EXECUTIVE SUMMARY

BACKGROUND

Efforts are made by the pulp and paper industry to reduce the chloroorganic and chloride discharges by the substitution of chlorine-containing chemicals with other more environmentally friendly bleaching agents such as hydrogen peroxide, oxygen and ozone. In response to the environmental concerns and stringent emission standards, modifications of the production process at the pulping and bleaching stages have been developed that can reduce the levels of absorbable organic halogen and toxic effect of the pulping and bleaching waste waters. The bio-utilization of industrial waste waters in production of high-value products such as enzymes and the use of enzymes in bio-bleaching to reduce the chemical consumption of chlorine-based bleaching agents present new environmentally sound technologies that can significantly minimize the environmental impact of the pulp and paper industry.

OBJECTIVES

- Development of a bioremediation and biobleaching technology to minimize the use of hazardous chlorine-based bleaching chemicals which would produce certain economical benefits as well as reduce the environmental impact of the pulp and paper industry.
- Development of a microbial fermentation technology of pulping waste waters to obtain high-value products such as enzymes to be utilized in a biobleaching process for environmental clean-up and upgrading the quality of pulp and paper products.

RESEARCH APPROACH

Remediation of industrial waste waters from the pulp and paper industry was investigated using bleaching with enzymes, biomimetic systems (polyoxometalates) and microbial fermentation processes. The waste waters under study were derived from the pulping and bleaching stages of pulp production. Two industrial pulp types were examined for their bleachability with enzymes: hardwood soda-aq pulp and bagasse soda-aq pulp. Following enzymatic treatments, pulp properties such as brightness, viscosity, kappa number, etc.

were determined according to the Standard Methods of the Technical Association of the Pulp and Paper Industry (TAPPI, Atlanta, USA). Most of the waste water analyses such as chemical oxygen demand, colour, solid content, etc. were carried out as described in the Standard Methods for Examination of Water and Waste Water (APHA, American Public Health Association, Washington, DC, USA). Fermentation experiments for enzyme production were carried out in shake flasks and bioreactors in batch and fed-batch cultures. Evaluation of cultivation conditions was based on the levels of xylanase activity produced. The efficiency of various approaches of waste water bioremediation was evaluated mainly based on the impact on chemical load, toxic effect, chloride content and chlorinated organic matter.

RESEARCH

Polyoxometalate-based waste water bioremediation

- Polyoxometalate (POM) pretreatment of hardwood soda-aq pulp enabled chlorine dioxide savings of 10% compared to alkaline oxygen control and 50% compared to the acid oxygen control while retaining brightness at the control level.
- POM pretreatment of bagasse soda pulp could replace the entire chlorine bleaching step without loss in final pulp quality. In addition, up to 50% of the hypochlorite charge could be reduced without deterioration of bagasse pulp properties.
- The use of POM in pulp bleaching represents an alternative bleaching technology that can offer a significant reduction of the consumption of chlorine-containing bleach chemicals with reduced environmental impact. However, further studies are required to demonstrate the reusability and economical viability and determine the environmental impact of this technology.

Xylanase-based waste water bioremediation

- It has been demonstrated that implementation of the enzyme bleaching technology in the pulp and paper industry could improve the existing technology of pulp and paper manufacture in a cost-effective and environmentally friendly way.
- Biobleaching of bagasse pulp with xylanase (X) afforded reductions in sodium hypochlorite (32%) and sodium hydroxide (20%). Similarly, reductions of chlorine

dioxide (30%) and sodium hydroxide (20%) were possible during biobleaching of soda-aq pulp.

- Overall improvements in the bleach filtrate quality could be achieved when xylanase treatment was employed prior to bleaching. The major impact of the reduction of the active chlorine charges during biobleaching was on the chloride, adsorbable organic halides (AOX) and toxic effect levels (as determined by the bacterial growth inhibition test) of the bleach waste waters. Overall, the AOX content correlated well with the bacterial growth inhibition caused by the bleach filtrates. It was evident that the use of chlorine containing chemicals during bleaching was the major cause of bacterial growth inhibition in the resulting waste waters. In addition, the reduction of the amount of chlorinated compounds would minimize also their teratogenic effect.
- Introduction of a washing step between X and D_1 stages during soda-aq bleaching might prevent problems such as the overloading of the plant waste water treatment system. The wash waters from the xylanase stage might be treated separately or even utilised for biotechnological applications. Alternatively, the xylanase-stage chemical oxygen demand (COD) can be sent to the recovery system of the mill where the organic matter will be utilized for heat generation and use in the mill.
- The reductions in the use of bleaching chemicals would not only minimize the impact of the pulp and paper waste waters on the environment, but also lead to cost savings for the industry. For instance, savings of 5.25 kg of ClO_2/t pulp and 1.4 kg NaOH/t pulp could be obtained as result of the enzyme bleaching. This can be translated into cost savings in excess of R2 million per annum.

Bio-utilisation of waste water for xylanase production with the fungi *Aspergillus oryzae* and *Aspergillus phoenicis*

- A comparison of xylanase activities obtained with *Aspergillus oryzae* NRRL 3485 showed that higher xylanase activities of up to 200 U/ml were obtained in batch cultures than in shake flasks (30 U/ml) cultures using the concentrated spent sulfite liquor (SSLc) as carbon feedstock at 20-fold dilution.

- The fed-batch cultivation of *A. oryzae* NRRL 3485 using SSLc as carbon substrate yielded activities of up to 200 U/ml, which was two-fold higher than activities obtained in batch cultures under similar conditions (40-fold dilution).
- The chemical composition of the SSL waste waters revealed that concentrating the waste water reduced the amount of acetic acid, thereby minimising the inhibitory effect the acid may have on microbial growth during utilisation of SSLc as carbon feedstock.
- The considerably high biomass concentrations obtained with SSLc as carbon feedstock could be attributed to the utilisation of additional carbon present in the SSLc, as is indicated by the total organic carbon (TOC) results.
- Xylanase production using SSLc as carbon feedstock indicated that the SSLc acted as inducer. Being a cheap carbon substrate, xylanase production costs would be greatly reduced and possibly enhance the economic viability of the biobleaching technology.
- Xylanase production using SSLc was favoured by a high culture pH of 7.5. The agitation rates between 400 to 800 rpm did not have any adverse effect on xylanase production. A better understanding of the limiting factor would enable even higher activities being achieved.
- The xylanases from both *A. oryzae* NRRL and *A. phoenicis* ATCC 13157 exhibited multiplicity. The *A. oryzae* xylanase showed unusual pH and temperature optima not generally exhibited by fungal xylanases. A higher level of pH stability was shown by the xylanase preparations from this fungus.
- The application of SSL-grown fungal xylanases in biobleaching resulted in a reduction in the use of active chlorine of up to 30 %. The xylanases increased the pulp brightness by up to 1.5 brightness points over the control. The application of these xylanase enzymes, produced with SSLc as carbon feedstock is highly significant.
- Xylanase production using SSLc as carbon feedstock indicated that the SSLc acted as carbon source and enzyme inducer. Overall, the xylanase yields in shake flasks obtained with both *A. oryzae* and *A. phoenicis* on SSL-based growth media were about 2-fold higher than those produced on xylan-based media. Furthermore, the xylanase activities induced in batch cultures on SSL and xylan were comparable.

- Since the carbon source in general constitutes 30-50% of the total enzyme production costs, the eventual replacement of xylan with SSL as inexpensive and abundant carbon substrate would result in significant cost reductions associated with xylanase production and enhance the economic viability of the biobleaching technology.

CONCLUSIONS

- It has been demonstrated that the implementation of the enzyme bleaching technology in the pulp and paper industry could improve the existing technology of pulp and paper manufacture in a cost-effective and environmentally friendly way. The use of enzymes can reduce the amount of chlorine-containing chemicals employed in bleaching. This impacts directly on the levels of toxic effects, chlorides and adsorbable organic halides of the waste waters.
- The use of polyoxometalates in pulp bleaching represents an alternative bleaching technology that can offer a significant reduction or complete elimination in the use of chlorine-containing bleach chemicals. However, further studies are required to demonstrate the reusability and economical viability and determine the environmental impact of this technology.
- The potential of pulp mill waste waters for biotechnical utilization has been demonstrated. The bio-utilization of these waste waters would alleviate problems associated with their discharge. Furthermore, the xylanase enzymes produced on the spent sulphite liquor could be successfully applied in biobleaching of pulp. This would further contribute to the overall reduction of the environmental impact of the bleach waste waters.