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Investigation of Electrocatalytic Water Purification from Formaldehyde Using Copper-Containing Catalyst

M. Z. DKHAN and YU. V. TSAREV

Ivanovo State Chemical Engineering University,
Pr. F. Engelsa 7, Ivanovo 153460 (Russia)

E-mail: tsarev@isuct.ru

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Abstract

Formaldehyde electrocatalytic oxidation of was studied on a copper-containing catalyst placed in an electrochemical cell. The effect of catalyst on the formaldehyde oxidation when changing parameters such as solution flow rate through the reactor, wherein the catalyst was placed, power density supplied and interelectrode spacing.

Key words: formaldehyde, waste water, purification, electrocatalysis

INTRODUCTION

The State Report on the condition of Water Resources in the Russian Federation [1], prepared by the Ministry of Natural Resources and Environment, noted that for some rivers the pollution level values exceed the MPC by 1.4 times with respect to such toxicants, as formaldehyde. Taking into account the fact that the compound was added to the list of substances those exhibit carcinogenic hazard for humans [2], the development of novel purification methods aimed at preventing the inflow of formaldehyde into the environment, is relevant.

The sources of formaldehyde entering into the environment are the woodworking and furniture production enterprises, as well as enterprises for the production of coke, for the processing of coal, oil and shale tar, for coal gasification.

In modern practice, preference is given to a combined water treatment using reagentless technologies, allowing one to carry out the processes of deep oxidation of organic matter, sorption of suspended solids and water disinfection within one unit [3–5]. The authors of [6] investigated the three-dimensional electrode system (TDES), so-called bulked electrode system. In this three-dimensional system the parts of electrodes in the form of pellets are placed within the space between common two-dimensional electrodes (into the interelectrode space). The authors of [6] noted that owing to a small distance between the granules, a high productivity level could be achieved in the electrochemical process. The authors of [7, 8] studied a combined process of the adsorption and electrochemical oxidation of organic compounds. In this case the activated carbon was located within the interelectrode space in fixed and suspended state. The authors of these studies have demonstrated that the use of combined techniques could increase the efficiency of wastewater purification from organic pollutants.

The authors of [9] noted that the use of the Fenton process for wastewater treatment is limited to a narrow range of pH values. In order to extend the operating range of the pH to neutral and basic one the authors of [9] propose to use as nanostructured Fe/Fe_2O_3 deposited onto carbon fibre (ACF) a cathode. The system with the cathode Fe/Fe_2O_3/ACF was investigated in the field of water purification from rhodamine dye with demonstrating a significantly higher rate than other electro-Fenton system at neutral solution pH values.

For the electrochemical oxidation of methylene blue (MB) in waste water the authors of [10] used kaolin modified with Fe_2O_3 and placed into an electrochemical reactor with graphite plates as electrodes. It was found that kaolin modified with Fe_2O_3 exhibits a high catalytic activity in the electrochemical degradation of wastewater containing MB. In other studies [11–13] the authors investigated the purification of wastewater containing methyl yellow dye (MF) and wastewaters of pulp and paper production in the system with iron and graphite electrodes, wherein $Co_2O_3{-}CuO{-}PO_4^3$ modified kaolin was placed. The experiment demonstrated that the oxidation proceeds efficiently at pH 3–5, with the current density amounting to 30 mA/cm^2. The purification efficiency in COD amounted up to 90–97 %. Similarly, the authors of [14] studied the effect of $KMnO_4$ and ferrous sulphate in contact with active bentonite, on the process of waste water purification from phenol.

The authors of [15] investigated the efficiency of a new electrochemical reactor with a bulked electrode, where through a gas was bubbled. As the object of investigation we chose model waste water containing formic acid. The results demonstrated that the purification efficiency according to COD is significantly higher compared with two-dimensional and three-dimensional electrodes without passing-through gas. The purification efficiency of COD is increased by 13.5 % by replacing nitrogen used as gas bubbled through the bulked electrode, by air that not only participated in some physical processes, but also played an important role in electrochemical reactions.

The authors of [16] used a new electrochemical heterogeneous catalytic reactor for the heterogeneous-catalytic purification of a model solution of nitrobenzene. The space between the graphite plates (anode and cathode, at a ratio of 1 : 3) was filled with bifunctional bulked electrode: activated carbon and alumina with 2 % of copper (II) oxide or iron (III) oxide. It was found that the purification of nitrobenzene is to a considerable extent dependent on applied potential, initial pH value and the concentration of background electrolyte. The results demonstrated that the efficiency of catalytic purification from nitrobenzene is higher than without the catalyst. The efficiency of water purification from nitrobenzene in the case of catalyst based on iron oxide only at $pH < 4$ is much higher than the efficiency a catalyst based on copper oxide. For neutral and alkaline pH values, this difference disappears. With an increase in pH increases the purification level.

In some publications [17] it is noted that in neutral and alkaline solutions, the formaldehyde oxidation in the electro-Fenton systems in the presence of Fe^{2+} occurs with the accumulation of formic acid. In acidic solutions at pH 2.2 and the temperature of 60 °C, a complete formaldehyde oxidation into CO_2 and water proceeds. At the same time the authors of [18, 19, p. 540] noted that the presence of Cu^{2+} results in increasing the oxidation level in the electro-Fenton process and in a more significant effect on the oxidation of aliphatic acids accumulated as intermediate oxidation products. The authors explain this by the fact that the much more ready oxidation of aliphatic acids could be connected with the formation of their complexes with Cu^{2+}.

Thus, a problem remains urgent concerning the development of electrodes those would provide the process of deep waste water purification from organic pollutants within a wide pH range. The investigation was aimed at studying the influence of alternating electric current upon the layer of copper-containing catalyst in the process of purifying a model solution from formaldehyde.

EXPERIMENTAL

As the object of the investigation, we used formaldehyde solution with the concentration of 800 mg/L, prepared from distilled water and technical grade formaldehyde (VM trademark, Oxiton Co., State Standard GOST 1652–89) containing 37 % of formaldehyde. To carry out the purification process, we prepared copper-containing catalysts supported on AG-2 grade activated carbon (AC) with granule size ranging within 0.5–1 mm, using impregnation. To a 500 mL flask were put 50 g of AC and was poured a solution of $Cu(NO_3)_2$ with the concentration of 410 g/L. The impregnation procedure was carried out in an incubator at 80 °C during 60 min. The AC granules impregnated with the solution were placed to an oven with the temperature of 150 °C for 60 min. After drying, the AC granules were placed to a muffle furnace and calcined at 350 °C for 1 h. The copper (II) oxide content in the catalyst obtained amounted to 8 %.

The purification of waste water was carried out in a flow-through reactor (Fig. 1), operating as a plug flow reactor. The reactor represented a tube of 1 cm in diameter, wherein the catalyst under investigation was placed. The bulked electrode was supported from both sides of the tube by current leads with mesh copper electrodes. The distance between the mesh electrodes was varied from 1 to 3 cm. The waste water flow rate was adjusted by a control valve *8*. In the reactor there was a catalyst *2* between placed the mesh electrodes *3* and *4*. Across the copper mesh electrodes, AC voltage (5–15 V) was applied. Amperage and voltage were registered using a milliammeter (A) and a voltmeter (V). Determining the input power density W (W/cm^3) for the reactor was calculated using the formula $W = UI/V$, where U is voltage, V; I is current strength, A; V is the volume of the catalyst bed, cm^3.

The current efficiency was determined from the formula

$$CE = XC_0VnF/Q$$

where X is the pollutant conversion level, C0 is the initial concentration of the pollutant, mol/L; V is the volume of purified solution, L; n is the number of electrons involved in the oxidation process; F is the Faraday constant, C/mol; Q is the amount of electricity, C.

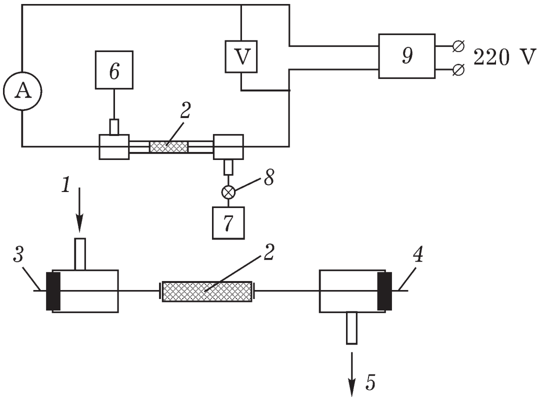

Fig. 1. Reactor and experimental setup for the electrocatalytic purification of waste water from formaldehyde: *1* – the model waste water inlet into the reactor, *2* – catalyst layer, *3*, *4* – current leads with mesh copper electrode on the end, *5* – the model of waste water outlet from the reactor, *6* – pressure camera with the model waste water, *7* – infeed chamber with purified waste water, *8* – valve for adjusting water flow, *9* – transformer; A – ammeter, V – voltmeter.

The concentration of formaldehyde was measured at the inlet and outlet of the reactor by a photocolorimetric method [20] using KFK-2MP unit. The method for determining formaldehyde is based on its reaction with chromotropic acid in acidic medium resulting in the formation of a compound making the solution purple. The formaldehyde content was determined with the use of photocolorimetry at the wavelength of 584 nm in an optical cell with the optical path length amounting to 0.5 cm. The pH value of the model waste water was determined using a Monomer I-130 pH meter. The initial pH value for the wastewater was equal to 5. The content of copper (II) ions at the outlet of the reactor was determined using Saturn AAC-3 atomic adsorption spectrophotometer. The qualitative determination of formic acid was performed via bleaching the solution of 0.1 M $KMnO_4$ as described in [21]. In order to measure the surface of the catalyst we used the method of selective low-temperature helium chemisorption of in the pulsed mode at the temperature of −136 °C. The measurement of the total surface area was carried out using a Tsvet-211 sorbtometer [22]. The specific surface for the activated carbon amounted to 1100 m^2/g, and that for the catalyst prepared was equal to 28 m^2/g.

RESULTS AND DISCUSSION

Figure 2 demonstrates the purification level of the model waste water on the passing time. Purifying the model solution containing formaldehyde was carried out in the flow-through reactor for 210 min at a constant specific power consumption equal to1.5 W/cm^3 and a flow rate of 0.08 mL/s. The height of the catalyst layer poured into the interelectrode space was equal to 1, 2 and 3 cm (the mass of the catalyst being 280, 590 and 850 mg, respectively).

In general, the dynamics of purifying the model waste water from formaldehyde indicates that since the initial moment of operating the reactor up to 1 h, the purification level with respect to formaldehyde amounted to 40–80 %. So, with increasing the height of the catalyst layer from 1 to 3 cm, the purification level increased, respectively. Basing on the data presented in Fig. 1 one could assume that at the initial stage (about 30–40 min) formaldehyde and its oxidation products adsorbed on the catalyst surface affect the formaldehyde oxidation via the formation of the catalyst surface and the participation of intermediates in the oxidation process. Low initial oxidation level values for formaldehyde and the subsequent increase of these are due to “flushing” a part of supported copper (II) oxide, which is confirmed by further experiments.

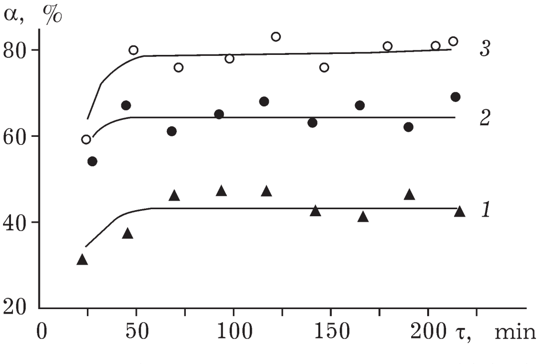

Fig. 2. Level of purification from formaldehyde (α) depending on time (τ). Supplied specific power amounting to 1.43 W/cm^3, the flow rate of the solution equal to 0.08 mL/s, alternating current, the catalyst bed height H, cm: 1 (*1*), 2 (*2*), 3 (*3*).

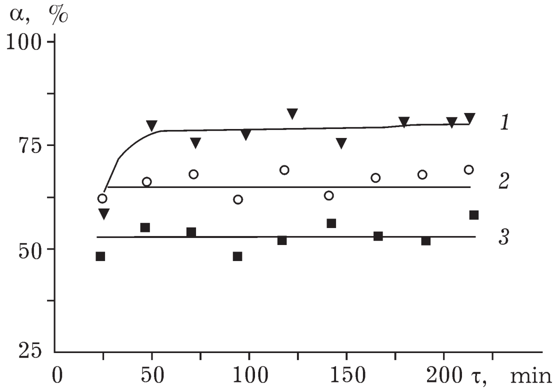

Fig. 3. Level of purification from formaldehyde (α) depending on time (τ) in the presence of bulked electrodes of various types, and without them: *1* – bulked electrode, the catalyst containing 8 % CuO, *2* – bulked electrode, AG-2 activated carbon, *3* – mesh electrodes in the absence of bulked electrode; interelectrode distance H = 3 cm, flow rate amounting to 0.08 mL/s.

Figure 3 demonstrates the purification level with respect to formaldehyde depending on time both in the presence of different type bulked electrodes, and without their use. Experiments were performed using the catalyst containing 8 % CuO on K-2 grade AC as a bulked electrode. In addition, an experiment was performed with a mesh electrode without the use of bulked electrode. In all the cases the interelectrode distance amounted to 3 cm. It was found that when AC with CuO applied onto the surface was used as a catalyst, the formaldehyde oxidation increased by 20–30 %. With using AC as the bulked electrode the purification level increases by 10–15 %.

In the course of the electrocatalytic cell operation for purification waste water from formaldehyde it could be possible that the copper oxide deposited on the surface of AC would pass in the purification solution. Figure 4 demonstrates the concentration of copper ions Cu^{2+} at the output of the electrocatalytic cell depending on the processing time for the model solution. For all the experimental conditions, copper (II) in water outgoing from the reactor is less than recommended standards for the sanitary and toxicological hazard index (1 mg/L) [23]. For the catalyst layer with the height of 3 cm, a decrease in copper content from 0.09 to 0.04 mg/L was observed during 1 h.

For the catalyst layers with the filling height of 1 and 2 cm, the content of copper (II) is about two-fold reduced, too. For the purification of the model solution we used a copper-containing catalyst with the copper content of 8 % as calculated for CuO content. As much as 960 mL were processed at a rate of 0.08 mL/s during 200 min. The concentration of copper in the purified model solution after passing through the catalyst bed 3 cm high at the input power density 1.8 W/cm^3 amounted to maximum 0.1 mg/L. The mass of the catalyst put into the reactor by the time of the experiment was equal to 810 mg. Consequently, only 0.2 % of the catalyst goes into solution. For the catalyst bed with the height of 1 and 2 cm, the loss of copper (II) oxide amounts to 0.1 and 0.2 % respectively.

One of the possible stages of formaldehyde oxidation consists in the formation of formic acid [6], which would to some extent affect the pH value of purified solution. In this connec-

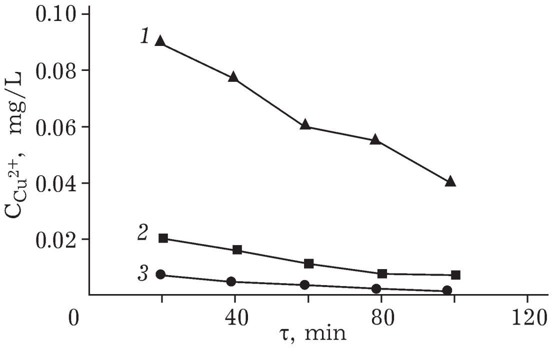

Fig. 4. Concentration of copper ions Cu^{+2} at the outlet of the electrocatalytic cell depending on the duration of waste water treatment, alternating current (AC). The height (*H*) of the catalyst bed, cm: 1 (*1*), 2 (*2*), 3 (*3*).

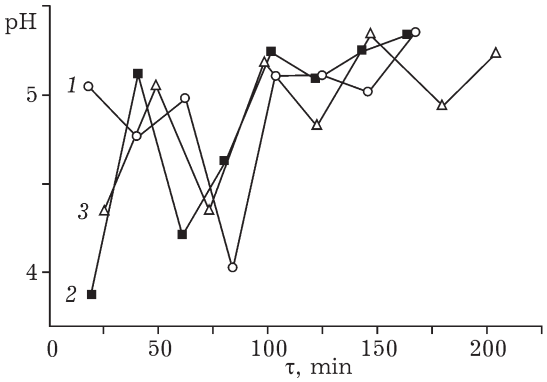

Fig. 5. Solution pH depending on the passing time of the model solution (the supplied specific power W = 1.43 W/cm^3, flow rate amounting to 0.08 mL/s, AC). The height (*H*) of the catalyst bed, cm: 1 (*1*), 2 (*2*), 3 (*3*).

tion, we obtained data concerning the pH value of the model solution at the outlet of the flow-through reactor depending on the passing time (Fig. 5). The pH value of the solution after purification during the entire operation time of the reactor changed insignificantly (pH 4.0–5.1); it could be characterized as weakly acidic.

In order to assess the influence of intermediate products formed upon the pH value of the purified model solution we have carried out a qualitative analysis of formic acid. It was established that the purified model solution does not contain formic acid. We can conclude that the formaldehyde oxidation proceeds completely to yield CO_2 and H_2O with forming an insignificant amount formic acid that could exist in the adsorbed state on the catalyst surface to affect the oxidation process. In general, changing the pH of the model solution at the outlet of the reactor is observed within the first hour of the unit operation. As mentioned earlier, this time interval corresponds to the formation of the catalyst surface due to washing-out a part of copper oxide from the catalyst surface. Increasing the concentration of ions in the solution may contribute to intensifying the processes at the electrodes, which ultimately results in the fluctuations of the solution pH value.

Basing on the data obtained we calculated the reaction rate constants for formaldehyde oxidation. The kinetics of formaldehyde oxidation is described by second order equation [8]:

$$dx/d\tau = k_2C_f(1 - x)^2$$

where k_2 is the effective second order rate constant, L/(mol · min); C_f is the initial concentration of formaldehyde, mol/L; τ is the time spent in the reactor, min; x is the conversion level.

The calculated rate constants values for the oxidation process in the flow-through reactor are presented in Table 1. Our data are comparable with the results presented in [8]. The authors of [8] carried out the formaldehyde oxidation using hydrogen peroxide generated in the porous gas diffusion cathode. The current yield for different experimental conditions ranged from 5 to 15 %.

The process of waste water purification of from formaldehyde was carried out at the current densities amounting to 500–3000 A/m^2. With increasing the current density, the puri-

TABLE 1

Effective rate constant values ofr formaldehyde oxidation, for different process conditions, L/(mol · min)

Height of the catalyst bed, cm	Supplied specific power (W_{sp}), W/cm^3			
	1.4	2.4	7.3	10.7
1	0.014	0.018	0.032	0.058
2	0.020	–	–	–
3	0.039	–	–	–

fication level of formaldehyde increased. It is noteworthy that the formaldehyde oxidation does not require for introducing any background electrolyte solution, since the granules of the copper-oxide catalyst placed into the interelectrode space exhibit electrical conductivity.

CONCLUSION

The process of formaldehyde oxidation on catalyst made of granular activated carbon coated with an active component such as copper oxide, placed in the interelectrode space, was investigated.

It is established that applying the alternating electric field on the catalyst layer in the course of passing-through the model solution allows one to perform the formaldehyde oxidation.

In the course of studying the process of model waste water purification on the copper-containing catalyst it was revealed that the increase of the input power density and current density results in increasing the formaldehyde oxidation level of in the flow-through reactor.

Basing on the kinetic model of plug flow reactor, rate constants of formaldehyde oxidation were calculated for second order reaction model.

Our results confirm the practical value of the combined method proposed for the purification of the model solution from formaldehyde.

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