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SELECTED PROBLEMS OF THE UTILIZATION OF WASTEWATER FROM WOOD INDUSTRY BY BIOLOGICAL PROCESSES

A review of literature data has been presented, concerning selected problems of the utilization of wastewater from woodworking industry with the participation of microorganisms. Special attention has been focused on the biodegradation of components contained in water extracts from natural wood, leachates from wood waste and industrial wastewater generated in manufacturing wood products. Significance of white-rot fungi in enzymatic decomposition of lignin complexes has been emphasized. Many of chemical compounds which have toxic effect on water organisms are present in wastewater from wood industry. Although a lot of these compounds are potentially biodegradable, the decomposition process, especially of adhesives, may be inhibited by their high and harmful concentrations.

1. INTRODUCTION

Wastewater from wood manufacturing, leachates from raw wood storage and woodworking contain various natural substances and xenobiotics having been introduced in the manufacturing processes. Natural wood consists of cellulose (approximately 51%), hemicellulose (23%) and lignins (22%). It contains resin, waxes, fatty acids, phenols, sterols and sterol esters (1–3%). Over 250 chemical compounds have been identified in papermaking wastes, including, among others, diterpene carboxylic acids, harmful to fish when $LC(EC)_{50}$ is about 1 mg/dm^3 [1]. Waste from wood manufacturing contains mainly adhesives, impregnants, insecticidal and fungicidal biocides, paints and varnishes. Over 500 substances derived from wood and wood-based materials have been identified in indoor air, including formaldehyde, phenol, resorcinol, benzene, toluene, ethanol, methanol, ethyl acetate, vinyl acetate, phthalates, acetone,

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methyl derivatives of hydrocarbons, and cyclohexanone. The literature data indicate that biological treatment of wastewater and leachates from processed wood might not ensure the appropriate quality of the treated effluent.

2. WOOD LEACHATES

Cellulose and hemicellulose are relatively easily biodegraded into saccharides as many microorganisms produce cellulolytic enzymes. Lignins are resistant to biochemical decomposition due to their aromatic structure consisting of phenylpropane units. It has been found, however, that some fungi, mainly white-rot fungi (*Basidiomycetes*) produce enzymes – laccases which participate in the biodegradation of the lignin complex. Laccase are oxidoreductase molecules contain 4 copper atoms in active sites. They cooperate with reaction mediators – simple phenols originating from lignin depolymerization [2]. Among the white-rot fungi capable of producing laccase, the following ones should be emphasised: *Stereum hirsatum*, *Ceriporiopsis subvermispora*, *Pleurotus ostreatus*, *Coriolus versicolor*, *Irpex lacteus.*

It has recently been discovered that fungi *Mucor racemosus* (*Zygomycetes*) isolated from seawater produced laccase in the medium containing 2% malt and 3% NaCl, i.e. in a saline environment [3]. Studying the laccase production process by *Cerrena unicolor*, Antecka et al. [4] observed a negative correlation between the enzyme biosynthesis and biomass growth. Glucose and L-asparagine which increased fungal biomass growth were applied as food substrates, whereas laccase was produced after the depletion of carbon and nitrogen sources. The phenomenon of production of laccase and cellulolytic enzymes on waste materials such as rice straw, wheat and rice bran, maize stems and leaves, using solid state fermentation (SSF) process [5] is of considerable interest. Delignification ability of fungi could be used for initial wood treatment in the biopulping process, before the formation of paper pulp. The research conducted by Dorado et al. [6] has shown that impurities such as triglycerides, resin acids, sterols, waxes, and esters were eliminated from softwood extracts subjected to the following white-rot fungi: *Bjerkandera* sp., *Stereum hirsutum* and *Trametes versicolor*. Toxicity of the extracts measured with the Microtox test was reduced by 7–17 fold. Van Beek et al. [7] have proven that during a 4 week initial spruce chips treatment by *Trametes versicolor*, the amount of resin acids and triglycerides was reduced by 40% and 100%, respectively. Harmfulness of the extract decreased as well.

It should be emphasized that during storage, leachates originating from wood contain numerous chemical compounds, including phenols, volatile fatty acids, lignins, tannins and resin acids which might transfer to waters and soils [8]. Content of volatile fatty acids, tanins and lignins may reach over 1600 mg/dm^3 and 5150 mg/dm^3, respectively, which corresponds to COD 14 250 mg/dm^3. Studies on the harmfulness of water washed compounds from the wood chips: phenols (up to 30 mg/dm^3), fatty acids (up to 90 mg/dm^3) and organic carbon (up to 2480 mg/ dm^3) have shown that the EC_{50} values for water organisms were in the range of 1–2% [8]. Chronic toxic effects of resin acids and unsaturated fatty acids occur already at the concentration of 20 µg/ dm^3 [9].

The toxicity of leachates depends on the type of wood, thus Libralato et al. [10] demonstrated that TU 50/72 h for oysters (*Crassostrea gigas*) was in the range from 2.4 (leachates from the tropical wood *Ponteria quianensis – Abiurana ferro*) to 53.76 (leachates from Norway spruce). It is commonly accepted that landfill sites for wood waste such as sawdust, bark, wood dust are the source of leachates containing compounds such as phenols, methylphenols, terpenes and tropolones being toxic to water organisms. Oak tannins contain glucose acid whereas acacia wood contains vanilla acid. Leachates from pinewood are rich in alcohols and ketones(C_7–C_{12}). However, at least 50% of the substances present in the compound mixture in the leachates are characterised by high BOD_5 levels which indicates their possible biodegradation [11]. Proven participation of white-rot fungi in the biodegradation of lignins and other wood components makes them suitable for practical application. The role of those fungi in removing refractory pollutants is increasing, as it has been proven that they are capable of PAH biodegradation. Decomposition of naphtalene, phenantrene and anthracene was observed due to the ligninolytic system including three main enzymes: lignin peroxidase, Mn-peroxidase and laccase [12].

3. WASTEWATER FROM WOODWORKING INDUSTRY

In comparison to leachates from wood, wastewater from wood adhesives and preservation production and paper-industry wastewater cause considerably bigger environmental problems. Polyurethane, polyvinyl, polyacryl, silicone and epoxide adhesives as well as adhesives based on phenol-resorcinol-formaldehyde resins and urea-formaldehyde resins are used in the production of particle boards, panels, multidimensional wood constructions and furniture. Wastewater from adhesives production is generated during adhesive preparation, spreading on the wood and hardening (pressing). According to PAN pesticides database [13], basic components of resins such as formaldehyde, melamine, styrene and urea are harmless to water organisms, in accordance with the accepted toxicity criteria. In general, phenol and resorcinol are of mild and acute toxicity, depending on the bioindicator examined. It should be emphasized, however, that concentrations of basic compounds are high in adhesive resins, and toxic effects of compound mixtures are additive. Formaldehyde is a group I carcinogen (according to International Agency for Research on Cancer – IARC), and its maximum permissible concentration in water must not exceed 2 mg/dm^3. Taking into account susceptibility to biodegradation, it should be stated that formaldehyde undergoes biochemical decomposition in both aerobic and anaerobic conditions. Eiroa et al. [15] obtained effective (99.5%) anaerobic formaldehyde removal by the activated sludge method with the initial concentration of 3168 mg/dm^3, as well as in a reactor with denitrifying granulated biomass (99.5%) with the initial concentration of 5000 mg/dm^3 [14]. Lu and Hagemann [16] investigated decomposition of formaldehyde with the addition of glucose and wastewater containing wood adhesive. The concentration of formaldehyde inhibiting gasification by 50% was to 300 mg/dm^3 (the glucose test) and 150 mg/dm^3 (the adhesive waste test). In the presence of phenol, formaldehyde biodegradation can be inhibited [17].

Phenol and styrene are relatively easily decomposed by microorganisms. BOD/TOD ratio of phenol accounts to 0.7, indicating its susceptibility to biodegradation. Jiang et al. [18] proved that phenol degradation in initial concentration of 1600 mg/dm^3 occurred within 76 h by *Alcaligenes faecalis* and Okamoto et al. [19] – styrene degradation of 600 mg/dm^3 in 48 h by *Pseudomonas putida*. Studies on the biochemical decomposition of polyurethanes have shown that the following esterases are involved in the process: intracellular esterase bound to cytoplasmic membrane, and extracellular esterase allowing ester bond hydrolysis in the polymer [20]. A synthetic polymer (polyvinyl alcohol) is applied to harden adhesives. This type of alcohol, as well as polyvinyl acetate and copolymers containing polyvinyl alcohol, inhibits biodegradation of wood waste. Nevertheless, it has been stated that the white-rot fungi (*Pycnoporus cinnabarius*, *Phanerochaete chrysosporium* and *Flammulina velutipes)* demonstrate the ability to decompose polyvinyl alcohol [21]. Studies with *Flammulina velutipes* have shown that these fungi depolymerize polyvinyl alcohol in culture on quartz sand due to Mn-peroxidase and laccase production.

Paper mill wastewater contains much organic pollution and the COD of this wastewater can even reach 11 000 mg O_2/dm^3. Amounts of the wastewater produced are significant, as the paper industry is a water-consuming one; the use of water is up to 60 m^3 per each ton of produced paper. In their review paper, Thompson et al. [22] described papermaking wastewater treatment system including aerobic, anaerobic, aero-anaerobic as well as alternative methods such as wastewater pre-ozonation. The following stages of treatment can be used: sedimentation of suspension or flotation, biological, mainly aerobic processes with activated sludge, clarifying and disposal to river. For the removal of colour, the remaining COD, and toxic compounds, wastewater before disposal is fed to the tanks where adsorption, ozonization, and coagulation occur. Vidal et al. [23] used an anaerobic filter colonized by a consortium of anaerobic bacteria for the treatment of wastewater from paper pulp production. The authors found that the method allows removal of nearly 100% harmful components such as endocrine stigmasterol and β-sitosterol. Nair et al. [24] studied the effect of phenol degrading *Alcaligenes* sp. on paper factory effluent. After the complete removal of phenol, the bacteria strain could also oxidize organic matter other than phenol in the effluent.

Chlorophenols are by-products of chlorine bleaching in the pulp and paper industry. A large variety of bacteria are known which can utilize chlorophenols as carbon and energy sources under aerobic condition. Several examples of aerobic cometabolism of chlorophenols have been reported. Many fungi and yeast are capable of metabolizing and cometabolizing chlorophenols. Selected examples of aerobic bacteria and fungi capable of chlorinated phenols biodegradation are presented in Table 1 [25]. Ecotoxic effects of chlorophenols are given in Table 2 [26, 27].

Table 1

Bacteria and fungi capable of biodegradation of chlorophenols
(adopted from [25])

Microorganisms	Congener
Bacteria:	
Alcaligenes xylosoxidant JH1	2-CP, 4-CP
Pseudomonas picketti LD1	2-CP, 3-CP, 4-CP
Rhodococcus opacus 1G	2-CP, 3-CP, 4-CP, 2,4-DCP
Streptomyces rochei 303	2-CP, 2,4-DCP, 2,6-DCP
Sphinogomonas strain	2,6-DCP. 2,4,6-TCP, 2,3,4,6- TeCP, PCP
Pseudomonas saccharophila	2,4,6-TCP, 2,3,4,6-TeCP
Preudomonas strains	4-CP, 2,4-DCP, PCP
Mycobacterium sp. CG-2	2,3,5- TCP, 2,3,5,6- TeCP, PCP
Fungi:	
Penicillium sp.	2-CP
Candida maltose	2-CP, 4-CP
Candida albicans	4-CP
Trichoderma harzianum	PCP
Gloeophyllum striatum	2,4-DCP
Trametes versicolor	PCP

CP – chlorophenol, DCP – dichlorophenol, TCP – trichlorophenol, TeCP – tetrachlorophenol, PCP – pentachlorophenol.

Table 2

Ecotoxicity of chlorophenols – $LC(\mathrm{EC})_{50}$ [mg/dm^3] [26, 27]

Congener	Algae	Crustaceans	Fisch
2-CP	50–170	0.3–25	4.5
3-CP	–	4,9	–
4-CP	8–29	0.6–8.6	–
2,4-DCP	4–37	3.3–13.8	8.0
PCP	–	–	0.24–0.36

Biodegradation of wastewater components from woodworking industry is a complex process, not only due to the diversity of chemical compounds but also because of their high concentration and possibly harmful influence on the biocenosis participating in the decomposition of pollutants. Thus, numerous papers have been published on the usage of advanced and highly efficient methods of chemical oxidation of wastewater compounds preceding the biological stages [28, 29].

4. CONCLUSIONS

Diversity of issues concerning wastewater utilization from wood industry requires the broadening of research on methods enhancing the biodegradation of components which are used for producing wood and wood-based materials. This concerns the use of fungi, including white-rot fungi, for the production of lignin complex enzymes as well as broadening the knowledge of factors increasing process efficiency, including cometabolism which has already been used in the decomposition of numerous refractory compounds. Studies on chemical formulae of e.g. adhesives are crucial for the reduction of their toxicity. Development of wastewater treatment methods is recommended, including not only biological methods but also the chemical ones.

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