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Effect of biological wastewater treatment on the molecular weight distribution of soluble organic compounds and on the reduction of BOD, COD and P in pulp and paper mill effluent

Tiina Leiviskä[a,*], *Hannu Nurmesniemi*[b], *Risto Pöykiö*[c], *Jaakko Rämö*[a], *Toivo Kuokkanen*[d], *Jaakko Pellinen*[d]

[a]*Department of Process and Environmental Engineering, University of Oulu, P.O. BOX 4300, FI-90014 University of Oulu, Finland*
[b]*Stora Enso Oyj, Veitsiluoto Mill, FI-94800 Oulu, Finland*
[c]*The Town Planning and Building Committee, Environmental Research Division, City of Kemi, Valtakatu 26, FI-94100 Kemi, Finland*
[d]*Department of Chemistry, University of Oulu, P.O. BOX 3000, FI-90014 University of Oulu, Finland*

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ABSTRACT

Pulp and paper mill wastewater was characterizated, before (influent) and after (effluent) biological wastewater treatment based on an activated sludge process, by microfiltration (8, 3, 0.45 and 0.22 μm) and ultrafiltration (100, 50, 30 and 3 kDa) of the wastewater samples into different size fractions. Various parameters were measured on each fraction: molecular weight distribution (MWD) using high performance size exclusion chromatography (HPSEC), total organic carbon (TOC), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total phosphorus (Tot-P), phosphate phosphorus (PO_4-P), electrical conductivity, pH, turbidity, charge quantity and zeta potential. The MWD, TOC and COD_{Cr} results indicated that the majority of the material present in both the influent and effluent was in the medium molecular weight (MW) range (i.e. MW < 10 kDa) with three main MW subfractions. There were no significant differences in the range of the MWD between the influent and effluent samples. The magnitude of the MWD in the effluent was about one half that in the influent, the greatest reduction being in the 6 kDa fraction. The 3 kDa fractions of both the influent and effluent showed a considerable increase in BOD_7, probably due to the removal of compounds harmful to bacteria in 3 kDa ultrafiltration. Influent turbidity decreased considerably in microfiltration (8–0.22 μm). As the turbidity was removed by 0.22 μm filtration, the anionic charge quantity started to decrease. Particles in the influent and effluent contained 19–29% and 14–20% of the total phosphorus, respectively. The major phosphorus fraction was in the form of soluble phosphate.

1. Introduction

The pulp and paper industry has been faced with ever-more stringent limitations on its discharges during the last few decades and the same trend will continue in the future. In Finland, the pulp and paper industry has been markedly successful in reducing discharges, biochemical oxygen demand (BOD), phosphorus and chemical oxygen demand (COD), even though the production of pulp and paper has increased considerably. In the 1980s, the activated sludge

* *Corresponding author*. Tel.: +358 40 5544531; fax: +358 8 5534507.
E-mail addresses: tiina.leiviska@oulu.fi (T. Leiviskä), hannu.nurmesniemi@storaenso.com (H. Nurmesniemi), risto.poykio@kemi.fi (R. Pöykiö), jaakko.ramo@oulu.fi (J. Rämö), toivo.kuokkanen@oulu.fi (T. Kuokkanen), pellinja@mail.student.oulu.fi (J. Pellinen).
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Abbreviations and notations

AOX	adsorbable organic halogen (mg/L)
ATU	allylthiourea
BOD	biological oxygen demand (mg/L)
BOD_7	a seven-day biological oxygen demand (mg/L)
COD	chemical oxygen demand (mg/L)
COD_{Cr}	chemical oxygen demand (mg/L), oxidation with dichromate
Da	Dalton
ECF	elemental chlorine-free
ELS	evaporative light scattering
ELSD	evaporative light scattering detector
eq/l	equivalent/litre
G	gas chromatography
HPLC	high performance liquid chromatography
HPSEC	high performance size exclusion chromatography
kDa	kiloDalton
kg/d	kilogram/day
mL/min	millilitre/minute
mm	millimetre
mV	millivolt
MW	molecular weight
MWCO	molecular weight cut-off
MWD	molecular weight distribution
NMWL	nominal molecular weight limit
NTU	nephelometric turbidity unit
O	an oxygen stage
P	Phosphorus (mg/L)
PO_4-P	Phosphate phosphorus (mg/L)
TCF	total chlorine-free
t/d	ton/day
TOC	total organic carbon (mg/L)
Tot-P	total phosphorus (mg/L)
SEC	size exclusion chromatography
S/m	siemens/meter
UF	ultrafiltration
μm	micrometre
UV	ultraviolet
WWTP	wastewater treatment plant

treatment was introduced in many mills. Furthermore, the replacement of chlorine (Cl_2) in bleaching by elemental chlorine-free (ECF) bleaching or total chlorine-free (TCF) bleaching has drastically cut discharges of absorbable organic halogens (AOX). The increasing need to reduce water consumption has forced pulp mills to develop more efficient techniques for pulp washing. In addition, the circulation of filtrates has increased and internal water treatment is also nowadays used.

In spite of the major process investments in environmental protection, the supplementary treatment of wastewater will become ever more important in the future. The decolorization of effluents, at least, should be performed. Conventional biological treatment processes have little or no effect on wastewater decolorization. The brownish colour is mainly attributable to lignin and its derivates, which are difficult to degrade naturally.

Fractionating wastewater components into different size fractions gives detailed information about wastewater characteristics and helps in the design of appropriate treatment technologies (Dulekgurgen et al., 2006; Engström and Gytel, 2000; Levine et al., 1991; Sierka et al., 1997; Skipperud et al., 1998; Sophonsiri and Morgenroth, 2004). The main aim of this work was to characterize the wastewater from an integrated pulp and paper mill before and after the activated sludge treatment process. This was carried out by microfiltration and ultrafiltration of the wastewater samples into different size fractions in order determine the size fractions in which the priority pollutants, BOD, COD, and phosphorus, occur. A large number of analyses were conducted on each fraction: molecular weight distribution (MWD) using high performance size exclusion chromatography (HPSEC), total organic carbon (TOC), BOD_7, COD_{Cr}, total phosphorus (Tot-P), phosphate phosphorus (PO_4-P), electrical conductivity, pH, turbidity, charge quantity and zeta potential.

2. Materials and methods

2.1. Wastewater sampling

Wastewater samples were taken from Stora Enso Oyj Veitsiluoto Mill, which is located in Northern Finland. The integrated pulp and paper mill produces ECF bleached soft and hardwood pulp (371,566 t in 2007), uncoated fine papers (514,385 t in 2007), coated printing papers (394,779 t in 2007) and sawn goods (149,566 m^3 in 2007). The pulp mill used 0.44 million m^3 of softwood, 0.94 million m^3 of hardwood and 0.36 million m^3 of sawmill chips in 2007. In the same year, the groundwood mill used 0.35 million m^3 of spruce pulpwood and the sawmill 0.31 million m^3 of pine logs. The wastewater from the pulp mill, the groundwood mill, and the disc filters of the paper machines (altogether 60,000 m^3/d) are treated biologically by the activated sludge method. Other wastewaters from the paper mill are treated chemically by flotation. The total wastewater load from Veitsiluoto Mill in 2007 was 3.3 t/d solids, 3.3 t/d BOD_7, 34.2 t/d COD_{Cr}, 24.4 kg/d phosphorus, 243 kg/d nitrogen and 0.13 t/d AOX. The permit conditions for all the parameters were met.

Grab samples were taken on two different occasions (May 7, 2007 and July 30, 2007), before (influent) and after (effluent) activated sludge treatment during stable operating conditions in the wastewater treatment plant (WWTP). The influent sample was taken immediately before aeration. The effluent sample was taken after the secondary clarifier.

2.2. Filtration experiments on the samples

Filtration was started on the same day as sampling. The samples were first passed through a 4 mm plastic sieve. They were then filtered sequentially, first by using a suction Millipore filtration device with a 47-mm diameter filter paper with pore sizes of 8, 3, 0.45, and 0.22 μm. Consequent ultrafiltrations were performed with a stirred cell (Amicon, Model 8400) using Millipore ultrafiltration (UF) membranes with nominal molecular weight limits, NMWL (also known as molecular weight cut-off, MWCO) of 100, 50, 30, and 3 kDa.