Treatment of wastewater containing formaldehyde from wood processing enterprises

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Abstract

The article presents the results of studies of treatment of wastewater containing urea-formaldehyde resins (UFR) from woodworking industry. Methods for purifying wastewater from pollutants are proposed. The paper presents the effect of pH, temperature and concentration of the components of UFR on the formation and precipitation of the condensation products of urea and formaldehyde. It is shown that UV-treatment in the presence of the powder of a composite material containing TiO_2 at a dose of exposure 10.8 J/cm^2 reduces the formaldehyde content by 97% at concentration of formaldehyde ranging from 10 to 150 mg/dm^3. Schematic diagram of treatment of wastewater containing components UFR are proposed.

Аннотация

В статье представлены результаты исследований очистки сточных вод деревообрабатывающих предприятий, содержащих компоненты карбамидо-формальдегидных смол (КФС). Предложены способы очистки сточных вод от загрязняющих веществ. Описано влияние pH, температуры и концентрации компонентов КФС на образование и осаждение продуктов конденсации карбамида и формальдегида. Показано, что УФ-обработка в присутствии порошка композиционного материала, содержащего TiO_2, при дозе облучения 10,8 Дж/см^2 снижает содержание формальдегида на 97% в диапазоне концентраций формальдегида от 10 до 150 мг/дм^3. Предложена принципиальная схема очистки сточных вод содержащих компоненты КФС.

Keywords: formaldehyde; urea formaldehyde resins, UV treatment; wastewater

Introduction

Most adhesives on woodworking factories, which are used in the manufacture of plywood, MDF, furniture boards, are obtained from urea-formaldehyde resins (UFR or UF resins). UF resins make up about 80% of all produced amino resins (Salamone, 1998). One of the problems for companies producing and using UF resins is the treatment of wastewater that contains condensation products of urea and formaldehyde and free formaldehyde.

Wastewater, which is formed during the process of washing of equipment and containers that are used at the stage of the preparation and dispensing of adhesives from urea-formaldehyde resin, is characterized by formaldehyde concentration 500-8000 mg/dm^3, chemical oxygen demand (COD) of the liquid phase accompanying 8000- 20000 mgO_2/dm^3 (Vossoughi, 2001, Kowalik, 2011). In the Republic of Belarus wastewater from the wood processing enterprises is characterized by concentration of formaldehyde - 1000-5000 mg/dm^3, COD of the liquid phase accompanying 15,0-60,0 gO_2/dm^3,content of UFR components - 50,0-80.0 g/dm^3. Wastewater is translucent liquid without extraneous suspended solids. The composition of the wastewater includes the uncured resin fraction in water-soluble form.

Wastewater has a specific odor of formaldehyde, its color changes from grey to light grey, pH is usually in the range between 5 and 7.

Despite the formation of small amounts of wastewater, treatment such water causes difficulties associated with unstable composition of wastewater, deposition of condensation products of UF resins on the walls of tanks and pipelines and significant change of formaldehyde concentration during a short time.

Because the oligomers UFR hydrolytically unstable, the main process affecting the composition of wastewater is the hydrolysis of components of UF resins. As the result, residual methylol group and ether bonds are converted into the methylene ether bonds with the formation of free formaldehyde and water.

Feature of wastewater, containing components of UFR, is high content of nitrogen in the solid and liquid phase, which can be up to 33% of dry mass weight.
While it is not possible to organize the re-use of such waters without pre-treatment, it is important to search for technological solutions that can provide at least their partial return to water rotation cycle of the enterprise.

It is known that for the neutralization of wastewater with the same or similar composition oxidation (vapor phase and liquid phase, electrochemical, biochemical, photochemical oxidation) (Kowalik, 2011, Oliveira, 2004, Barbusiński, 2005, Kajitvichyanukul, 2006) as well as physical and chemical (adsorption, flotation, coagulation, etc.) (Salman, 2012) purification methods are used. However, in practice these methods have limited application, which is associated with considerable costs, insufficient extent of purification. Most often wastewater is not subjected to purification and after dilution is discharged into the sewer for further treatment at centralized wastewater treatment plant.

The aim of the research is to develop technology for the removal of cured components of UFR in a form that would be suitable for further re-use, and reduction of formaldehyde concentration to levels at which wastewater can be used or disposed to centralized wastewater treatment plant without dilution.

Methods of control and materials

Methods of control

Formaldehyde concentration was determined by the sulfite method using automatic titration unit (Rice, 2012), pH value was determined by potentiometric method (Rice, 2012), the dry residue was determined gravimetrically, COD was determined according to ISO 6060. Determination of the elemental composition of the dispersed phase was carried out on CHNS - analyzer VarioEL cube.

Materials

Wastewater was characterized by content of formaldehyde - 1000 mg/dm^3, components of UF resins - 60000 mg/dm^3, COD of the liquid phase - 20000 mgO$_2$/dm^3 and pH 5.

Treatment was carried out at the experimental setup by source of UV radiation. The experimental setup is shown in Figure 1. The reactor represented a vertical cylinder made of stainless steel. Inner part of the cylinder had quartz cover, in which ultraviolet lamp DRT-400 was installed.

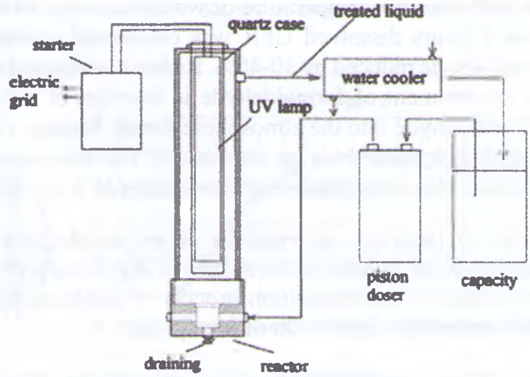

Figure 1 Experimental setup for the UV treatment of wastewater

The course of study and the results

Stabilization of wastewater

Because hydrolysis process influences the composition of wastewater, one of the tasks of the research was to determine the conditions under which maximal condensation of UFR in the form of fine particulate material occurred. This was achieved by stabilization of wastewater by preventing subsequent condensation of UFR and by obtaining the lowest possible concentration of formaldehyde.

The main methods of condensation of dissolved oligomers are raising the temperature or lowering pH to a certain values. Polycondensation process is well studied for solutions of UFR, which are characterized by a high concentration of oligomers. For dilute solutions of UFR, the selection of special conditions is required. These conditions should provide polycondensation with maximum removal of oligomeric products from the solution and be suitable for obtaining of a particulate precipitate.

The condensation process is the formation of cross ethylene and methylene ether bonds between macromolecules of UFR by reacting of the methylol groups CH_2OH with each other and hydrogen of amide group. In this process three-dimensional structures are formed, which fragment is shown in Fig.2 (Salamone, 1998).

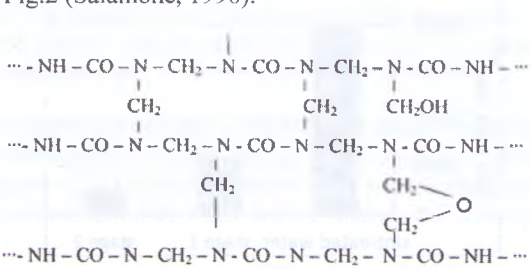

Figure 2 Fragment of three-dimensional structure of cured UF resins

Investigations of curing process of UFR in wastewater at the increasing temperature have shown that in the liquid phase, containing oligomers and formaldehyde, several parallel reactions occurs. The reactions of attachment, condensation and hydrolysis are characterized by different mechanisms, rates and equilibrium constants.

The results show that when the temperature of wastewater was in range 40-60 ± 2 °C and the reaction time was 2 hours dissolved UFR was condensed to 60-70%, while the initial concentration of formaldehyde reduced by 30-40%. Reduction formaldehyde concentration can be explained by the involvement of formaldehyde in reaction of polycondensation, and the partial emission of formaldehyde into the atmosphere during heating. However, the hydrolysis of formed sludge was accelerated with an increase of the temperature of wastewater that presumably could increase the concentration of formaldehyde in the solution.

We established that in carrying out reaction of polycondensation by reducing pH of wastewater to the value 2.0, the condensation degree of dissolved UFR could be substantially increased due to the division of the deposition process of condensation products into several steps, each of which finished by a separation of precipitate.

Experiments were carried out using 1000 cm^3 of wastewater, which pH was lowered to a value of 2.0. We observed intense formation of the disperse phase (stage 1) consisting of a cured resin. UFR concentration in solution decreased by 70%. After sedimentation of dispersed particles the solution became clear. After separation of the precipitate the secondary process of polycondensation was activated in the remaining supernatant (stage 2). After separation of the formed precipitate, the composition of wastewater was stabilized. Changes in the content of components of UFR in a solution at a two-stage separation of the precipitate are illustrated on Figure 3.

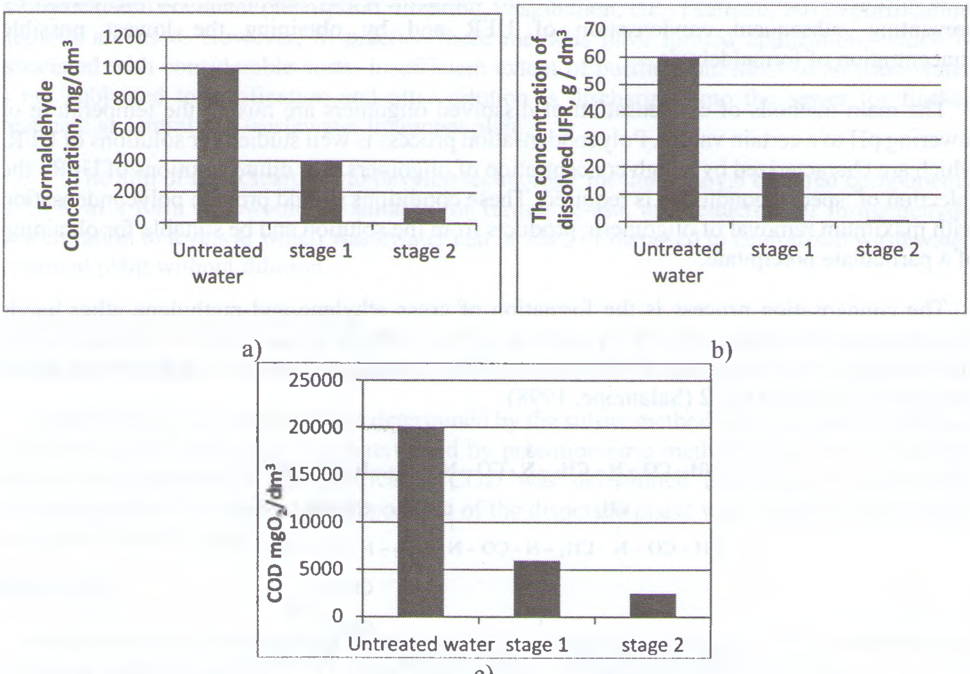

Figure 3 The content of pollutants in the wastewater during stabilization

The 98.8% decrease in the concentration of dissolved UFR was achieved by the use of a two-stage separation of the precipitate. This provided a deeper decrease of the concentration of free formaldehyde in solution (90%) as formaldehyde participated in the reaction of polycondensation of components of UF resins. The concentration of formaldehyde in stabilized wastewater (line 2) practically did not change for a long time if to compare with the untreated wastewater (line 1) figure 4.

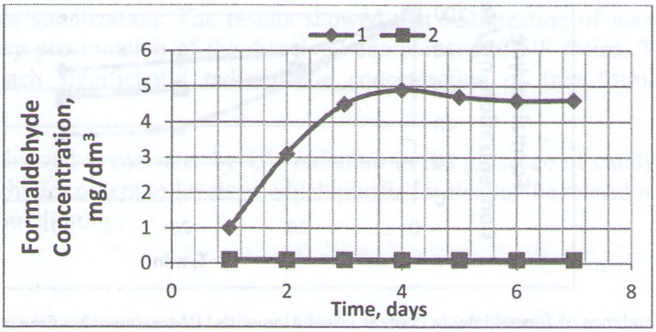

Figure 4 Time depending changes of formaldehyde content

Wastewater sludge is a white hygroscopic mass, which chemical composition is represented by a cured UF resins with a mass fraction of moisture from 70 to 80%. The precipitate contains a fairly large amount of nitrogen, which is a part of amino groups. Elemental analysis of the composition of solid state showed the following results: nitrogen - 35%, carbon - 31%, oxygen - 28%, hydrogen - 6%. Due to high nitrogen content, the precipitate can be considered as a potential nitrogen fertilizer.

After separation of the oligomeric products of UF resins wastewater was a transparent liquid with stable composition, and the formaldehyde content did not exceed 100 mg/dm^3. The supernatant after stabilization of wastewater was neutralized to pH 7 with $Ca(OH)_2$.

UV treatment of wastewater

Obtained stabilized wastewater was used in the experiments on wastewater treatment from formaldehyde. In the work for the removal of formaldehyde the UV treatment using a catalytic TiO_2 was applied.

It is known that the main factor, effecting the initial rate of destruction of formaldehyde, is a pH value. The initial stage of the oxidation of aqueous formaldehyde solution proceeds via a radical mechanism. The depth of degradation increases at high concentrations of radicals (Shin, 1996, Kowalik, 2011). The changes in pH level lead to a significant increase of the initial rate of the process. In most cases it occurs with the increase of the concentration of hydroxyl radicals in an alkaline environment.

Two mechanisms of photodegradation of organic compounds involving the use of catalyst are possible. The first mechanism includes adsorption of organic substances onto the catalyst with subsequent oxidation of the hydroxyl radical. The second mechanism is a formation of hydroxyl radicals in the interaction of water with a catalyst and subsequent oxidation of the organic substrate.

Effect of catalyst on the process of photodegradation of formaldehyde was illustrated in Figure 5 and 6.

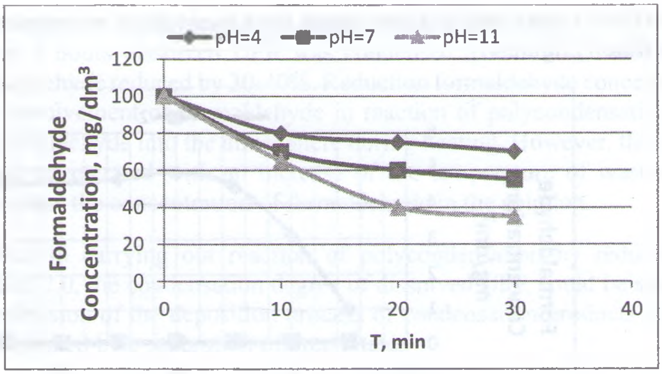

Figure 5 Dependence of formaldehyde content in solution with UV treatment by time and pH values: 1) pH=4, 2) pH=7, 3) pH=11

As seen from Figures 5 and 6 the degradation rate of formaldehyde in presence of the catalyst and alkaline pH value increased.

During processing, the initial pH decreased (Table 1), indicating the formation of the intermediate product of formic acid by a mechanism which is shown below.

Table 1 Change of pH during treatment of wastewater by UV light

pH	T, min			
	0	10	20	30
pH=7	7	6,9	6,9	6,8
pH=11	11	10,9	10,7	10,5

According to (Kowalik, 2011, Hong, 2005), photocatalytic oxidation of formaldehyde proceeds with participation of OH· radicals, which interact with the adsorbed molecule of HCHO as described by the following reactions:

$$HCHO + OH\cdot = HCO\cdot + H_2O \quad (1)$$
$$HCO\cdot + OH\cdot = HCOOH \quad (2)$$
$$HCOOH + 2h^+ = CO_2 + 2H^+ \quad (3)$$

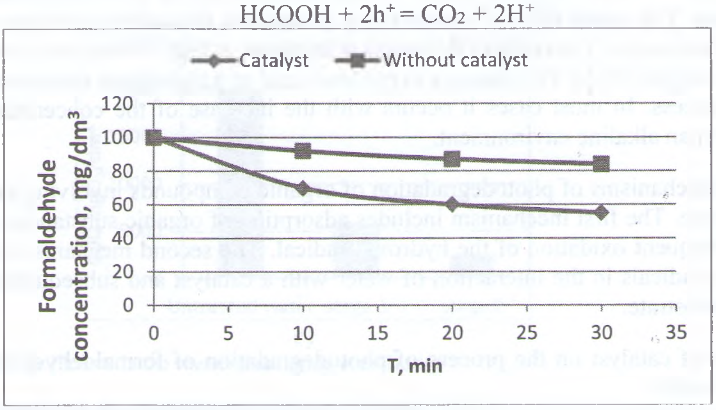

Figure 6 Effect of the catalyst on the degradation of formaldehyde at pH 7.

Conclusion

We determined conditions for almost complete precipitation of dissolved UF resins from wastewater and their stabilization. The results showed that stabilization of wastewater was achieved by two step precipitation of the dissolved components of UF resins. The two step precipitation approach significantly reduced the concentration of free formaldehyde in solution.

Treatment of stabilized wastewater by UV radiation in the presence of catalyst TiO_2 can reduce the formaldehyde content to levels at which purified water can be reused or discharged into sewerage without diluting.

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