BIO-TECHNOLOGY - APPLICATIONS IN WASTE UTILISATION AND POLLUTION ABATEMENT

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ABSTRACT

Bio-technology, in simpler terms, means the technological use of biological agents and encompasses much more than genetic engineering. In the paper and pulp industry, it includes many aspects of the growing of trees, facets of processing wood and pulp, the utilization of the wastes and the byproducts. In wood processing, bio-technology offers the tentalising prospects of bio-pulping, bio-bleaching and biological improvement of mechanical pulps. Alternative uses of wood through bio-processing can also be envisioned, particularly for wood that is unsuitable for pulping and wood residues generated during the harvesting and processing of forest produce. Yet another example of the potential of bio-technology is in decolourising of the pulp mill waste water.

The pulp and paper industry already depends on microbial technology. Oxidation ponds, lagoons and activated sludge basins are some of the examples which have already gained wide acceptance.

The role of micro-organisms in waste utilisation and pollution abatement are discussed in the paper. The results of SPB-PC's research efforts in this area are also briefly discussed in the paper.

INTRODUCTION

Bio-technology, in simpler terms, is the use of biological agents. Human progress in mastering nature has been slow mainly due to the difficulties in harnessing the biological process. The biological organism are intricately interconnected with our day-to-day life. Domestication and breeding of animals, cultivation of crops, preservation of food and feed materials are only a few to mention.

Delignification has been one of the main hurdles faced by the paper and pulp industry. This is currently brought about by high

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energy demanding physico-chemical processes. However in nature, the same is brought about by the micro-organisms without the need for any external source of energy. This is achieved mainly by the 'enzyme machinery' which these microbes are endowed with.

Besides cellulose, lignin is the next most abundant organic compound in nature. The biological degradation of lignin is one of the most important part of the biospheric carbon and oxygen cycle. Much of the lignin biosynthesised by the plants is mineralised and returned to atmosphere as carbon-di-oxide. Accumulated evidence suggests that lignin degradation by micro-organisms proceeds by way of extra cellular mixed function enzymes oxygenases and dioxygenases. These catalyse the demethylation, hydroxylation and ring-fission reactions.

The range of micro-organism that can degrade lignin include a wide variety of fungi and bacteria. Excellent reviews that primarily discuss the lignin decomposing group of organisms have been published (Kirk, 1971). Lignin is, structurally, a complex three-dimentional polymer of phenyl proponoid groups that are not easily degradable. There are many organism that are capable of degrading lignin partly. The fungi are the most important of the many group of organisms.

Bio-technology has the potential that can be put to beneficial use by the paper and pulp industry, in many areas. The industry already depends on microbial technology to treat its manufacturing wastes. Oxidation ponds, lagoons, Unox reactors, activated sludge treatment, rotating biological contractors and others are all unit operations making use of mixed populations of microbes to destroy or detoxify wastes.

LIGNIN DEGRADATION BY MICRO-ORGANISMS

In nature there is a continuous degradation, of dead plant material by saprophytic micro organism. To degrade woody material is mainly a task for fungi. Different types of fungi give rise to different types of rots. One normally distinguishes between soft-rot, brown-rot and white-rot fungi. The blue staining fungi are also associated with wood damage.

SOFT-ROT FUNGI

A variety of ascomycetes and fungi impercti belong to this group. Soft-rot fungi is characterised by attack on wood under moist conditions. The decay is frequently accompanied by a softening of the surface Distinct cavities can be identified in the secondary wall layer. Lignin degrading ability of these have been reported to be anywhere between minimal to substantial (Eslyn et al.,1975).

BROWN-ROT FUNGI

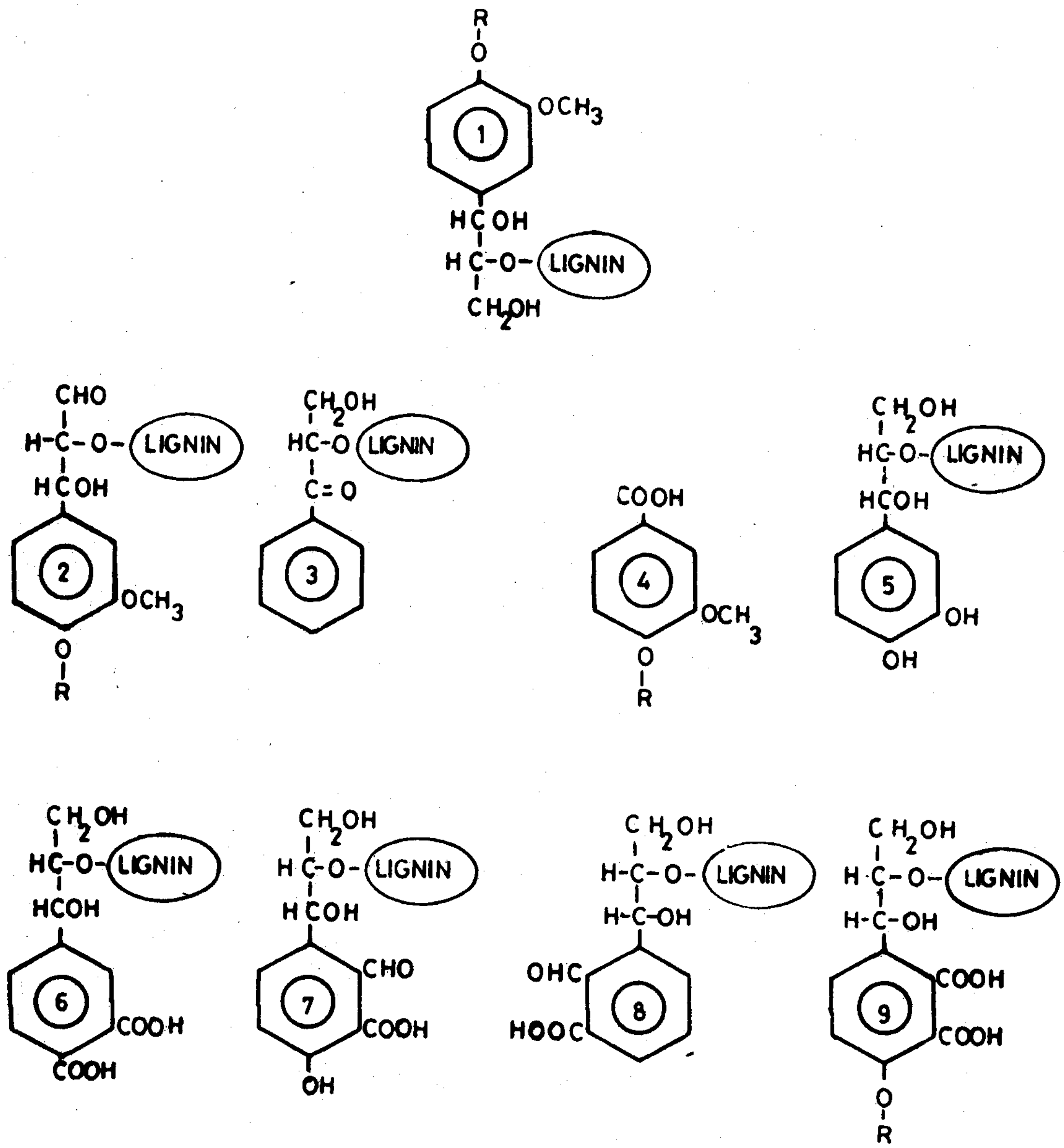
Numerous basidiomycetes are included in this group. All these fungi preferentially degrade cellulose when compared to lignin. Lignin is depleted only slightly (Kirk, 1975).

WHITE-ROT FUNGI

This group is mainly composed of the basidiomycetes. These fungi have emerged as the only micro-organism with the conclusively proven capability of totally degrading lignin to carbon dioxide and water (Kirk, 1971). It has been demonstrated that under optimal environmental conditions, these fungi can completely decompose lignin.

The mode of degradation by white-rot fungi has been more or less well worked out. The enzymology of lignin degradation is now beter understood. The types of reactions which proceed are indicated in Fig. 1. The following steps are believed to take place:

1. Terminal Alcohol Oxidation
2. Carbonyl Formation.
3. Side Chain Shortening
4. Demethylation to O-diphenolic Structure
5. Ortho ring clevage - I
6. Meta ring clevage
7. Ortho ring clevage - II



R– REPRESENTS H OR AN ETHERIFIED INTERMONOMERIC LINKAGE.

1. UNALTERED C-9 GUIACYL UNIT
2. TERMINAL ALCOHOL OXIDATION
3. CARBONYL FORMATION
4. SIDECHAIN SHORTENING
5. DEMETHYLATION
6. ORTHO RING CLEVAGE-I
7. META RING CLEVAGE
8. ORTHO RING CLEVAGE-II

KINDS OF OXIDATIVE REACTION PRODUCTS CHARACTERISTIC OF WHITE ROT LIGNIN DEGRADATION

FIG. 1.

UTILISATION OF BYPRODUCTS

Microbial technology offers new approaches to the utilisation of wood residues from harvesting and manufacturing wastes. Lignin serves as a tremendous renewable raw material for various processes. Bio-conversion produces a variety of chemicals, many of which are presently derived from petroleum industry. As oil resources dwindle and price for oil-based chemicals continue to rise, alternative raw materials will have to be found. Lignin is a logical choice not only because of its structural properties but also because of its abundance as a waste and its value as a renewable resource.

Kraft lignin, in particular, can be utilised as a source of fuel (Hoyt et al., 1975). Waste lignin such as lignin sulphonates and kraft lignin are now used for the synthesis of a variety of products. Products like emulsifiers, stabilisers, grinding aids, binders and dispersants use these reactive lignins as additves which enhance the properties of the specific products.

One of the many important bio-conversion processes may be in the production of low molecular weight compounds from waste lignin. A number of these can act as suitable substitutes for products derived from petroleum (Goheen, 1971). Compounds such as vanillin, dimethyl sulphonates, dimethyl sulphoxide, furfural, methylmercaptan etc can be produced in low quantities by controlled hydrolysis of waste lignosulphonates. Phenolics can also be produced by pyrolysis.

FERMENTATION

Although originally this term was used to describe the release of carbon dioxide during wine-making, it is now commonly applied to any large scale industrial microbial process. Classical fermentation requires that the cellulose and the hemicellulose be hydrolysed to simpler sugars by direct acid treatment of the wood. Unfortunately, the yield of glucose by this process is at the most 50 % and further byproducts formed, interfere with the fermentation process. In contrast enzymatic hydrolysis by fungi and other micro organism render the cellulose and the hemicellulose more accessible for reaction and can give yields close to the theoretical maximum. The intereference by byproducts can also be over-come by this. The resulting sugars are suitable for any type of fermentation. An approach that has received considerable attention is a single stage fermenter. Certain microbes are being studied that can both hydrolyse the polymer and ferment the resulting sugars (Zeikus, 1980). Technology is emerging rapidly for the fermentation of pentoses that are released from hemi-celluloses by mild acid hydrolysis. A combination of these alongwith hexoses has profound effect on total wood hydrolysis.

Further, advances can be expected with utilisation of immobilised enzymes and cells and novel methods of fermentation. Major research problems in the bio-conversion of wood include development of pro-cesses for -

a) Economical pretreatment
b) Cost effective cellulose production and recovery
c) Improved yield and rates in pentose fermentation
d) Improved product recovery

Direct conversion of wood into food is possible by the degradat-ion of lignin into smaller units by fungi. Production of microbial proteins which can be used as fodder, appears to be a distinct possi-bility (Bailey and Jones, 1971). The second largest commercial pro-duction of the mushroom Lentinus edodes is on wood residues. These were cultivated on small diameter Oak billets. Recent research has shown that the growth of the mushroom can be increased ten-fold by raising them in a mixture of the wood and its bark. This is Japan's largest agricultural export.

POLLUTION ABATMENT

Pulp mills contribute substantially to the pollutants in the waste water. Although most of the pulp mill liquor are recycled to produce heat and steam and for the recovery of the inorganic chemicals, the small portion of the liquor fraction that is not recovered plus the inevitable spillovers and the wash-ups still contribute to nearly a third of the pollution load from the mill. The overall bleaching process involves the solubisation of and removal of the non-fibrous components from the unbleached pulp. Lignin and its derivatives are the major contributors to the colour, BOD and COD. The chromophore-containing compounds in the E_1 stage effluent are predominantly polymeric chlorine-containing oxidised lignin fragments with a low aromatic content (Sundman et al., 1981). In addition, the effluents from this stage also contribute to the solids load.

As a consequence of the oxidation by chlorine, most of the residual lignin and small amounts of the carbohydrates in the unbleached pulp are degraded into water and alkali soluble substances. These components mainly consist of phenolic and carbohydrate oligomeres and neutral and acidic derivatives of phenols due to ring clevage.

The most common method of effluent treatment is to treat them in conjugation with the effluents derived from other sources in the mill. The known approaches to the removal of the colour include coagulation, membrane process, absorption to other colloids, ion exchange, photochemical process and ozonisation. However, the high cost involved in all these processes serve as the major draw back in commercial exploitation.

An example of the potential application of bio-technology is in decolourizing of the effluent. Fungi have been shown to break-down the chromophore bearing polymers into low molecular weight colourless, soluble/volatile products (Sundmann et al., 1981). The white-rot fungi have been used in these processes.

In view of the fact that most of these studies have been carried out using an isolate of Sporotrichum pulverulentum which is a temperature species, a systematic study with a number of isolates of indigenous origin has been taken up. India, being a tropical country; the isolates are expected to be more efficient in their decolourising ability.

RESEARCH EFFORTS BY SPB-PC

Under an arrangement with Tamil Nadu Newsprint and papers Limited (TNPL), SPB-PC has undertaken a long-term research programme on the applications of bio-technology in the Pulp and Paper industry. Treatment and management of wastes, forms a priority area of the research works.

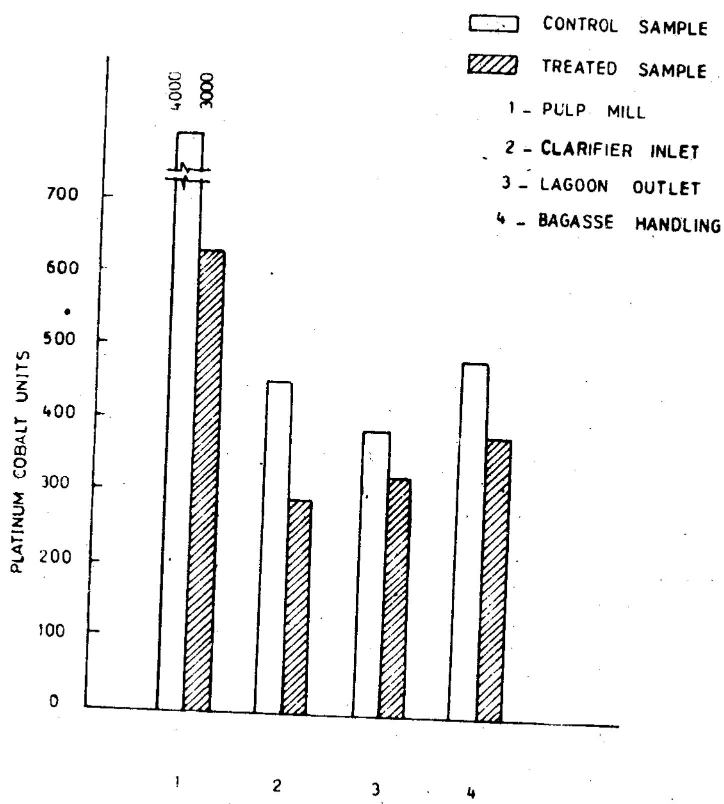
A number of collection trips were taken up and more than 20 white-rot fungi were collected. Initial screening indicated the suitability of an isolate SPVR 439 which has been used in the experiments reported here. The isolate is yet to be identified. Standard mycological techniques are being used for the isolation and maintenance of the cultures (Rawlins, 1933).

In the preliminary study, the following effluents were taken up for the study:

1. Pulp mill washings and screenings
2. Clarifier inlet
3. Bagasse handling and wet pile storage.
4. Aerated lagoon outlet.

As the retention time in the lagoon is about ten days, the treatment period was restricted to only six days, and beyond this period, the experiments were discontinued. In one set, the raw effluent, as such, was used and in another 1 % glucose was added to serve as an additional carbon source. The results are presented in Fig. 2. The addition of glucose as a supplementary carbon source has a significant effect in all the samples.

In the next set of experiments, various carbon sources were also included in addition to glucose. The carbon sources used were glucose, cellulose, pith and pulp. In the second set, nitrogen was also supplemented in the form of urea and diammonium phosphate. They

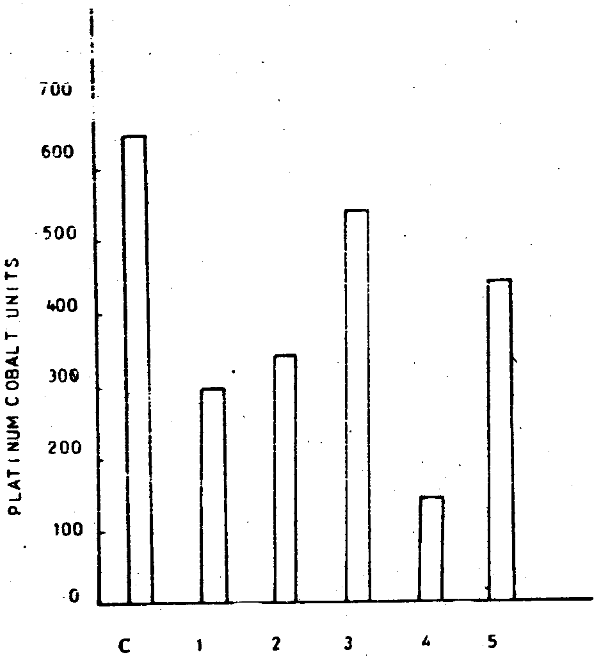


EFFECT OF FUNGAL TREATMENT ON VARIOUS EFFLUENTS.

FIG.2

were added in the ratio of 100 BOD units: 5 Nitrogen : 1 Phosphate. In the third set of experiments, the initial pH of the effluent was adjusted to 5 and only the various carbon sources were supplemented. The results are presented in Figs. 3,4 and 5.

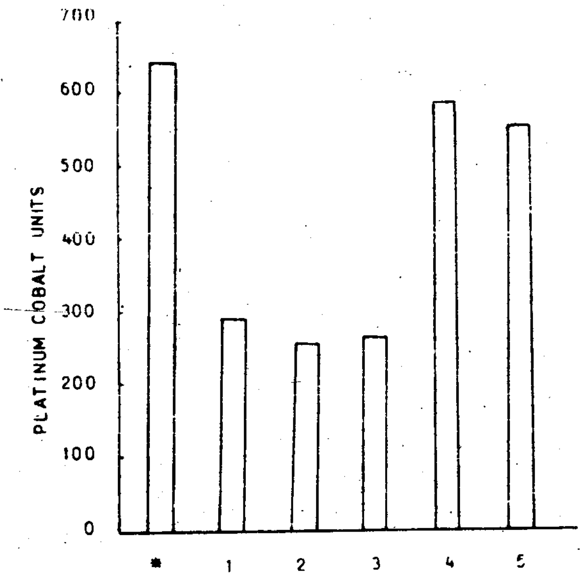
As was seen in the earlier experiment, addition of carbon influenced the rate of discolourization. Glucose caused 43 % to 58 % reduction in the colour, while pith had the most pronounced effect at 78 % reduction.



C-CONTROL, 1-1% GLUCOSE, 2-2% GLUCOSE, 3-1% CELLULOSE, 4-1% PITH.
5-1% PULP

EFFECT OF FUNGAL TREATMENT ON PULP MILL EFFLUENT SUPPLEMENTED WITH VARIOUS CARBON SOURCES.

FIG. 3.



* - CONTROL
1 - 1 % GLUCOSE, 2 - 2% GLUCOSE, 3 - 1% CELLULOSE, 4 - 1% PITH
5 - 1 % PULP.
NITROGEN WAS IN THE FORM OF UREA AND DI AMMONIUM PHOSPHATE

EFFECT OF FUNGAL TREATMENT ON PULP MILL EFFLUENT SUPPLEMENTED WITH CARBON AND NITROGEN.

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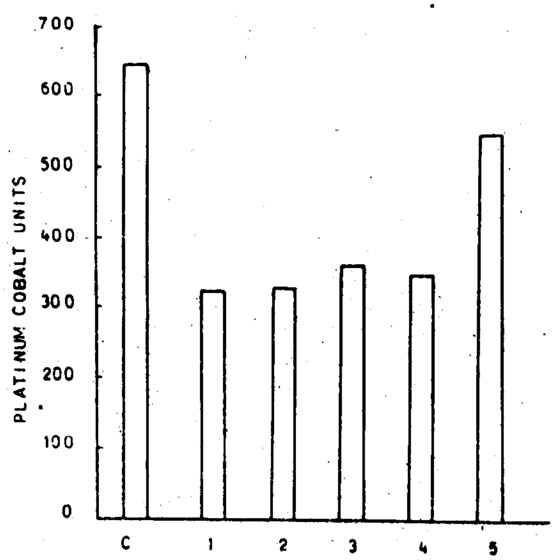

C - CONTROL, 1 - 1% GLUCOSE, 2 - 2% GLUCOSE, 3 - 1% CELLULOSE
4 - 1% PITH, 5 - 1% PULP.

EFFECT OF FUNGAL TREATMENT ON PULP MILL EFFLUENT INITIAL pH ADJUSTED TO 5.

FIG. 5.

In the second batch experiments with additional nitrogen sources, 56-61 % reduction could be achieved in a number of combinations.

If the initial pH is adjusted to 5, 40-50 %, reduction in the colour could be seen in most of the combinations.

However, the drawback of these experiments was that the addition of glucose significantly contributed to the BOD loads while the addition of pith reduced the pH to very acidic level. Hence these supplements have not been added in the subsequent experiments. The earlier experiments showed that fungal treatment has an effect on the waste water properties. Hence the sample volume was increased to 1 m^3. Aeration of the sample was included as another treatment. The results are presented in Fig.6. A reduction of 62 % colour could be achieved. The BOD and the COD reduced significantly by more tha 80 %. The BOD and the COD reduced significantly by more than 80 %. The BOD of the sample after treatment was only 25. However, caution is required in the interpretation of the data as the influence of the continuous aeration of the BOD cannot be ruled out. Experiments are underway to evalueate these and other parameters.

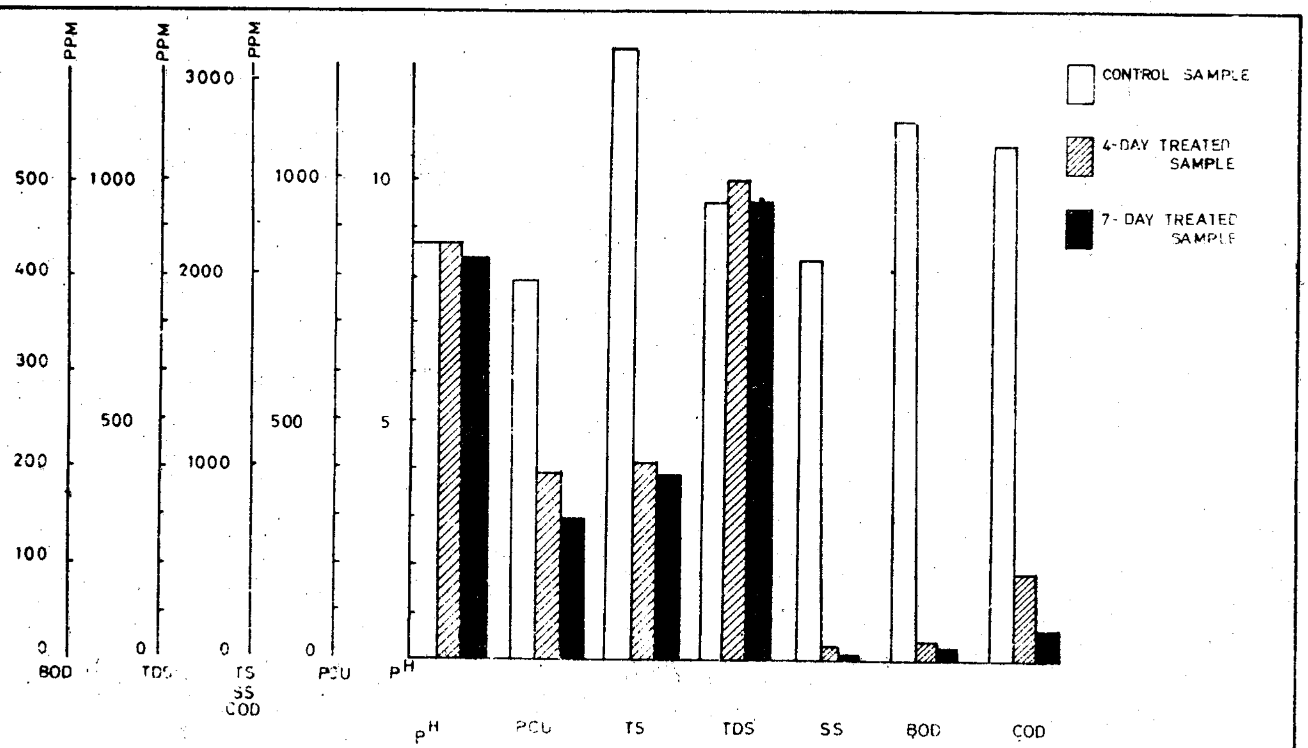

FIG.6. EFFECT OF FUNGAL TREATMENT ON THE WASTE WATER CHARACTERISTICS. (CLARIFIER INLET)

CONCLUSION

Bio-technology has the potential that can be put to beneficial use by the pulp and paper industry in many ways including the growing of superior trees, the processing of wood and pulp, the utilization of the wastes and the management of the wastes.

A survey of the total amount of sugars available from wood based industries in United States of America indicated that:

1. Roughly 1.2 million metric tonnes of sugar could be annually available from sulfite mills.
2. About 1.5 million metric tonnes of cellulosic material could be recovered from primary sludges in kraft mills; and
3. Hardboard and insulation board plants produce about 150,000 metric tonnes of non-utilised sugar annually.

Thus, the amount of wastes that could be bio-converted into useful products is mind-boggling. The key to this vast domain obviously lies in basic research aimed at the physiology of the micro organism and their mode of action. We have yet to even scratch the topsoil.

The current waste water treatment methods are highly cost and energy intensive, and here bio-removal of the colour can have an important role to play. In future, more novel approaches may be used for the treatment of waste effluents.

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