УДК 661:882

A. V. Dubina, V. N. Martsul'
Belarusian State Technological University

PHOTOCATALYTIC WASTEWATER TREATMENT FROM FORMALDEHYDE

The article presents the results of studies of treatment of wastewater at woodworking companies which is formed during manufacture and application of adhesives based on urea-formaldehyde resins. There presented a method of wastewater purification from pollutants such as dissolved components of urea-formaldehyde resins and free formaldehyde. This paper describes a method of pre-stabilization of wastewater for further treatment, which is achieved by precipitation of the condensation products of urea and formaldehyde. Stabilised wastewater is further subjected to processing by UV-radiation. Investigations were carried out with the wastewater, which were selected at the wood-processing enterprises of Belarus and wastewater has the following composition: formaldehyde content – 1.0–5.0 g/dm^3, chemical oxygen demand (COD) of the liquid phase – 15.0–60.0 g O_2/dm^3 of components UFR – 50.0–80.0 g/dm^3.

Various treatment options of stabilized wastewater by UV-radiation are investigated. It was established that UV-treatment of wastewater containing formaldehyde in the presence of powder composite material comprising TiO_2, at a dose of irradiation of 10.8 J/cm^2 and and pH value being equal to 11 to reduced the formaldehyde content to 97% formaldehyde at concentrations ranging from 10 to 150 mg/dm^3.

Schematic diagram of wastewater treatment containing components UFR are proposed.

Key words: wastewater, formaldehyde, wastewater treatment, UV-treatment, catalyst.

Introduction. At the enterprises of Belarusian woodworking industry, most adhesives used in the production of veneer chipboard, MDF, furniture boards, etc., are prepared from urea-formaldehyde resins (UFR). UFR constitute about 80% of the produced amino resins [1]. For enterprises producing and using UFR, an important issue is the treatment of wastewater, which contain condensation products of carbamide, formaldehyde and free formaldehyde.

Main part. Wastewater generated during the washing process of technological equipment and containers used for preparation and dosing of adhesives from carbamide-formaldehyde resin, which characterized by the content of the formaldehyde – 0.5–8.0 g/dm^3, chemical oxygen demand (COD) of the liquid phase – 8.0–20.0 O_2 g/dm^3 [2, 3]. Wastewaters under consideration selected at woodworking enterprises of the Republic of Belarus, are characterized in formaldehyde content – 1.0–5.0 g/dm^3, chemical oxygen demand (COD) of the liquid phase – 15.0–60.0 g O_2/dm^3, content of UFR components – 50.0–80.0 g/dm^3. They are a semi-transparent liquid without extraneous suspended inclusions. The composition of the wastewater includes the uncured resin fraction in water-soluble form and free formaldehyde. They have the specific smell of formaldehyde, their color changes from light gray to dark gray, the pH is usually in the range from 5 to 7.

Despite small amounts of wastewater, their treatment raises a number of difficulties associated with an unstable structure, deposition of condensation products of UFR on the walls of containers and pipes, changing the concentration of formaldehyde in a wide range for a short time.

Since UFR oligomers are unstable hydrolytically, the fundamental process that influences the composition of the wastewater is hydrolysis of UFR components. As a result of this process, the residual methylol groups and ether bonds are converted into methylene and methylene-ether bonds with the formation of free formaldehyde and water [4].

Since the organization of reuse of these waters is not possible without pretreatment, it is urgent to find the technological solutions to ensure their return to the water rotation cycle of the enterprise.

It is known that for sewage sanitation similar or close to composition, such purification methods as oxidation (vapor phase, electrochemical, biochemical, photochemical oxidation) and physicochemical (adsorption, flotation, coagulation etc.) are used [3, 5, 6, 7, 8].

In practice, however, these methods are of limited use because of the large cost, insufficient purification efficiency. More often waste waters do not subject to purification and after dilution they are discharged into the sewer for subsequent purification in centralized treatment facilities of the settlement.

The aim of this work is to study the effectiveness of the use of UV-treatment in the presence of the catalyst for purification of formaldehyde wastewater.

The object of study – waste water selected at the wood-processing enterprises of the Republic of Belarus, and solutions of CFR.

Formaldehyde sulphite concentration was determined by using BAT-15, the pH of solutions was determined on a pH meter pH 150, the dry residue was found by gravimetric method, COD was found by bichromate method [9].

Purification of investigated wastewater under UV radiation is possible after the removal of suspended particles and preventing from forming the dispersed phase directly during the processing.

Our studies have established the parameters under which the wastewater is almost completely purified from water-soluble components of urea-formaldehyde resin by converting them into insoluble components and their subsequent precipitation. Thus there is a stabilization of the wastewater composition.

It was found that when using a two-stage separation of the residue, one may reach concentration decay of UFR by 98.8% as well as concentration decay of free formaldehyde in solution by 90%, as it participates in the polycondensation reaction of UFR components. The concentration of formaldehyde in water stabilized (Fig. 1) (curve 2) practically does not change for a long time in contrast to the untreated waste water (curve 1).

After separation of the oligomeric products of UFR, wastewater represents transparent stable composition liquid with a formaldehyde content not more than 100 mg/dm^3.

Waste water obtained after the separation of oligomeric products was used in experiments on wastewater treatment from formaldehyde. The paper deals with UV treatment of waste water using a catalyst containing TiO_2, which was introduced into the reactor as an aqueous suspension. The source of ultraviolet radiation was a mercury-quartz lamp DRT-400, emitting in the range 240–320 nm and the power of the radiant energy of 36 watts. Dose of irradiation (J/cm^2) was calculated as a product of radiation intensity I (mWt/cm^2) and exposure time t (s). As a catalyst the composite core SiO_2 was used – shell TiO_2 (catalyst composition in recalculation terms on oxides (wt %): SiO_2 – 68, TiO_2 – 29, H_2O – 3. Specific surface is 150 m^2/g [10].

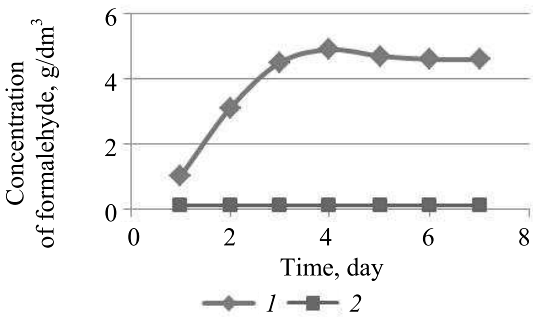

Fig. 1. Changing the formaldehyde content depending on the storage time

Purification from formaldehyde was carried out at 20°C, pH value from 4 to 11, as it is known that, depending on their choice oxidation can proceed to the formation of carbon dioxide and water, or lead to the formation of formic acid. Their processing was carried out on the installation for ultraviolet treatment of water shown in Fig. 2.

The reactor of installation is a vertical stainless steel cylinder having inside a quartz cover intended to protect the ultraviolet lamp from contact with water in which an ultraviolet lamp DRT-400 is installed.

The radiation dose ranged from 0.15–10.8 J/cm^2. The decisive influence for the initial velocity of the formaldehyde degradation is pH index.

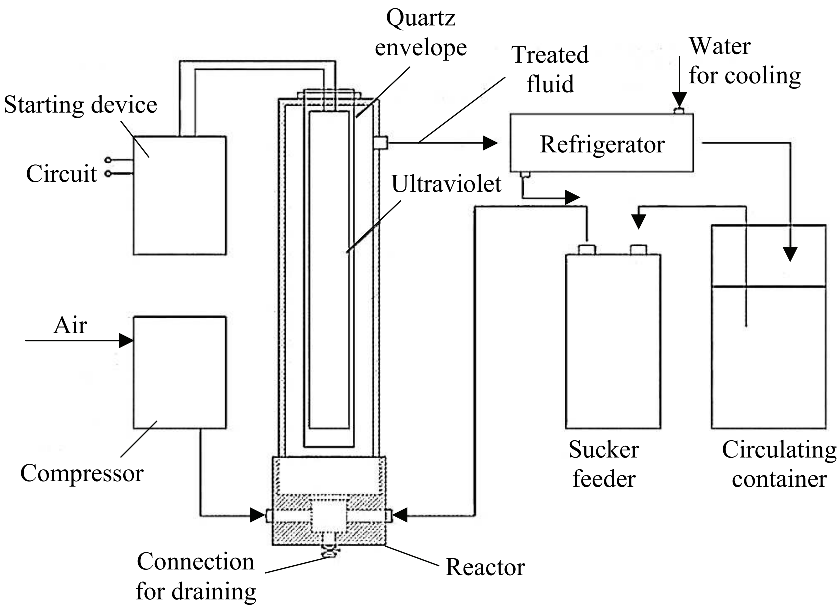

Fig. 2. Installation for UV neutralization of polluted water

It is known that the initial stage of the oxidation of aqueous formaldehyde solution occurs via a radical mechanism. Changing the pH value to 11 results in a significant increase in the initial rate of formaldehyde oxidation, mainly due to the increase in the concentration of hydroxyl radicals in an alkaline environment. At the same time the residual formaldehyde concentration decreases.

Fig. 3 shows the results of wastewater treatment by UV without using a catalyst at different pH values.

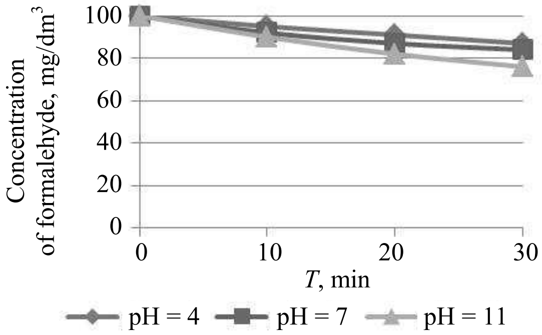

Fig. 3. Changing of the formaldehyde concentration in the wastewater depending on pH

With increasing pH in the solution the oxidation rate of formaldehyde is increased, but the degree of wastewater treatment remains insignificant.

In the presence of a catalyst, there are two basic ways of formaldehyde oxidation i.e. adsorption on the catalyst with further oxidation by hydroxyl radical or the generation of hydroxyl radicals in the reaction of water with the catalyst with subsequent oxidation of the organic substrate [11]. At the core of the catalyst photoactivation is formation of active particles, significantly accelerating the formation of hydroxyl radicals OH· due to the reactions:

$$TiO_2 + h\nu = h^+ + e; \quad (1)$$

$$H_2O \text{ (ads.)} = OH^- + H^+; \quad (2)$$

$$OH^- + h^+ = OH\cdot. \quad (3)$$

The consequence of the presence of the catalyst in the wastewater is increase in the concentration of OH· radicals. The influence of the photocatalyst on the formaldehyde oxidation process is shown in Fig. 4.

In the process of wastewater treatment initial pH value decreased (Table), which indicates on the formation of the intermediate product namely formic acid.

Changing the pH in waste water treatment by UV radiation

pH	*T*, min			
	0	10	20	30
7	7	6.9	6.9	6.8
11	11	10.9	10.7	10.5

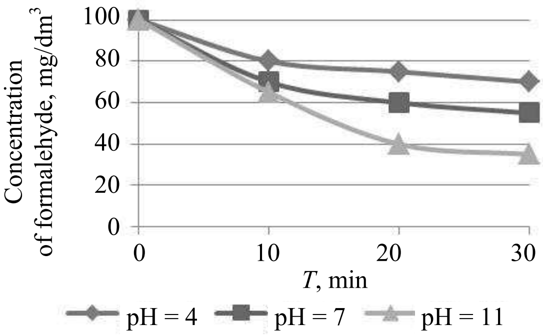

Fig. 4. Changing of the formaldehyde concentration in the wastewater in the presence of catalyst depending on pH

This is confirmed by the available data [12], according to which the photocatalytic oxidation of formaldehyde takes place with the participation of radicals OH·, interacting with adsorbed HCHO molecule by the following reactions:

$$HCHO + OH\cdot = HCO\cdot + H_2O; \quad (4)$$

$$HCO\cdot + OH\cdot = HCOOH; \quad (5)$$

$$HCOOH + 2h^+ = CO_2 + 2H^+. \quad (6)$$

As it can be seen from Fig. 4, the concentration of formaldehyde in the effluent at UV treatment decreases with increasing treatment time in the presence of a catalyst. While to the greatest extent it occurs when the pH value = 11. While the treatment of wastewater for 60 min (Fig. 5), which corresponds to a radiation dose of 10.8 J/cm^2, the degree of purification from formaldehyde was 97%.

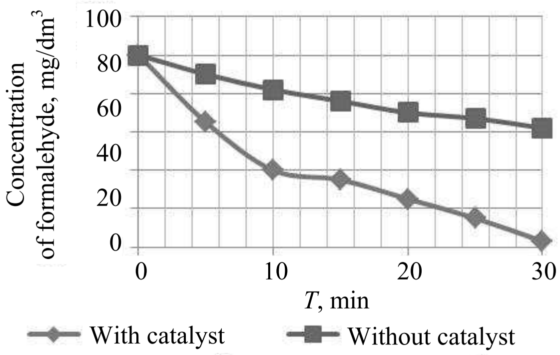

Fig. 5. Effect of catalyst on the concentration on formaldehyde in the wastewater at pH = 11

Conclusion. Thus, the UV treatment of waste water, from which water-soluble components of UFR are removed beforehand in the presence of a catalyst, containing TiO_2, provides a high degree of purification (by 97%) from formaldehyde.

It is found that in the conditions studied, maximum rate of formaldehyde oxidation is achieved in an alkaline environment in the presence of photocatalyst. It was shown that the degradation of an aqueous solution of formaldehyde is a complex multistage process running on radical mechanism. The rate of formaldehyde degradation is dependent on external factors. The results of the work indicate the reasonability for using this method for waste water purification from formaldehyde at the enterprises of the Republic of Belarus.

References

1. Salamone J. C. Concise polymeric materials encyclopedia. *CRC press*, 1998, vol. 11, pp. 8496–8501.

2. Vossoughi M., Borgheai M., Salehi H. Combined Chemical and Biological Processes for the Treatment of Industrial Wastewater Containing Formaldehyde. *Scientia Iranica*, 2001, vol. 8, no. 3, pp. 223–227.

3. Kowalik P. Chemical pretreatment of formaldehyde wastewater by selected Advanced Oxidation Processes (AOPs). *Challenges of Modern Technology*, 2011, vol. 2, pp. 42–48.

4. Doronin Yu. G., Miroshnichenko S. N., Svitkina M. M. *Sinteticheskiye smoly v derevoobrabotke* [Synthetic resins in wood processing]. Moscow, Lesnaya promyshlennost' Publ., 1987. 224 p.

5. Raja Priya K., Sandhya S., Swaminathan K. Kinetic analysis of treatment of formaldehyde containing wastewater in UAFB reactor. *Chemical Engineering Journal*, 2009, no. 148, pp. 212–216.

6. Moussavi G., Bagheri A., Khavanin A. The investigation of formaldehyde removal from aqueous solutions use of electrofenton process by alominium and iron electrod. *J. Kordestan Univ. Med. Sci*., 2012, vol. 17, pp. 72–81.

7. Kajitvichyanukul P., Lu M., Liao C., Wirojanagud W., Koottatep T. Degradation and detoxification of formaline wastewater by advanced oxidation processes. *J. Hazard. Mater*, 2009, vol. 135, pp. 337–343.

8. Salman M. Removal of formaldehyde from aqueous solution by adsorption on kaolin and bentonite: a comparative study. *Turkish Journal of Engineering and Environmental Sciences*, 2012, vol. 36, no. 3, pp. 263–270.

9. Standard methods for the examination of water and wastewater Washington, DC, American Public Health Association, 2012. 1496 p.

10. Murashkevich A. N., Lavitskaya A. S., Alisienok O. A., Zharskiy I. M. Synthesis and properties of mesoporous composite based on TiO_2 and SiO_2. *Neorganicheskiye materialy* [Inorganic materials], 2009, vol. 45, no. 10, pp. 1–7.

11. Shin E.-M., Senthurchelvan R., Munoz J., Basak S., Rajeshwar K. Photolytic and photocatalytic destruction of formaldehyde in aqueous media. *J. Electrochem. Soc.*, 1996, vol. 143, pp. 1562–1570.

12. Hong Q. I., Sun D., Chi G. Formaldehyde degradation by UV/TiO_2/O_3 process using continuous flow mode. *Journal of Environmental Sciences*, 2007, vol. 19, no. 9, pp. 1136–1140.

Information about the authors

Dubina Aleksandr Valentinovich – assistant, Department of Industrial Ecology. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: dubina@belstu.by

Martsul' Vladimir Nikolaevich – Ph. D. Engineering, associate professor, Head of the Department of Industrial Ecology. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: martsul@belstu.by

Received 23.02.2015