under the following reaction conditions: initial concentration of HCHO, C_O – 50 mg dm^{-3}; amount of the oxidant – 5 ml dm^{-3}; temperature, 20°C. The electronic absorption spectra and their first derivatives (D1) of the formaldehyde solutions are displayed in Fig.6, as they have been registered in the course of chemical oxidation with NaOCl.
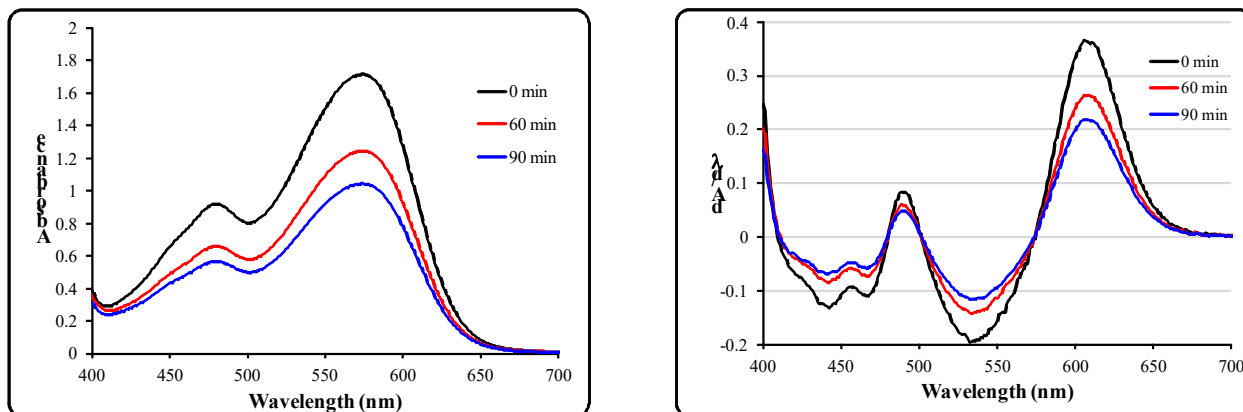
Fig. 6. UV-Vis spectrum profiles and their D1 derivatives in the course of chemical oxidation of HCHO with NaOCl (50 mg/L HCHO, 5 ml/l NaOCl, 20∘C)

The calculated degree of conversion of formaldehyde at 60th min and at 90th min, 27% and 39%, respectively, have been unsatisfactory. This has directed us to examine the possibility for increasing the effectiveness of the oxidation process through bringing a catalyst into the system.

3.2.2. Catalytic oxidation of HCHO with NaOCl over CoO_x

The results of the comparative study of the kinetics of oxidation of HCHO in various systems are displayed in Fig.7. The changes observed in the UV-Vis spectrum of HCHO in the course of catalytic oxidation on CoO_x as well as its first derivatives, are presented in Fig.8.
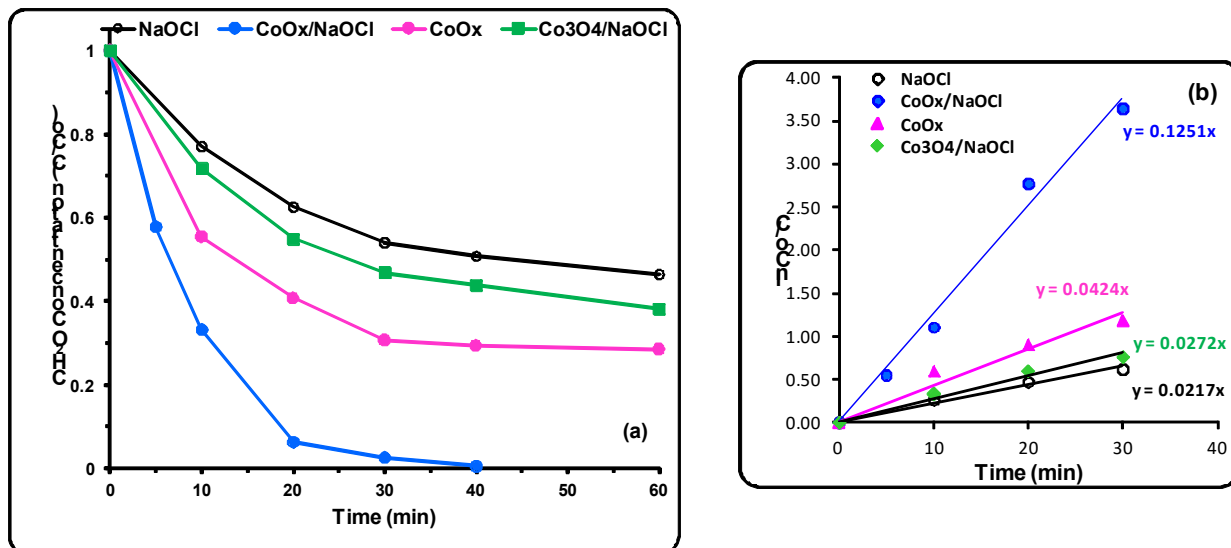

Fig. 7. (a) Comparative kinetics of chemical, depletive and catalytic oxidation of HCHO; (b) Corresponding linear transformation of the kinetic curves (50mg/l HCHO, 15 ml/l NaOCl, 1.5 g/l catalyst, 20°C)

It is seen from the presented data that in the absence of catalyst the oxidation of formaldehyde has proceeded with low rate – only 53% degree of purification of the solution has been achieved in one hour. In the presence of CoO_x but without addition of oxidant (depletive oxidation), nearly 70% of HCHO has undergone oxidative degradation up to 30 min, after that its concentration in the solution has remained unchanged. Under these conditions, HCHO has been oxidized by the active oxygen of

the catalyst and, at its depletion (confirmed by chemical analysis), the oxidation process has been stopped. The behavior of the catalytic system CoO_x is different in the presence of an oxidant in the reaction system. A considerable accelerating of the oxidation process has been observed as for the same reaction period (30 min) over 98% degree of purification of the solution of HCHO has been achieved. This presumes that NaOCl has provided a permanent regeneration of the active oxygen of the catalyst that has been consumed in the course of oxidation of formaldehyde. The participation of O* from CoO_x in the oxidation process has been also confirmed by the considerably lower catalytic activity of Co_3O_4 obtained with thermal treatment of CoO_x at 300ºC. The active oxygen concentration in that sample has been insignificant (below 2%) which explains the commensurable rate of the oxidation process with its participation with that one of chemical oxidation by HCHO. The linear plots of $\ln(C_o/C)$ versus time (Fig. 7b) confirm the assumed first-order kinetics.
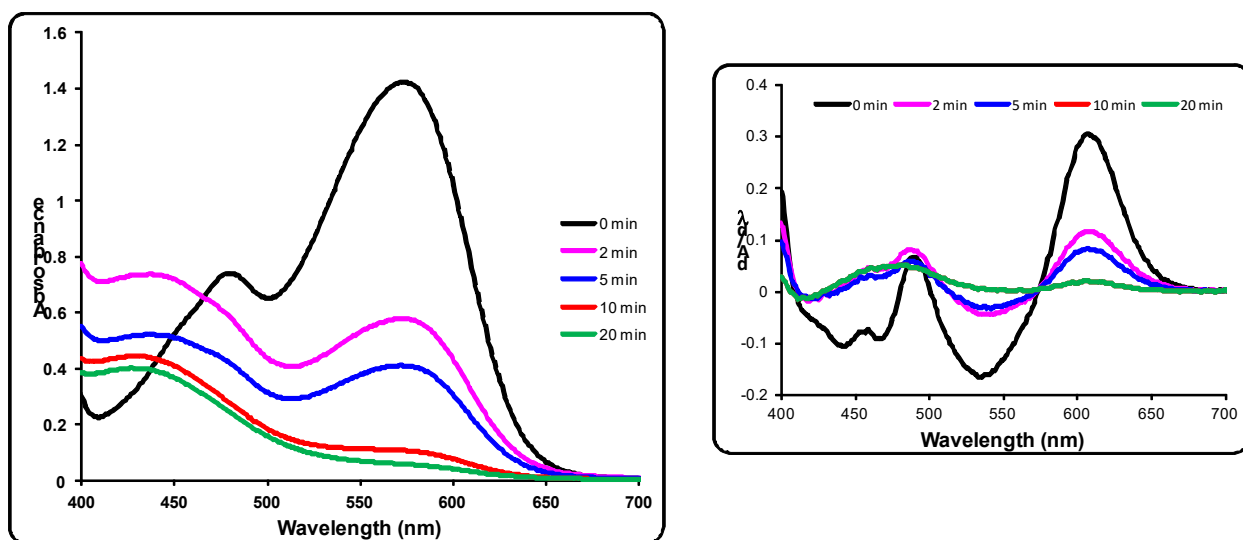

Fig. 8. UV-Vis spectra and their D1 derivatives recorded during the catalytic oxidation of HCHO on CoO_x (50mg/l HCHO, 15 ml/l NaOCl, 1.5 g/l catalyst, 20ºC)

The method of planned experiment has been applied for determination of the optimum conditions for complete catalytic oxidation of formaldehyde in wastewaters with the inclusion of the synthesized CoO_x catalytic system. The planning and modeling of the experiment have been carried out by means of statistical methods for modeling and optimizing multi-factor objects. As variable factors have been chosen: X_1 – concentration of the catalyst, expressed in g dm^{-3}; X_2 – concentration of the oxidant, ml dm^{-3}; X_3 – temperature, ºC. For aim functions, through which the effectiveness of the applied method has been assessed, Y_1 and Y_2 have been chosen respectively, for the degree of purification of water solutions from HCHO in the 20 min from the start of the process (α_{20}, %) and the rate constant of the oxidation process (k, min^{-1}). The basic levels of the factors and the intervals of their variations, determined on the base of analysis of the results of preliminary experiments, are presented in Table 2.

Table 2. Basic levels and intervals of variation of the factors

Factors	$[X_i]$	Interval of variation, λ_i	Levels of the variables		
			$X_i = -1$	$X_i = 0$	$X_i = +1$
X_1	g dm^{-3}	0.5	0.5	1.0	1.5
X_2	ml dm^{-3}	5.0	5.0	10.0	15.0
X_3	ºC	5.0	20	25	30

The practical realization of the experiment has been realized on the base of the composed plan-matrices following the principle of randomization of the trials. It has been worked with double trials in order to make it possible to check for the homogeneity of the dispersions throughout the entire factor space. The results are presented in Table 3 obtained in studying the influence of the three factors on the degree of purification from HCHO in 20 min from the beginning of the process; in Table 3b – on the rate constant calculated according the kinetic equation for first-order reactions.

Table 3. Plan-matrices and results from experiments with participation of CoO_x catalytic system: (a) aim function – α_{20}, %; (b) aim function – k, min^{-1}

(a)

№	X_1 g/dm^3	X_2 ml/dm^3	X_3 ℃	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$	$\alpha^I_{20'}$	$\alpha^{II}_{20'}$	$\alpha_{20',cp.}$	$\sum S_u^2$
1	0.5	5.0	20	+	+	+	–	52.4	49.8	51.1	3.38
2	1.5	5.0	20	–	–	+	+	70.25	68.9	69.58	0.91
3	0.5	15.0	20	–	+	–	+	81.0	78.9	79.9	2.42
4	1.5	15.0	20	+	–	–	–	95.4	92.1	93.75	5.45
5	0.5	5.0	30	+	–	–	+	53.8	54.12	53.96	0.05
6	1.5	5.0	30	–	+	–	–	70.35	70.25	70.3	0.005
7	0.5	15.0	30	–	–	+	–	89.65	89.41	89.53	0.03
8	1.5	15.0	30	+	+	+	+	96.32	95.96	96.33	0.26

(b)

№	X_1 g/dm^3	X_2 ml/dm^3	X_3 ℃	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$	k-I	k-II	$k_{cp.}$	$\sum S_u^2$
1	0.5	5.0	20	+	+	+	–	0.036	0.032	0.034	0.00001
2	1.5	5.0	20	–	–	+	+	0.056	0.062	0.059	0.00002
3	0.5	15.0	20	–	+	–	+	0.076	0.072	0.074	0.00001
4	1.5	15.0	20	+	–	–	–	0.121	0.128	0.125	0.00002
5	0.5	5.0	30	+	–	–	+	0.035	0.041	0.038	0.00002
6	1.5	5.0	30	–	+	–	–	0.089	0.079	0.084	0.00005
7	0.5	15.0	30	–	–	+	–	0.102	0.109	0.106	0.00002
8	1.5	15.0	30	+	+	+	+	0.271	0.267	0.269	0.00001

The coefficients of the following regression equations have been calculated on the basis of the obtained results:

$Y_1 = 75.51 + 6.89x_1 + 14.23x_2 + 1.93x_3 – 1.82x_1x_2 – 1.19x_1x_3 + 1.03x_2x_3 – 0.66x_1x_2x_3$

$Y_2 = 0.098 + 0.036x_1 + 0.045x_2 + 0.026x_3 + 0.018x_1x_2 + 0.017x_1x_3 + 0.018x_2x_3 + 0.012 x_1x_2x_3$

The analysis of the obtained regression equations has shown positive effect of the studied factors on the effectiveness of the catalytic process with the strongest influence being on the amount of the oxidant (Fig.9).
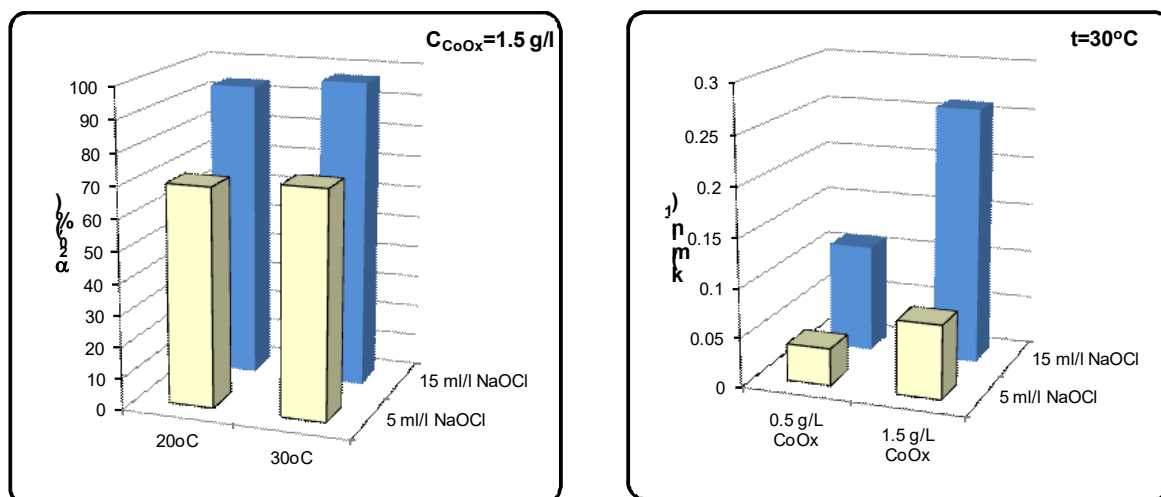
Fig. 9. Combined effect of the studied variable factors on the degree of catalytic purification of the HCHO solution at 20th minute with participation of CoO_x

The following basic conclusions can be drawn on the grounds of the results from the carried out studies:

–   complete oxidation of HCHO to CO_2 and H_2O has been practically attained with all combinations of the factors – concentration of the catalyst (g/dm^3), concentration of the oxidant (ml/dm^3), and reaction temperature (^{o}C) (Table 3) – proved with gas-chromatographic analysis for different reaction periods. The oxidation process has passed with the lowest rate at trial No.1 (low level of the factors) – complete oxidation of formaldehyde has been attained in *ca.* 90 min;

–   maximum purification effect for shortest time (*ca.* 20 min) has been achieved at upper level of the three factors (concentration of the catalyst, 1.5 g/dm^3, concentration of the oxidant, 15 ml/dm^3, and temperature, 30°C);

–   the factor X_2 – concentration of the oxidant – has exerted the most powerful influence on the rate of the catalytic process. The rate constant has increased *ca.* 3 times with increasing concentration of the oxidant from 5 ml/dm^3 to 15 ml/dm^3 with identical other factors – temperature and concentration of the catalyst;

–   the results have revealed that the proposed new method is effective and can be adapted for purification of wastewaters from the formalin production.

What conditions will be chosen for the practical application of the catalytic method for purification of wastewaters containing HCHO depends on: the output of wastewaters; the concentration of HCHO in the wastewaters; the capacity of the purification installations; the financial resources.

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