

Role of Biotechnology in the Pulp & Paper Industry : A Review Part 3 : Effluent Treatment

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ABSTRACT:-- This is the third part of a three part review of Role of Biotechnology in the Pulp and Paper Industry. Various effluents from kraft pulp and paper factories have the potential to colour the receiving water. Bleaching waste water supplies most of the total colour loading, with caustic extraction stage being responsible for 70-75% of it. The conventional physicochemical colour removal processes based on precipitation, adsorption, chemical oxidation or concentration of colour bodies are relatively expensive and have not been a satisfactory solution to the colour problem. On the other hand, effluent treatment has been a stronghold of biotechnology for reducing BOD, COD, AOX and colour from effluents. New, research on the use of bacteria and fungi to degrade and detoxification of chlorinated organics in the effluent may yield technologies that the industry can apply.

In part 1 and 2 of this series, biotechnology was defined as the use of biological organisms in bio-pulping¹ and bio-bleaching². Hence, we continue with a review of bio-technology research in effluent treatment. Pulp and Paper industry discharges a huge amount of waste water per day into receiving waters. The major pollutants in the effluent are bio-chemical oxygen demand (BOD), chemical oxygen demand (COD), colour and total organic chlorine (TOCl). These pollutants

discharge of oxidizable, soluble organics³. Characteristics of the effluents depend upon the raw materials used and pulping and paper making process. The pollution load from hardwood is lower than for softwood. Higher BOD, COD, TOCl reduction efficiencies were achieved for hardwood bleaching effluent. Characteristics of effluents from large intergrated mills based on bamboo and hardwood, newsprint, agrobased and waste paper mills is given in Table⁴-1.

Table-1⁴

Characteristics of effluent from Pulp and Paper Mills

Particulars	Waste Paper Based Mills	Agro based Small Paper Mills	Newsprint Mills	Integrated Pulp and Paper Mills
Raw Materials	Waste Paper	Rice straw, wheat straw, Bagasse etc.	Bamboo, Salai, hardwoods	Bamboo & hardwoods
Waste water (m ³ /Tonne)	70-150	200-380	200	250-350
pH	6.0-8.5	6.0-8.5	7.2-7.3	6.0-9.0
BOD ₅ (Kg/Tonne paper)	10-40	85-270	42-45	35-50
COD (Kg/tonne paper)	50-90	500-1100	130-135	150-200
Suspended solids (Kg/Tonne paper)	50-80	90-240	95-100	100-150

have caused serious water quality problems in receiving waters. Some of the problems are sludge banks caused by suspended solids and organic matter such as bark, fine and fibre, fish kills due to oxygen depletion and toxicity and slime infestations resulting from the

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Pulping, Bleaching and Paper making are the three major waste water sources for the Industry. In the modern pulp and paper mill, the pulp mill effluent is burned in the recovery system to recover pulping chemicals and energy. Effluent from paper making machines is reduced by internal measures such as the installation of savealls to recover the fibre and additives and by white water recycling to save water and energy costs. The low molecular weight fraction of the chlorolignins is the main contributor to the effluent BOD and acute toxicity, while the high molecular weight portion for colour, COD and chronic toxicity^{5,6}. High molecular weight chlorolignins are resistant to bio-degradation & have a potential to be bio-accumulated in the environment, or they are degraded at a very slow rate resulting in the possible production of low molecular weight toxic intermediates.

Future effluent regulation may require the pulp and paper industry to substantially reduce non-conventional pollutants such as colour and total organic chlorine (TOCl). TOCl and colour can be reduced by (a) Process modification can range such as improved pulp washing, modified pulping for extended delignification, oxygen bleaching and high chlorine-di oxide substitution in the chlorination stage. In plant, a variety of effluent treatment schemes have been studied, including Chemical precipitation, Ozonation, Carbon adsorption, Ion exchange resin adsorption, Ultra filtration, and Reverse osmosis⁷. Even though some of these methods are excellent colour removal processes, all of them have certain basic problems such as excessive cost per unit volume of effluent treated or unreliability.

Inherent problems associated with each process will probably deter their use as a colour removal technology within the pulp and paper industry. To date, microbiological treatment is the best available technique for reducing the colour and toxicity of the effluents.

Biological colour removal may hold considerable promise in decolourisation technology. The cost of biological effluent treatment is usually about one order of magnitude less expensive than either chemical or advanced waste water treatment. The biological treatment systems currently used in the pulp & paper industry are successful in reducing BOD.

However, within the time frame of a biological treatment system, bacteria cannot significantly reduce the COD or colour of the effluent. Bacteria are capable of metabolizing soluble sugars and some low molecular weight compounds in the effluent, thereby reducing the BOD, but they do not have an enzyme system capable of oxidizing lignin rapidly.

Ganczarczk,^{9,10} et.al., propose that lignin fragments present in a simulated kraft mill effluent, when subjected to aeration, are oxidatively condensed to produce higher molecular weight products that may be precipitated or absorbed onto the bacterial biomass in a biological treatment system. The principal method of lignin removal in an activated sludge process can be attributed to physical absorption onto the bacterial biomass followed by removal concurrent with sludge wasting.

Joyce, et.al.¹¹, have demonstrated that the biological treatment using activated sludge does not significantly change the chemical character of the colour bodies. Algae in environmental waters may play a significant role in the natural reduction of colour originating from pulp mill effluent. Algae cultures when incubated in a diluted nutrient solution of effluent reduced the colour content by approximately 50% over a 20 day period.

In contrast to bacteria and algae, fungi are capable of oxidizing lignin to low molecular weight degradation products, even to CO₂ and water in a relatively short time span. The fungi possess the most active ligninolytic enzyme system known and therefore present a largely unexplored and untapped potential for a new type of biological treatment.

Eaton, et.al.¹², have demonstrated that *Phanerochaete chrysosporium*, a white rot fungus can decolourise the highly coloured E₁, stream originating in the kraft bleach plant. This fungus has some basic nutrient growth requirements which include calcium, magnesium, nitrogen, phosphorous and a primary carbon source such as glucose or cellulose. The mycelium growth stage requires nitrogen, while decolourization is reduced in the presence of nitrogen. The colour removal process is a secondary metabolic pathway which requires a primary carbon source as glucose or cellulose for energy.

Presumably, the energy requirements of the organism are not met in the degradation of colour bodies. *Phanerochaete chrysosporium* is capable of reducing the colour in the E₁ stream by 60% in 2-4 day. Livernoche et.al.¹³ and Royer et.al.¹⁴ have experimented with another white-rot organism, *coriolus versicolor*, they also reported 80% colour removal in three days of treatment. The combined treatment of *coriolus versicolor* with ozone effectively destroyed effluent chromophores but the fungal attack resulted in greater degradation, as expressed in terms of COD removal of dialysed macromolecules¹⁵.

Pulp and Paper mill effluent was decolourised by growth of *Aspergillus niger*. Adding glucose and ammonium hydrogen phosphate improved decolourization by the fungus and reduced the BOD₅ (43%) and the COD (41%) of the effluent after 48 hrs of incubation, Table-2¹⁶. Prasad et.al.¹⁷ studied the effect of *Trichoderma* sp. on lignin degradation and decolourising the hardwood extraction-stage bleach plant effluent. The results show that under optimal conditions, total colour and COD decrease by almost 85% and 25% respectively, after cultivation for three days. Glucose was the most effective carbohydrate utilised by the fungus, as it stimulated substantial colour reduction without any increase in COD.

Bergbauer et.al.¹⁸ have demonstrated that the Coelomycete *Stagonospora gigaspora* degrades lignin derivatives within pulp mill bleachery effluent. Besides dechlorination, 90% of the colour was removed from CEH bleachery effluents. Lignin derivatives in the effluents of EOP bleaching stages revealed more persistent against fungal attack.

Toxicity of both effluents was diminished significantly by *S. gigaspora*. Preliminary studies^{19,20} conducted on other white rot fungi such as *Polyporus* & *Fomes* showed substantial colour reduction for mill effluents. Beslare and Prasad²¹ demonstrated the decolourisation efficiency of *Schizophyllum commune*.

In order to maintain a continuous colour removal process, the fungi must remain in the secondary metabolic state for long periods. A rotating biological surface or contactor (RBC) is the most promising technology for fungal growth. The high oxygen requirements of the fungus can be easily satisfied by contacting an enriched oxygen atmosphere with the biomass as it rotates. The RBC effectively mixes the effluent while providing a continually renewable interface between the fungus and the effluent.

Disposal of fungal biomass from a continuous flow system could be a potential problem. The used or spent mycelium can be heat-sterilized and reused as a source of nutrients. *P. chrysosporium* grown in a medium made from heat-sterilized mycelium, decolorised E₁ at the same rate as a control in a normal nutrient system²².

Fungi have extremely active ligninolytic enzyme in comparison to bacteria. This feature makes them especially interesting for biological applications in which lignin or its degradation product must be chemically altered. The potential benefit of a fungal bio treatment system to pulp and paper industry is enormous. The BOD and COD are each reduced by 50% concurrent with 60% decolourisation in the treated effluent.

Table-2¹⁶

Effect of different concentration of glucose on decolourisation of the paper mill effluent both alone and by the action of *Aspergillus niger* after 48 hr of incubation

Characteristics	Uninoculated					A niger inoculated			
	0	0.5	1.0	1.5	2.0	0.5	1.0	1.5	2.0
Glucose (g/l)	0	0.5	1.0	1.5	2.0	0.5	1.0	1.5	2.0
pH	7.3	7.1	6.8	6.8	6.6	6.4	6.0	5.7	5.5
Colour units	1000	900	870	820	750	470	380	260	190
BOD ₅ (mg/l)	152	140	131	127	120	124	106	97	87
COD (mg/l)	321	312	298	284	279	259	244	202	191

Colour Units - Platinum - Cobalt units.

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