



Adhesives based on formaldehyde – environmental problems

MARIA ŁEBKOWSKA, MONIKA ZAŁĘSKA-RADZIWIŁŁ, AGNIESZKA TABERNACKA*

Division of Biology, Faculty of Building Services, Hydro and Environmental Engineering,
Warsaw University of Technology, Warszawa, Poland

Abstract

Adhesives are substances that increase the surface adhesion of bonded items. Unfortunately, they also emit volatile organic compounds (VOCs) which negatively impact upon human and animal health. VOCs have carcinogenic and mutagenic properties and can cause migraines, irritation to the eyes, nasal passages, mouth, and lungs, and respiratory problems. Wastewater from adhesive production is characterized by high levels of pollutants and contains high concentrations of compounds including formaldehyde that are toxic to water biocenoses. Moreover, its purification causes many problems and requires the application of specific methods. This review presents data concerning the toxicity and ecotoxicity of selected adhesives components. VOC emission rates from adhesives and wooden construction elements with adhesives are also discussed and assessed. Current knowledge on the treatment methods for wastewater containing adhesive components is reviewed. Finally, the treatment and disposal methods for solid wooden waste containing adhesives are also analyzed and discussed.

Key words: adhesives, formaldehyde, wastewater treatment

Introduction

Adhesives are substances that increase the surface adhesion of bonded items. The main component of adhesives is a natural or synthetic polymer in colloid state dispersed in a solvent or in a mixture, together with hardeners, plasticizers and other compounds modifying the composition.

There should be strong cohesion between the particles of an adhesive. The highest conjugation energy is found in ionic or atomic bonds. Substances built from elements connected in this way are resistant and durable, and are difficult to melt or dissolve. The liquid form of adhesives is produced by using solvents or liquid dispersion agents.

The main goal of using adhesives is to form a thin layer of congealed adhesive with good mechanical characteristics between bonded items. Adhesives can be categorized by the method of adhesion into: solvent-based adhesives; polymer dispersion adhesives (resins); and mixed adhesives. Synthetic adhesives include resorcinol adhesives based on resorcinol resin, phenol resin and

formaldehyde resin, amine adhesives based on melamine resin, urea-formaldehyde (UF) resins, polyurethane adhesives, polyvinyl adhesives, phthalic adhesives, polyacrylic adhesives, and silicone-based and epoxide adhesives. Adhesives are widely used in the production of wooden (structural) construction elements, such as girders, rafters, columns and trusses, and in the production of plywood, particleboards, fiberboards, wood veneers, joiner boards, wood flooring and furniture. Currently, the most commonly used adhesives are those based on urea-formaldehyde resin, polyurethane, epoxide, polyester and polyvinyl acetate (McDermott et al., 2007).

Adhesives are a source of volatile organic compounds (VOCs) which negatively impact upon human and animal health as a result of inhalation and skin contact. They may cause allergic reactions and have carcinogenic and mutagenic properties. It has been found that VOCs have strong neurotoxic effects and can cause allergies, migraines, irritation to the eyes, nasal passages, mouth, and lungs, and respiratory problems. Small doses of toluene, hexane and methyl ethyl ketone have

* Corresponding author: Division of Biology, Faculty of Building Services, Hydro and Environmental Engineering, Warsaw University of Technology, Nowowiejska 20, 00-653 Warszawa, Poland; e-mail: agnieszka.tabernacka@is.pw.edu.pl

been shown to damage membranes of human neurons in as few as five days (McDermott et al., 2007). Wastewaters from adhesive resin production are characterized by high levels of pollutants and contain high concentrations of compounds that are toxic to water biocenoses.

In this study, the toxicity and ecotoxicity of selected wood adhesive components are presented, including the emission of formaldehyde (FA) and VOCs, from wood elements of interior design to indoor air. The methods of treating wastewater from formaldehyde resin production and wood waste are also described. It should be noted that there are few data available concerning the impact of adhesives on organisms and ecosystems, or the ecological consequences of storing and landfilling used wood products.

Toxicity and ecotoxicity of selected adhesive components

Toxicity

At room temperature, formaldehyde is a colorless gas with a very characteristic pungent odor. It is very unstable and its chemical reactivity is very high. At concentrations of 1 ppm (1.23 mg/m^3) in air, formaldehyde strongly irritates the mucous membranes and eyes, but the threshold concentration that results in eye irritation is much lower, $12 \text{ } \mu\text{g/m}^3$. It is known that at a concentration of 60 mg/m^3 formaldehyde damages pulmonary tissues; chronic obstructive pulmonary disease (COPD) has been diagnosed in employees working for at least five years in particleboard production exposed to an FA concentration of 0.47 mg/m^3 in air. Mice exposed to FA concentration of 3.6 mg/m^3 for 10 minutes experienced a lowering of their breathing rate by 50%. Pursuant to the acute toxicity data from the PAN Pesticide Database this chemical is considered highly toxic.

FA inhibits reproduction in both animals and humans, causing an increase in the incidence of menstrual disorders, inflammatory diseases of the reproductive tract, and sterility, and increased risk of spontaneous abortion and adverse developmental effects during pregnancy, such as low birth weights among offspring (Duong et al., 2011; TOXNET Database). It is categorized as a known human carcinogen by the International Agency for Research on Cancer (IARC). It is associated with nasal sinus cancer and nasopharyngeal cancer, brain

cancer, prostate cancer, and the development of leukemia, particularly myeloid leukemia. It has been found that the exposure of rats to FA concentrations of $6.8\text{--}17 \text{ mg/m}^3$ for over 18 months, 6 hours a day and 5 days a week resulted in the formation of nasal cancer. Chromosome aberration and genotoxicity are also observed under FA inhalation. Results of research on FA toxicity are presented in Table 1. The FA lethal dose (LD50) when swallowed is 500 mg/kg for humans and 800 mg/kg for rats.

Phenol is a white crystalline solid, soluble in water. It is absorbed into an organism by the respiratory system and through skin contact. The substance has harmful neurotoxic effects on the central nervous system, but also damages the intestines, liver and kidneys. It is considered highly toxic and genotoxic. Retention of phenol vapor in the lungs is as high as 70-80%. The lethal digested dose is 167 mg/kg for humans and 915 mg/kg for rats (Safety Data Sheet, NIOSH Database, TOXNET Database).

Benzene, an organic chemical compound and aromatic hydrocarbon, is absorbed by the respiratory system and through skin contact. Its vapor retention in the lungs is 80%. It is accumulated in adipose tissue and has a narcotic effect on humans. It damages bone marrow and weakens the immunological functions. While this substance is considered only slightly toxic according to acute toxicity studies, it is nevertheless a carcinogen which, among other things, causes blood cancer (PAN Pesticide Database). Lethal doses for humans and rats when digested are 500 mg/kg and 5700 mg/kg , respectively.

Vinyl chloride (VC) is a gas with the sickly sweet odor of chloroform. It is difficult to solve in water and easily polymerizes to polyvinyl chloride. It is absorbed through skin contact and by the respiratory system. The reactive metabolites of vinyl chloride – chloroethylene oxide and chloroacetate aldehyde – react with DNA, acting as mutagens and thus initiating carcinogenesis. VC has narcotic effects, irritates skin and mucous tissues, damages the liver and causes cancer of the lungs, brain and blood. According to acute toxicity data, it is considered only slightly toxic. LC50 for rats is 700 mg/m^3 .

Styrene is a colorless oily liquid with an irritating, sweet smell. It is poorly soluble in water. It is absorbed by the respiratory system, has neurotoxic properties and can cause depression in humans. It is classified as a mu-

Table 1. Toxic effects of the exposure to formaldehyde [PAN Pesticide Database, ATSDR 1999]

Species	Route	Parameter	Result	Units
Mouse	inhalation	LC50	400.0	mg/m ³
Rat	inhalation	LC50	590.0	mg/m ³
Rabbit	dermal	LD50	270.0	mg/kg
Mouse	oral	LD50	42.0	mg/kg
Rat	inhalation 13 wk 5 d/wk 6 hr/d	LOAEL*	3.69	mg/m ³
Rat	inhalation 13 wk 5 d/wk 6 hr/d	NOAEL**	1.23	mg/m ³
Mouse	inhalation 24 mo 5d/wk 6hr/d	NOAEL	2.46	mg/m ³
Mouse	inhalation 24 mo 5d/wk 6hr/d	LOAEL	6.88	mg/m ³

*LOAEL – lowest observed adverse effect level; **NOAEL – no observed adverse effect level

Table 2. Average concentrations of formaldehyde in indoor and outdoor air

City and country	Environment	Average concentration [µg/m ³]	Additional comments	Reference
Hong Kong, China	indoor	18 38 43 (20-180)	homes, offices shopping malls restaurants	Lee et al. 2002
	outdoor	10 19 43 (20-130)	homes, offices shopping malls restaurants	
Pinnacles, Shenandoah National Park, Virginia, USA	outdoor	1.21 (0.018-3.200)	rural area	Munger et al. 1995
California, USA	indoor	43 88.56-95.94	homes mobile homes	Sexton et al. 1986
Germany	indoor	119	homes	Salthammer et al. 1995
Los Angeles, USA	outdoor	3.69-52.89		Grosjean 1982
Denver, USA	outdoor	2.83-4.82		Anderson et al. 1996
Cairo, Egypt	indoor outdoor	107.8-130 35.7-45.5	flats	Khoder et al. 2000
Isesaki, Japan Annaka, Japan Kyoto, Japan Tokyo, Japan Niigata, Japan Miyazaki, Japan	outdoor	3.3-5.4 2.2-5.1 4.0 4.1 2.3 2.4	(winter-summer) small city small city	Tago et al. 2005
Athens, Greece	outdoor	9.7-17.2		Bakeas et al. 2003
Birkenes, Norway Mace Head, Ireland Waldhof, Germany Kosetice, Czech Donon, France Ispra, Italy	outdoor countryside areas	0.4-1.1 0.5-1.2 0.7-2.0 1.2-2.3 0.8-2.2 2.5-6.5	winter-summer	Solberg et al. 2001

tagen, because its oxides form adducts with DNA and proteins. The lethal digested dose (DL50) in rats is 5000 mg/kg. The results of acute toxicity studies classify it as a moderately toxic compound.

There are not many data in the literature concerning the toxicity of adhesive compounds and solvents. Those compounds that have been researched and analyzed are acrylamide (Yang et al., 2005), 2,5-hexanedione (Kihale et al., 2005), terpenes and aldehydes (Gminski et al., 2010), and resins from conifers (Söderberg et al., 1996).

Ecotoxicity

The ecotoxicity of adhesive compounds on aquatic organisms has been determined based on mortality rate, growth inhibition, and ontogenesis (PAN Pesticide Database, Safety Data Sheets, NIOSH Database).

Formaldehyde is a compound that is moderately toxic to aquatic organisms. LC(EC)50 for the crustacean *Daphnia magna* is in the range 50-60 mg/dm³. FA does not exert harmful effects on molluscs and zooplankton in concentrations smaller than 100 mg/dm³. For specific fish species, the lowest LC50 values of FA are 2.3 mg/dm³ for white cloud mountain minnows (*Tanichthys albonubes*) and 22 mg/dm³ for orfe (*Leuciscus idus*).

Phenol is either not toxic or only slightly toxic to some species of fish, while being highly toxic to other fish species. The LC50 values are in the range of 0.1-500 mg/dm³. For crustaceans, LC50 concentrations are in the range of 0.005-175 mg/dm³.

Benzene is a slightly or moderately toxic compound for aquatic organisms. LC50 concentrations are in the range of 9-425 mg/dm³ (fish), 10-200 mg/dm³ (insects), and 18-373 mg/dm³ (*Daphnia magna*).

Styrene is toxic to fish *Pimephales promelas* at a concentration of 4.02 mg/dm³ (LC50/96 h), to the crustacean *Daphnia magna* at a concentration of 4.7 mg/dm³ (LC50/48 h) and to algae *Pseudokirchneriella subcapitata* 4.9 mg/dm³ (EC50/72 h). Urea is an easily biodegradable compound and its impact on organisms is insignificant.

Emission of volatile organic compounds

Adhesives that are widely used in construction (carpentry and joinery) and interior design are the major source of volatile organic compounds in indoor air.

In indoor air, more than 500 different compounds have been identified, including formaldehyde, phenol,

resorcinol, benzene, toluene, trimethylbenzene, ethanol, methanol, phenoxyethanol, methyl acetate, ethyl acetate, vinyl acetate, dibutyl phthalate, acetone, 2-butanone, methylpentane, dimethylpentane, methylhexane, cyclohexanone and methylcyclohexane. These compounds may originate from paints, lacquers, floor coverings, wallpapers and other materials. Croute and coworkers (Croute et al., 2002) noted that painting, staining and lacquering can produce VOC air concentrations of up to 1000 mg/m³. This concentration is a million times higher than typical concentrations in outdoor air (Table 2). Zhu and coworkers (Zhu et al., 1999) analyzed VOC emission from hydrocarbon solvent-based indoor materials used for coating wood surfaces. The analyzed materials were placed in a fume hood with a low ventilation rate to mimic indoor air movement until weight loss was no longer observed. Measurements of the weight loss of the analyzed materials and total VOCs emitted indicated that the initial emission rates were in the range of 186.9-201.2 mg/h and that 54-57% of the VOCs contained in the wood material containing polyurethane and organic solvent-based dyes evaporated within 7 hours. Data from China indicate that 27% of total VOC present in the air results from emissions from industrial plants that use paints and 14% of total VOC results from emissions from industrial plants that use adhesives (Wei et al., 2008). The use of urea-formaldehyde resins during particleboard production can cause contamination of 7 800 000 m³ of air per 1 m² of produced particleboard (dos Santos et al., 2014).

Many factors can impact upon the emission of FA and other VOCs into the air: the type of resin, especially the molar ratio between FA and other compounds in the adhesive, such as urea; the type of wood; condensation rates; water content; type and quality of additions; conditioning methods, and application of external wood coverings. Operational conditions and factors, such as temperature and humidity, efficiency of the air-conditioning system, the use of premises or any interior renovation and equipment restoration may also have a significant impact on VOC emission.

Que and coworkers (2007) analyzed FA and urea-formaldehyde resin emission depending on the molar ratio between FA and urea. They examined the FA-urea molar ratio in the range of 0.97-1.27. At the hot-pressing temperature of 150 °C and when the FA-urea molar ratio

was 1.05, FA emission was E1 quality (the second – middle class in accordance with German standards) ≤ 9 mg/100 g. When the FA-urea molar ratio was 1.19 or 1.27, the emission level increased, reaching E2 quality (the third – worst class), which is $9 \text{ mg/100 g} < \text{E2} \leq 30 \text{ mg/100 g}$. Currently, there is a tendency to decrease the FA content in urea-formaldehyde resins, while ensuring that the FA-urea molar ratio is 1.1:1 or lower.

The FA-urea molar ratio in resins is not the only factor influencing FA emission. It has been proven that an increase in specific gravity (SG), shelling ratio and pressure augment the FA content in air. It has been shown that a high beech particle content in particleboards results in lower FA emissions than from particleboards consisting of high amounts of pine particles (Nemli and Öztürk, 2006).

Research carried out by Kim and Kim (Kim and Kim, 2005) proved that the addition of melamine-formaldehyde resin to urea-formaldehyde resin dramatically reduced the level of formaldehyde emission from wood fiber made from Korean pine (*Pinus densiflora*). Urea-formaldehyde resin produces approximately 23% more emissions of formaldehyde than melamine-urea-formaldehyde resin (Silva et al. 2015). A decrease in FA emissions can also be achieved using polymeric 4,4'-methylene diphenyl isocyanate (PMDI) and phenol-formaldehyde (PF) resins to manufacture particleboard from recycled wood-waste chips for use in indoor environments. The research showed that formaldehyde emissions decreased linearly with an increasing PMDI/PF particle ratio. FA emissions were below 0.3 mg/dm^3 when the weight percentage of PMDI/particles was 7:3 (Wang et al., 2007). Lignocellulosic ethanol residue (a by-product of lignocellulosic ethanol production) may be used as a valuable resource to partially replace phenol (in the range of 10-70%) in the preparation of lignin-phenol-formaldehyde adhesive (Zhang et al., 2013). Ghaffar and Fan (Ghaffar and Fan, 2014) used lignin from straw to form phenol-formaldehyde resins for plywood, particleboard and other composites.

Some finishing treatment methods for wood products, such as their coating with paints, foils, laminates and veneer used to reduce water adsorption, may decrease FA and VOC emissions. Surface materials such as vinyl films or melamine impregnation reduce the FA emissions from wood based products. However, total VOC (TVOC) emissions of the coated materials can be

higher, because the finishing materials (such as urethane and lacquer) emit their own VOCs. However, Kim and coworkers (Kim et al., 2010) proved that PVC appeared to be a very efficient coating material, reducing both FA and VOC emissions.

The amount of FA and VOC emissions also depends on the manufacturing technology, such as open-mold and closed-mold processes. Di Tomasso and coworkers (Di Tomasso et al., 2014) noted that open-mold gel-coating used in the manufacture of fiber-reinforced polymer matrix composites produced high amounts of styrene to be used as a linking agent for the unsaturated polyester resins. The closed-mold technologies reduced the measured styrene levels from 28-70 ppm to 0.23-0.37 ppm. Closed-mold gel-coating is a route to reducing the environmental impact of VOCs (Rogers et al., 2014).

A very important issue in the assessment of FA emissions is the proper monitoring of emissions from a variety of wood products (Böhm et al., 2012; Marć et al., 2012). Guo and coworkers (Guo et al., 2002) proved that the total VOC concentration from wood products was in the range $18\text{-}408 \text{ } \mu\text{g/m}^3$ in indoor air, including emissions of $34\text{-}352 \text{ } \mu\text{g/m}^2/\text{h}$ from hardboards, $88 \text{ } \mu\text{g/m}^2/\text{h}$ from particleboards and $65 \text{ } \mu\text{g/m}^2/\text{h}$ from plywood. Guo et al. (2002) demonstrated typical FA and TVOCs emissions from different types of materials (Table 3). The differences in emission rates are caused by the types of wood, adhesives and resins and the applied measurement methods.

Table 3. Typical FA and TVOC emission rates from selected wood materials

Material	Emission rate [$\mu\text{g/m}^2/\text{h}$]	
	FA	TVOC
Medium-density fibreboard	733-2292	–
Hardwood plywood panelling	62.5-1417	34-352
Particleboard	83-1042	88
Softwood plywood	10-30	65

Among many factors influencing the emission of organic compounds from wood, it is temperature, humidity and the air exchange rate that play significant roles. Lin and coworkers (Lin et al., 2009) tested wooden flooring composites made from hardwood and plywood. Within six days, when the room temperature had increa-

sed from 15 °C to 30 °C, the specific VOC emission rate increased 1.5-129-fold. An increase in humidity from 50% to 80% resulted in VOC concentrations and emission rates increases of up to 32-fold. When the air exchange rate increased from 1 to 2 per hour, VOC concentrations decreased by 9-40% and the specific VOC emission rates increased by 6-98%.

An and coworkers (An et al., 2010) measured FA and VOC emissions from flooring with an adhesive (melamine-urea-formaldehyde resin). The flooring heating system was constructed with MDF with a bottom panel, heater sheet and engineered flooring. An oven dryer with a fan was used for the air circulation system. The floor surface temperatures were set to 20 °C, 26 °C and 32 °C, respectively. The rate of FA emissions from the flooring was the highest when the temperature was 32 °C, and then it decreased with time. The flooring emitted benzene, toluene, ethylbenzene and xylene, as well as other, unidentified VOCs. Sampling emission rates using different indoor heating systems (floor heating systems both with and without an air circulation system) showed higher FA emission rates when floor heating lacked an air circulation system, while VOC emission rates were higher when the floor heating had an air circulation system. FA and VOC emission rates from engineered flooring depend on the temperature of floor heating and air circulation. Table 4 presents the differences in FA and TVOC emission rates from engineered flooring depending on the length of time when the air is circulated and floor is heated. TVOC emission rates from engineered flooring with adhesives was higher when an air circulation system was applied than in the case of a floor heating system.

There are several types of wood flooring, including solid wood flooring, laminate wood flooring with high-density fiberboard (HDF) as the core material, and engineered flooring. Engineered flooring consists of plywood with a thin veneer bonded to the face of the plywood using melamine-formaldehyde and/or urea-formaldehyde resins as hot-press adhesives. Further research by An and coworkers (An et al., 2011) showed that FA emissions from laminate flooring were the highest at the temperature of 32 °C. Flooring with a floor heating system emitted more FA than an air circulation system. The VOC emission rate was higher with an air circulation system than with floor heating without air circulation.

Wiglusz and coworkers (Wiglusz et al., 2002) compared FA and VOC emission rates at various temperatures – 23 °C, 29 °C and 50 °C – from two types of laminate flooring: a bonded laminate on top of a particle-board substrate (A); and thermofused saturated papers on top of a high density fiber substrate (B). At lower temperatures, no FA emission was detected while the VOC emission rate was low. At 50 °C, flooring A showed high initial FA and VOC emissions, which then decreased with time. However, an increase in temperature did not increase VOC emissions from type B flooring. The results showed that the chemical composition of the laminate flooring, together with the level of floor heating, contributed to the contamination of indoor air.

The VOC emission rate depends on the quality of buildings. Guo and coworkers (Guo et al., 2002) described literature data which show that average VOC concentrations in indoor air in buildings were 1130 $\mu\text{g}/\text{m}^3$. In new buildings, concentrations could be as high as 4000 $\mu\text{g}/\text{m}^3$; in newly renovated properties, concentrations were 19565 $\mu\text{g}/\text{m}^3$ after 1520 h, but then decreased to 11 $\mu\text{g}/\text{m}^3$ after 2550 h. The largest contribution to the VOC concentration was from the air ventilation system (39%), and then from inhabitants' activities (37.3%) and the building materials (23.7%). Table 5 presents differences in TVOC emission rates from office buildings, based on research by Zuraimi and coworkers (Zuraimi et al., 2004).

It is assumed that a reduction in VOC emissions can be achieved by using construction materials tested for air pollutant emission and maximum air exchange rate, and by reducing the use of materials requiring adhesives. Guo and coworkers (Guo et al., 2003) showed that in houses with a high air exchange rate (those with efficient ventilation) and built using construction materials with low VOC emission rates, the VOC emission rate is in a range from 0 to 43 $\mu\text{g}/\text{m}^3$. The published data show that average emission levels in new buildings in Nordic countries and in the USA range from 0.48 to 31.7 mg/m^3 . In Paris, 61 flats were tested for the presence of aldehydes in indoor air. The pollution levels depended on the time of renovation, the age of wall and floor coverings, cooking, smoking, temperature, humidity and carbon dioxide levels. The average FA concentration in rooms in Paris dwellings was 34.4 $\mu\text{g}/\text{m}^3$, acetaldehyde concentration 10.7 $\mu\text{g}/\text{m}^3$, and hexanal and

Table 4. FA and VOC emission rates from engineered flooring depending on the temperature of floor heating and air circulation

Compounds	System	Emission rate after 1 day and after → 7 days at the set temperature of: [$\mu\text{g}/\text{m}^2/\text{h}$]		
		20°C	26°C	32°C
FA	air circulation system	63 → 22	75 → 30	105 → 42
	floor heating system	60 → 28	110 → 45	179 → 49
TVOC's	air circulation system	430 → 200	580 → 210	70 → 220
	floor heating system	380 → 100	410 → 250	610 → 280

Table 5. Differences in TVOC emission rates from office buildings in Singapore depending on the air conditioning system and personnel activities [Zuraimi et al., 2004]

Place of measurement	TVOC emission rates [$\mu\text{g}/\text{m}^2/\text{h}$]
Construction materials	1462-7883
Air conditioning systems without personnel present	1336-14732
Air conditioning systems with personnel present	1601-15629

pentanal were $33.5 \mu\text{g}/\text{m}^3$ and $8.9 \mu\text{g}/\text{m}^3$, respectively (Clarisse et al., 2003).

Based on the measurements of six PVC materials and four adhesives, Järnström and coworkers (2008) showed that individual materials had significantly lower VOC emissions and ammonia emission rates than the complete constructions. The permeability of the PVC products for VOCs and the type of adhesive used in the product affected the VOC emission rates of the individual PVC materials.

In homes, FA and VOCs are emitted not only from flooring, walls, adhesives and covering materials, but also from paints. Kim and coworkers (Kim et al., 2011) measured VOC and FA emissions from oil-based paints, emulsion paints and water-dispersion paints. The emission rate depended on the amount of paint needed to coat walls, and this was higher for coatings of $300 \text{ g}/\text{m}^2$ than $121 \text{ g}/\text{m}^2$. The FA emission rate was low. The VOC emission rate was much higher for oil-based paint than for emulsion paints and water-dispersion paints.

The problem of setting an appropriate indoor air exposure limit for formaldehyde is currently widely discussed in the literature. In the EU, the indoor exposure limit has been based on nose and throat irritation thresholds of $0.1 \text{ mg}/\text{m}^3$ (0.08 ppm; LOAEL), NOAEL of

$0.03 \text{ mg}/\text{m}^3$ (0.025 ppm) and an assessment factor of 30, including a factor of 3 for the higher sensitivity of children. The threshold for sensory irritation is 1 ppm, which is a higher concentration than the nose and throat irritation thresholds of $0.1 \text{ mg}/\text{m}^3$. Arts and coworkers (Arts et al., 2008) proposed an FA concentration of 0.1 ppm ($0.12 \text{ mg}/\text{m}^3$) as a safe and appropriate indoor air level. This concentration is 100-fold higher than the safe exposure concentration advised by the European Commission ($1 \mu\text{g}/\text{m}^3$). It is worth mentioning that the EC's indoor air limit for FA is lower than the FA levels generally encountered in the atmospheric air in many European countries, which are in the range of $1.3\text{--}17.2 \mu\text{g}/\text{m}^3$. The indoor air limit for TVOCs depends on the country, e.g. $300 \mu\text{g}/\text{m}^3$ (Germany) and $500 \mu\text{g}/\text{m}^3$ (Australia) (Table 6). Similarly, there are different legal limits for VOC and formaldehyde emissions from interior construction products into indoor air, which usually apply after 28 days of storage in a ventilated test chamber. TVOC concentrations differ from $20 \mu\text{g}/\text{m}^3$ (Finland) to $>2000 \mu\text{g}/\text{m}^3$ (French regulations class C) and FA concentrations from $10 \mu\text{g}/\text{m}^3$ (Finland, French regulations class A+) to $>120 \mu\text{g}/\text{m}^3$ (French regulations class C) (Eurofins Scientific, 2015).

Table 6. Comparison of the regulation and guidelines concerning formaldehyde pertinent to indoor environments [ASHRAE Standard 2010]

Organisation	Air concentration in average time of 8 hours [ppm]
Enforceable and regulatory levels	
OSHA	0.75 2 (15 min)*
MAK	0.3 1 (never to be exceeded)
Guidelines and reference levels	
Canadian	0.1
WHO/Europe	0.081 (0.1 mg/m ³) (30 min)*
NIOSH	0.016 0.1 ppm (15 min)*

* Numbers in brackets refer to averaging times less than 8 hours

Current scientific research is focused mostly on methods for reducing FA emissions from adhesives, including the widely applied urea-formaldehyde resins. Boran and coworkers (Boran et al., 2011) analyzed the effect on the FA emission rates from MDF panels of adding different amine compounds to UF resin. The addition of cone particles from stone pine improved the water resistance of the panels and reduced FA emissions from urea-formaldehyde resins (Buyuksari et al., 2010). Çetin and Özmen (Çetin and Özmen, 2002) observed that the partial substitution of phenol with lignin in phenol-formaldehyde resins does not affect their physical properties.

Lee (Lee, 2012) developed a procedure for producing a nano-sized, porous UF polymer powder which did not generate formaldehyde. Kim (Kim, 2010) proposed a method of reducing FA and VOC emissions from wood-based flooring by using a green adhesive based on a cashew nut shell liquid (CNSL). Jang and coworkers (Jang et al., 2011) suggested that formaldehyde-free adhesives could be produced using renewable materials, such as soybean. The soy-based adhesive developed by Jang et al. consists mainly of soy flour and a small amount of polyamidoamine-epichlorohydrin resin as a curing agent.

In parallel to the development of new adhesives, intense research is being carried out on resin modification, including urea-formaldehyde resin. Park and Jeong (Park and Jeong, 2011) published a study investigating the relationship between the hydrolytic stability and the

crystalline regions of cured UF resins with different FA-urea mole ratios to better understand the hydrolysis of cured UF resin adhesives responsible for FA emissions in service.

Treatment of wastewater from the production of formaldehyde-based resin adhesives

A very important issue in the impact assessment of formaldehyde-based resin adhesives on the environment is the treatment of wastewater derived from their production. Wastewater from the production of adhesives contains high concentrations of both base substances and additional organic compounds. Many of these pollutants are characterized by high ecotoxicity and resistance to biodegradation. FA concentrations detected in effluents are in the range of 100-10 000 mg/dm³ (Guimarães et al., 2012), and sometimes even higher, up to 30 000 mg/dm³ (Herrera Melián et al., 2008). Similarly, phenol may be present in raw wastewater in high concentrations, up to 60 g/dm³ (Agarwal et al., 2009). Garrido and coworkers (Garrido et al., 2001) noted that wastewater from formaldehyde-urea adhesive factories can contain 4000 mg FA/dm³ and urea concentrations can be up to 805 mg TKN (Total Kjeldahl Nitrogen) /dm³. Due to the high toxicity of phenol, wastewater containing this compound in concentrations higher than 60 g/dm³ should be chemically pre-treated, e.g. in an extraction process. Industrial wastewater can be first treated in a local chemical pre-treatment plant and then discharged to a sewer system.

FA, phenol and ammonia concentrations in treated wastewater (data from Poland) should not exceed 2 mg/dm³, 0.1 mg/dm³ and 10 mg/dm³, respectively. Therefore, it is necessary to use treatment technologies that remove the pollutants to the level required by law. To eliminate pollutants from wastewater, biological or chemical methods (or a combination of the two) are used.

Formaldehyde is easily biodegraded both in aerobic and anaerobic conditions, if its concentration does not inhibit metabolic activities of microorganisms participating in the wastewater treatment. Tister and Zagorc-Koncan (Tister and Zagorc-Koncan, 1997) proved that EC50 for FA inhibiting microbial respiration in wastewater was 34.1 mg/dm³. Other studies indicate that FA biodegradation occurs in higher concentrations following

the adaptation of microorganisms. Effective 99.5% FA removal using activated sludge was reported by Eiroa et al. (Eiroa et al., 2005). The initial FA concentration in the raw wastewater was 3168 mg/dm³. Łebkowska and coworkers (Łebkowska et al., 2011) obtained 55% FA removal from wastewater containing 2880 mg FA/dm³ using activated sludge. Eiroa and coworkers (Eiroa et al., 2004) used a denitrifying granular sludge blanket reactor to treat wastewater with an initial FA concentration of 5000 mg/dm³. The efficiency of the process was 99.5%.

In aerobic conditions, microorganisms oxidize formaldehyde to formic acid and methanol and then to CO₂ and H₂O. Due to the high level of toxicity of FA, if it is present in high concentrations in wastewater, enzymatic detoxification must be carried out to enable its use as a source of carbon and energy. Mitsui et al. (Mitsui et al., 2005) investigated the cultivation of a methylotrophic strain, *Methylobacterium* sp. MF1, and proved that detoxification and growth on extracellular FA requires not only enzymes related to oxidation and assimilation of this compound, but also a means of its transfer inside the cells without damaging cell membranes. Herrera Melián and coworkers (Herrera Melián et al., 2008) showed that an application of combined aerated biological filters and wetland reactors resulted in an almost complete removal of the high FA concentration from wastewater and in wastewater detoxification, which indicated that no toxic intermediates were formed.

Biodegradation of formaldehyde can be carried out in aerobic conditions, but the application of anaerobic and combined aerobic-anaerobic processes is also possible. Kaczala et al. (Kaczala et al., 2010) constructed a biological system consisting of a lab-scale anaerobic-intermittently aerated reactor. The authors achieved 65% removal of COD (Chemical Oxygen Demand) and 93% FA elimination; nitrification and denitrification processes were carried out simultaneously. As an alternative to aerobic methods of wastewater treatment, Priya et al. (Priya et al., 2009) used an upflow anaerobic fixed film reactor (UAFF) to eliminate FA from wastewater.

The treatment of wastewater from phenol-formaldehyde resin production was investigated by Moussavi et al. (Moussavi et al., 2010). They proposed a novel moving-bed sequential continuous-inflow reactor (MSCR) to degrade wastewater containing high concentrations of phenol and formaldehyde (each at concentrations of 1300 mg/dm³). An over 97% reduction of both com-

pounds was noted when the loading rates were 1.2 kg/(m³·d) for each compound.

Lofty and Rasched (Lofty and Rasched, 2002) observed that in wastewater from phenol-formaldehyde resin production, phenol had a toxic impact on biochemical reactions and its transformation was inhibited by the presence of FA. They proposed the addition of sodium sulfite which reacts with FA forming sodium formaldehyde bisulfite, a biodegradable substance which is non-toxic to microorganisms.

Due to the toxic characteristics of wastewater from resin production, some attempts to apply advanced oxidation processes (AOPs), usually prior to biological treatment, have been made. Guimarães et al. (Guimarães et al., 2012) investigated FA degradation in a water solution (400-1200 mg/dm³) by photolysis and AOP processes – UV/H₂O₂, Fenton process and photo-Fenton process. AOPs resulted in the removal of 98% FA and 65% DOC from the solution.

To eliminate phenolic compounds from wastewater generated during alkydic resin production, Schwingel de Oliveira et al. (Schwingel de Oliveira et al., 2007) used Fenton and photo-Fenton processes. The best results were obtained with the photo-Fenton process assisted with solar radiation, and this resulted in the removal of 99.5% COD, 99.1% TOC and 95% phenols.

Combining AOPs and biological methods to treat wastewater containing FA has proved to be effective in the removal of high concentrations of pollutants. Mousavi et al. (Moussavi et al., 2009) showed that the efficiency of the catalytic advanced oxidation process (CAOP) of O₃/MgO/H₂O₂ was 79% in FA removal and 65.5% in COD removal for a solution with an initial FA concentration of 7000 mg/dm³. Post-treatment in an SBR (Sequencing Batch Reactor) system with a total cycle time of 24 h resulted in complete FA removal and a 98% reduction of COD; the COD concentration in the effluent was below 60 mg/dm³.

Aparicio et al. (Aparicio et al., 2007) analyzed the ozonation process of wastewater from a resin-producing factory and, afterwards, the biodegradability of the ozonated effluent was studied under anoxic conditions. It was proved that a combined post-ozonation and biological treatment can be applied to recalcitrant wastewater from a resin-producing factory. The ozonation step enhances the biodegradability of wastewater compounds.

It should be noted that the wastewater treatment efficiency cannot be based on FA removal alone. Other parameters such as BOD₅ (Biochemical Oxygen Demand), COD, TOC (Total Organic Carbon) and TKN should also be considered to determine the quality of treated wastewater and its environmental safety.

Treatment of waste products and serviced woods

Environmental protection problems arising from the use of resin-based adhesives also include the treatment and disposal of waste products that contain adhesives. Wood and wood waste may contain not only resin-based adhesives, but also paint, surface coatings, coverings and natural oils, toxic compounds in wood preservatives, insecticides, antibacterial and antifungal agents, such as arsenic compounds or creosote, tebuconazole, propiconazole, cyfluthrin and alkyd resins. Research on the leaching of those compounds to water from impregnated wood proved their high toxicity for water biocenoses (Łebkowska et al., 2003). Biological treatment of wastewater containing wood preservatives, e.g. from a sawmill, has been scarcely investigated in the literature; advanced oxidation processes are recommended for its decontamination (Munoz et al., 2014). The removal of these pollutants from wastewater usually requires a multi-step treatment and a careful choice of treatment methods to ensure that pollutant levels are not greater than the legally permitted concentrations.

Singh and Singh (Singh and Singh, 2014) stated that it is possible to use wood-rotting fungi for the removal of toxic compounds from treated and serviced wood. The wood can then be processed to generate fibers for biocomposites and chemicals such as lignin degradation products as antioxidants or adhesives. In Germany, only 26% of the recovered wood is suitable for re-use (Höglmeier et al., 2013).

One of the main methods of disposing waste wood is combustion. This may lead to emissions of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). PCDDs and PCDFs are formed via precursors such as phenols and lignins during reactions with chlorine. The highest concentrations of dioxins are noted from the combustion of ammonium chloride hardened plywood or PVC-coated plywood. Measurement of PCDD and PCDF emissions showed that their concentrations in air ranged from 0.005 to 4 ng

I-TEQ (International Toxic Equivalents)/m³ (Lavric et al., 2004).

It should be noted that during combustion natural wood may also emit dioxins in concentrations above the legal threshold (0.1 I-TEQ/m³). It has been shown that the total amounts of PCDDs and PCDFs in plywood combustion gasses are in the range of 35-529 ng/Nm³, and are higher from plywood made using softwood trees than those using broadleaf ones (Muto and Sugawara, 2001).

PCB emissions have been measured during the combustion of wood samples from radiata pine, camphor laurel, chipboards and MDF (Bhargava et al., 2002). MDF contained phenol, resorcinol or cresol, formaldehyde, urea or melamine. Chipboard contained bonding agents, such as phenolic and urea resins. PCB emission rates for camphor laurel, MDF and chipboard were 17, 40, and 48 µg/kg of wood, respectively.

Conclusions

Adhesives based on formaldehyde are a source of many pollutants which negatively impact upon both human and animal health and the environment. Wastewater and wastes from their production cause a lot of problems and require the application of specific methods for their elimination. In recent years, significant progress has been made in the development and production of adhesives, especially in limiting the concentration of formaldehyde and other harmful/toxic compounds. In terms of environmental protection, a very attractive option is to produce adhesives from renewable materials. Also, new wood coatings have been proposed and developed that reduce VOC emissions to indoor air. Moreover, new methods to treat wastewater from adhesive resin production have been proposed, and these may enable the efficient removal of harmful pollutants from the aquatic environment.

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