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Enzymatic and Microbial Treatment of Concentrated and Recycled Pulp Mill Effluents

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Enzymatic and Microbial Treatment of Concentrated and Recycled Pulp Mill Effluents

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Wearing, J. T. and Francis, D.W.
PAPRICAN

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ABSTRACT

The pulp and paper industry is moving toward recycling of process waters to reduce effluent discharge into the environment. However increased levels of dissolved and colloidal substances (DCS) in the process waters will result from water systems closure. This will cause a series detrimental effects on the products quality and papermachine runnabilty.

Our research carried out at the Chair of Forest Products Biotechnology, UBC has shown that the detrimental substances present in the TMP pulp/newsprint mill process water are primarily derived from phenolics and lipophilic extractives. The level of detrimental substances will increase as the mill water system move toward the closure. The potential of using fungal enzyme treatment system to remove the detrimental DCS substances has been examined. This treatment system is capable of dealing with a large amount of process water under mill operation conditions. Most of the detrimental substances have either been degraded or converted to less harmful components. The fungal enzyme treatment shows promise as one way of decreasing the detrimental substances present within a closed water system.

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Developing a detailed protocol for analyzing the dissolved and colloidal substances (DCS) present in TMP pulp/newsprint mill process water

A clear knowledge of the composition of a "typical" TMP process white water will give us a better understanding of the influence the DCS components have on the paper properties. This will also help to design appropriate treatment technologies. In the earliest stage of this project, a detailed analytical protocol (Fig. 1) was set up based on previous studies, from which DCS component groups: carbohydrates, lignin, inorganics and extractives (resin and fatty acids, lignan and sterols, steryl esters and triglycerides), present in the white water samples can be quantified. Other properties of the white water, such as chemical oxygen demand, total organic carbon, colour unit, colloidal particle size distribution, turbidity, water surface tension and cationic demand can also be determined through this protocol.

Investigation of the effects of DCS components on the paper properties

Making recycled white waters

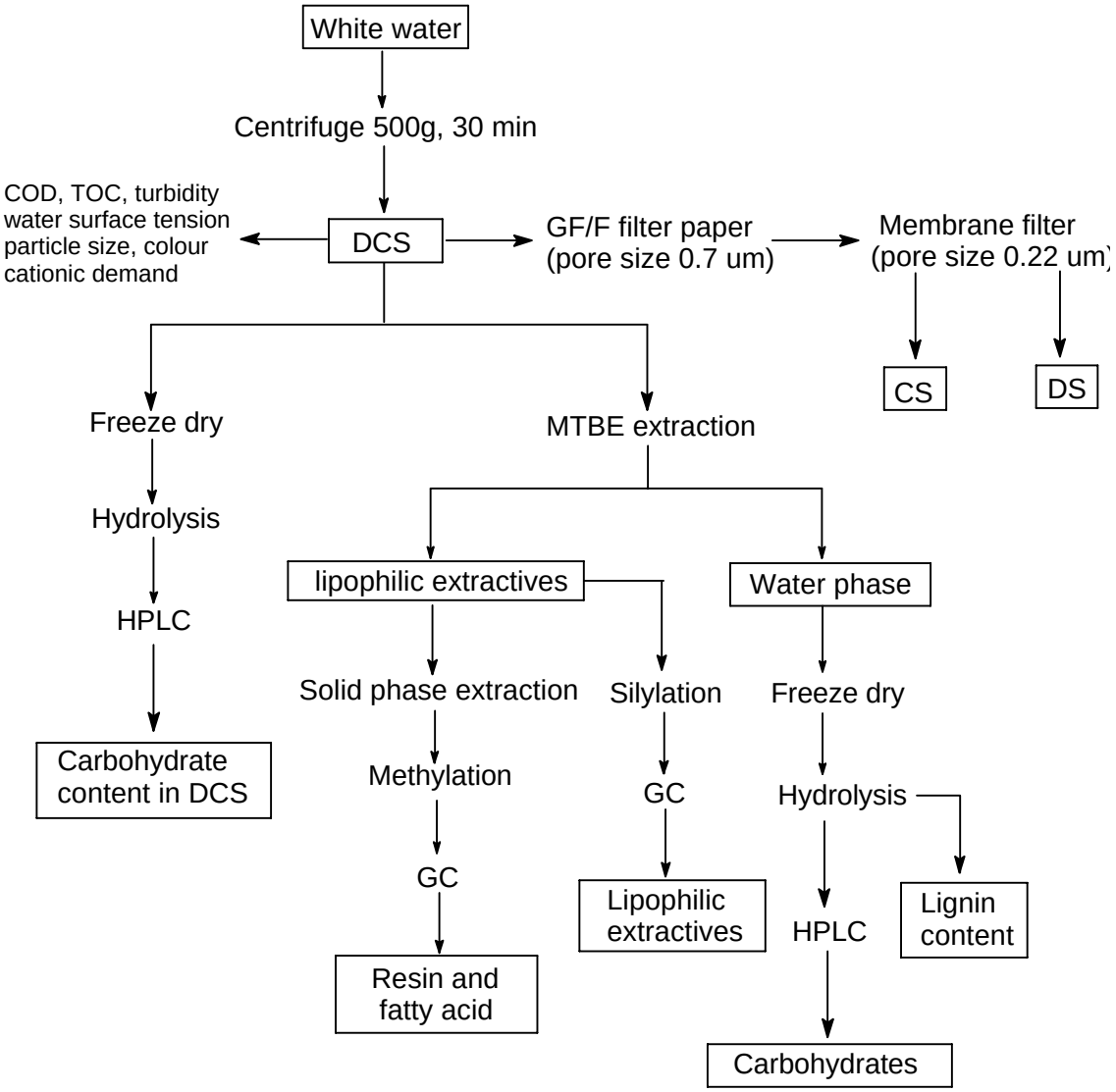
The diversity and complexity of different white waters due to the different furnishes, different processes, and different grade of products, etc. make it difficult to define a representative white water sample for studying the overall impact that the detrimental substances will have on the pulp and paper making process. Model recycled white water from 1 to 5 recycle steps was made in the PAPRICAN pilot plant (Appendix 1). A "typical" mill white water was obtained from the Howe Sound Pulp and Paper mill. The compositions of these waters were analyzed and the results showed a different distribution of the DCS components. Both white waters were used to prepare paper sheets.

Chemical nature of DCS components affecting paper properties (appendix 1)

The paper properties of the handsheets prepared by using model recycled white water and mill white water were tested and compared to the paper sheets formed by distilled water. Because of the different distributions of DCS component groups (carbohydrate, lignin, resin and fatty acid, lignan, steryl ester and triglyceride) present in the two waters, we were able to investigate the effects of different DCS components on the paper properties. The results showed that: 1) The concentration of dissolved and colloidal substances increased significantly with white water recycling. 2) The lignin component of the DCS was primarily responsible for the decrease in papersheet brightness whereas the presence of RFAs reduced wet web strength properties, as a consequence of their ability to decrease water surface tension. 3) The presence of lipophilic substances caused decreases in sheet density and interfibre bonding which resulted in reduced tensile

strength. 4) The presence of enhanced amounts of carbohydrates in highly recycled white water acted to counteract some of reduced bonding caused by the lipophilic extractives.

Figure 1. Protocol for analyzing dissolved and colloidal substances present in mechanical pulp/newsprint mill white water



Physical form of DCS components affecting paper properties (appendix 2)

During our investigation on the effects of different DCS components on the paper properties, it was recognized that physical properties of the paper sheets was not only determined by the chemical nature of DCS components, but also the physical form of these substances present in the white water. A 0.22 µm membrane filter was used to separate newsprint mill white water colloidal particles from the dissolved substances. The chemical and physical constitutions of these two fractions were then determined. Both the

original white water and white water containing only the dissolved substances, obtained after membrane filtration, were used to prepare handsheets. The physical properties of these two types of handsheets were tested and compared to the handsheets made using distilled water. In this manner, the separate effects of the dissolved and colloidal fractions in white water on the paper properties were determined. The results showed that: 1) The white water contained a significant amount of colloidal substances ranging in size from 250nm to 1000nm. 2) The lignin and ester-bonded extractives (steryl esters and triglycerides) were the main constituents of colloidal particles, while the neutral saccharides and lignans were predominantly dissolved in the white water. 3) Dissolved substances mainly caused the reductions in the paper strength properties, whereas the colloidal substances were primarily responsible for the impairment of paper surface and optical properties.

Screening fungi for activity against detrimental DCS

Twenty-three fungal strains were screened through a two step-process. The first screening was based on the growth of these fungi on agar plates containing white water without supplementation of additional nutrients. This initial step helped us to eliminate some of the strains which cannot survive on the white water due to the deficiency of nutrition or the inhibition effects from white water DCS components. The secondary screening was aimed at determining the ability of the remaining strains to decrease extractive content, which is one of major detrimental substances present in white water. From the two screening steps, the white-rot fungus *Trametes versicolor* showed both the highest growth on white water and highest activity against the DCS components present in the TMP white water.

Fungal enzyme treatment of DCS components present in the mill white water and model recycled white water

Effects of fungal removal of DCS components (appendix 3)

The efficiency of fungal removal of white water DCS components was tested. The results showed that most carbohydrates and extractives were depleted after 2-3 days of treatment under 30°C. However, the lignin content remain unchanged even after 7 days treatment. The long retention time and limited temperature range of fungal treatment make it impossible to be used in a mill situation. Compared to fungal treatment, enzyme treatment has the advantage of quick reaction time and resistance to higher temperature. A combined fungal enzyme treatment system was proposed to be used as an internal treatment “kidney” in a integrate paper mill with a closed water system. The principle of this system is shown in appendix 4. A small portion of the white water will be cooled down and fed into a bioreactor used to grow the fungi. The water components will be consumed during fungal growth and enzymes required to break down the substrates will be released into the water. By collecting the culture filtrates at the appropriate time, a

highly active fungal culture filtrate (FCF) could be obtained. Because DCS substances present in white water are the only nutrition source for the fungi, the enzymes produced in the culture filtrate should be specific for the DCS components. The FCF produced will continuously decant into the process water so the enzymes can react with the DCS components while the whole paper making process continues.

The efficiency of fungal culture filtrate removal of DCS components (appendix 5)

Fungal culture filtrate (FCF) produced from *Trametes versicolor* was used to treat the model recycled white water and mill white water. A significant decrease in total dissolved and colloidal substances, and carbohydrates in both water samples was observed. The FCF also showed considerably high activity against most extractives present in the white water, with a reduction of more than 90% for the lignans, steryl esters and triglycerides and about 20-50% for the resin and fatty acids.

Pure enzyme treatment of white water (appendix 2)

To obtain a better understanding the impact of the FCF as well as different groups of enzymes on process waters, we treated model recycled white water and colloidal free white water with commercial sources of the three main types of enzymes (hemicellulase, oxidative enzymes and lipases) found in the *Trametes versicolor* culture filtrate. The results showed that laccase treatment degraded most of the extractives while lipases specifically hydrolyzed ester-bonded extractives present in the colloidal fraction.

SUMMARY

Through two and half years work, the detrimental effects that dissolved and colloidal substances present in mechanical pulp/newsprint mill process waters will have on the paper properties have been clearly defined. A combined fungal enzyme treatment has shown a great potential to remove most of these detrimental substances from mill process water system. The future work will be: 1) To assess the continuous operation of treatment reactor; 2) To determine the half-life of each enzymes present in the fungal culture filtrate at elevated temperatures; 3) To determine which DCS components are recalcitrant to enzyme treatment; 4) To scale up of the treatment to pilot plant level

ARTICLES IN PEER-REVIEWED JOURNALS

Zhang, X., Beatson, R.P., Cai, Y.J. and Saddler, J. N., " Accumulation of Specific dissolved and Colloidal Substances During White Water Recycling Affects Paper Properties." Journal of Pulp And Paper Science 25(6):206-210 (1999).

Stebbing, D., "The Potential of Fungal Culture Filtrate to Reduce Extractive Levels in Newsprint White Water System." Pulp And Paper Canada 103(3): 46-49 (1999). (*Winner Paper for National Undergraduate Student Problem Solving Award from the Pulp and Paper Technical Association of Canada*)

RESEARCH PAPERS INCLUDED IN CONFERENCE PROCEEDINGS

Beatson, R.P., Zhang, X., Stebbing, D. and Saddler, J. N., " The Dissolved and Colloidal Fractions of White Water: Impact on Paper Quality and Degradation by Enzymes" 10th International Symposium on Wood and Pulp Chemistry, Yokohama, Japan, June 7-10, 1999. Vol. I:200-203 (Oral Presentation)

Saddler, J. N., Zhang, X., Stebbing, D. and Beatson, R.P., "The Different Effects of White Water Dissolved and Colloidal Fractions on Paper Properties and Effects of Enzyme Treatments on Their Removal." PACWEST Conference, Whistler, BC Canada, May 19-22, 1999, Session 4A, Paper 2. *(Oral Presentation)*

Zhang, X., Beatson, R.P., Chalmers, B.G., Francis, D.W. and Saddler, J. N., "Paper Quality Problems Caused by the Different Organic Components of Newsprint White Water. Can they be Solved by Enzymes?" In Proceedings of the 1999 Sustainable forest Management Network Conference p680, Edmonton Albert, February 14-17, 1999. *(Oral Presentation)*

Zhang, X., Beatson, R.P., Stebbing, D. and Saddler, J. N., "The Different Effects of White Water Dissolved and Colloidal Fractions on Paper Properties." In Proceedings of the 1999 Sustainable forest Management Network Conference p811, Edmonton Albert, February 14-17, 1999. *(Post Presentation)*

Zhang, X., Cai, Y.J., Stebbing, D., Beatson, R.P., and Saddler, J. N., "Influence of Accumulated Dissolved and Colloidal Substances on Paper Properties and the Potential of Enzyme Treatment for Component Removal." 7th International Conference on Biotechnology in the Pulp and Paper Industry, Vancouver, BC Canada, June 16-19, 1998, Vol. C:151-154 *(Post Presentation)*

Cai, Y.J., Zhang, X., de Jong, E., Beatson, R.P., and Saddler, J. N., "Fungal Treatment of Organic Contaminants Present in the White Water of a Thermomechanical Pulp Mill." 7th International Conference on Biotechnology in the Pulp and Paper Industry, Vancouver, BC Canada, June 16-19, 1998, Vol. C:155-158 *(Post Presentation)*

APPENDICES (Hard copy only)

Appendix 1: **Zhang, X., Beatson, R.P., Cai, Y.J. and Saddler, J. N.,** " Accumulation of Specific dissolved and Colloidal Substances During White Water Recycling Affects Paper Properties." Journal of Pulp And Paper Science 25(6):206-210 (1999).

Appendix 2: **Beatson, R.P., Zhang, X., Stebbing, D. and Saddler, J. N.,** " The Dissolved and Colloidal Fractions of White Water: Impact on Paper Quality and Degradation by Enzymes" 10th International Symposium on Wood and Pulp Chemistry, Yokohama, Japan, June 7-10, 1999. Vol. I:200-203 (Oral Presentation)

Appendix 3: **Cai, Y.J., Zhang, X., de Jong, E., Beatson, R.P., and Saddler, J. N.,** "Fungal Treatment of Organic Contaminants Present in the White Water of a Thermomechanical Pulp Mill." 7th International Conference on Biotechnology in the Pulp and Paper Industry, Vancouver, BC Canada, June 16-19, 1998, Vol. C:155-158 *(Post Presentation)*

Appendix 4 (poster and paper): **Zhang, X., Cai, Y.J., Stebbing, D., Beatson, R.P., and Saddler, J. N.,** "Influence of Accumulated Dissolved and Colloidal Substances on Paper Properties and the Potential of Enzyme Treatment for Component Removal." 7th International Conference on Biotechnology in the Pulp and Paper Industry, Vancouver, BC Canada, June 16-19, 1998, Vol. C:151-154 *(Post Presentation)*

Appendix 5: **Stebbing, D.,** "The Potential of Fungal Culture Filtrate to Reduce Extractive Levels in Newsprint White Water System." Pulp And Paper Canada 103(3): 46-49 (1999). (*Winner Paper for National Undergraduate Student Problem Solving Award from the Pulp and Paper Technical Association of Canada*)