CHARACTERIZATION AND BIODEGRADABILITY OF LIGNIN CONTAINING WASTEWATER FROM FOREST INDUSTRY

J. PELLINEN* AND M.S. SALKINOJA-SALONEN
Department of General Microbiology, University of Helsinki
* Present address The Finnish Pulp and Paper Research Institute, Box 136 Helsinki, Finland

Summary. Lignin derived compounds originating from forest industry represent the major organic constituent in waste streams into Finnish recipient waters. Pulping and bleaching of pulp transforms the lignin of wood chips into a variety of aromatic polymer molecules widely differing in size (MW from $10^2$ to $10^5$) and properties. The aim of this study was to see, whether the different wastewater lignins also differ in their biodegradability. We monitored the molecular weight distributions of lignins in waste streams from different stages of pulping and different bleaching processes at four different pulp mills and also in the recipient water. Our method of analysis was high performance size exclusion chromatography (HPSEC), shown to give reliable results on the molecular weight distribution of lignins, provided that precautions are taken to avoid hydrogen bonding and lipophilic or electrostatic interaction. The wastewater lignins proved poorly degradable by bacteria if used as sole substrate.

1. INTRODUCTION.
Wastewaters from forest industry have a dominant role in the pollution of surface waters in Finland. In 1983 about 90 % of the BOD$_7$ released into the watercourse was from forest industry (1). The most important wastewaters are those from debarking of wood and from washing and bleaching of chemical pulp. The major organic constituent of these wastewaters is lignin or lignin-like material.

Lignin in the effluents is very heterogeneous material consisting of a large spectrum of molecules of different sizes containing many phenolic and acidic groups (2,3). From the annual production of about $5\times10^6$ tons of chemical pulp (of which $3\times10^6$ tons of bleached pulp) the amount of chlorinated lignin released by the forest industry can be estimated to be approximately 150 000 tons per year in Finland.

The high-molecular weight lignin has been seen as potential environmental problem because toxic or mutagenic compounds may be formed from it in the nature or in the chlorination of drinking water (4,5). Chlorolignin seems very stable in the aqueous environment (5,6). One harm caused by pulp mill effluents is that the absorption of light is increased due to its colour which may affect water ecosystem (5).

Biodegradation studies may give us new information on the fate of lignin in the environment and make possible to develop better ways to treat lignin containing wastewaters. Since the biodegradability of organic compounds depends on the size and chemical structure of the molecules, the biodegradability of wastewater lignins can be expected to vary depending on the process and chemicals used in the industry. This paper describes the results of a study undertaken to evaluate the molecular weight distribution (MWD) of various lignins and its effect on biodegradability using recently developed high-performance size exclusion chromatography (HPSEC) methods (7,8). The HPSEC method was used also to follow the changes in the MWD of lignin in recipient water systems.

2. EXPERIMENTAL
Chromatography. The chromatography of water-soluble samples was performed as described in ref. 7 using TSK PW type columns (Toyo Soda Manufacturing Co., Tokyo,Japan). The mobile phase was NaHCO$_3$ (0.025 M)-NaOH buffer (pH 10.5) with
0.5g/l of polyethylene glycol 6000 (Fluka AG, Buchs, Switzerland) and 0.5 g/l of ethylene glycol (E. Merck, Darmstadt, FRG). Poly(styrene sulfonate) standards were used for calibration (Pressure Chemicals Inc., Pittsburgh, Pa., USA).

The water-insoluble samples were chromatographed as described in ref. 8 using Ultrastyragel columns (Waters Associates Inc., Milford, Mass., USA) with tetrahydrofuran as mobile phase (Rathburn, Walkerburn, Peeblesshire, Scotland, HPLC-grade). The calibration was done with poly(styrene) standards (Pressure Chemicals Co.).

UV-absorption detector was used at 280 nm. The chromatograms were normalised to equal area with a microcomputer.

Fig. 1. Structure of the tetrameric lignin model compound used in this study, 1,1'-(4,4'-dihydroxy-5,5'-dimethoxy-3,3'-biphenylene)-bis- 2-(2-methoxyphenoxy)-1,3-propanediol (MW 638)

Samples. The bleaching liquors were all from bleaching of kraft pulp. The bleaching sequences were the following: mill 1 (D/C)EHED, mill 2 (D/C)EHED, mill 3 OCE (prebleaching). The effluent from the mill 4 was combined from two bleacheries with sequences (C/D)EHDED and (C/D)EHPD. The kraft lignin from birch (mill 2) was purified by precipitation at pH 3, filtered, washed, dissolved in 0.1 N NaOH and ultrafiltered with an Amicon UM 2 filter (Amicon Corp., Danvers, MA, USA) with a nominal cut-off of 1000 dalton. The filtrate was used in the experiments. Indulin AT-R softwood kraft lignin was obtained from Westvaco Corp., North Charleston, SC, USA. Humic acid was from Fluka (Buchs, Switzerland).

The tetrameric lignin model compound 1,1'-(4,4'-dihydroxy-5,5'-dimethoxy-3,3'-biphenylene)-bis- 2-(2-methoxyphenoxy)-1,3-propanediol (MW 638, Fig.1) was synthesized as described in the literature (9,10). It was characterized by MS and NMR spectra.

Analyses. Total organic carbon (TOC) was determined with Ionics Mod 1258 analyzer using acetic acid for calibration. Total organic chloride (TOCI) was determined by burning the sample in oxygen after adsorption to activated carbon and titrating the formed hydrochloric acid coulometrically.

3. RESULTS AND DISCUSSION

Tables 1 and 2 and Figs. 2 and 3 show data of the lignins of various waste streams from four kraft pulp mills. The bleaching liquor lignins from the four millshave an average molecular weight varying from Mn 300 to 1700 and Mw of 1350 to 4400. The smallest molecules were found in the chlorination stage effluent.