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Short Communication

Dehalogenation and decolorization of wheat straw-based bleachery effluents by *Penicillium camemberti*

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This paper examined the capability of *Penicillium camemberti* to dechlorinate and decolorize wheat straw-based pulping and bleaching effluents. In batch tests, the highest removals for CEH (Chlorination-Extraction-Hypochlorite) bleaching sequence [65% organic halides (AOX) 84% color] were obtained with 2 g/l acetate concentration in 10 days under non-shaking conditions. Experiments in shaking flasks containing Tween 80 produced 60% AOX, 79% color removals in 10 days. This removal efficiency was also in accord with gas chromatography analysis indicating drastic reductions at low molecular weight adsorbable organic halogen compounds.

Key words: Straw, bleaching, adsorbable organic halogens, pulping, *Penicillium camemberti*.

INTRODUCTION

Compared with wood; hemp, ramie, straw, bagasse, kenaf, flax, cotton and rag fibers are generally lower in lignin, higher in silica and ash with equivalent cellulose content. Different plant species produce different pulp types suitable for a variety of products. For example bagasse and straw are used to produce predominantly low grade pulps, whereas hemp, kenaf and flax are often used in higher quality and speciality papers such as banknotes, tea bags, dialectric paper and cigarette papers (Van Roekel, 1994).

Nonwood pulps are easier to bleach than wood pulps. Shorter bleaching sequences and lower chemical charges are used to bleach nonwoods. Globally, most nonwoods still are bleached using chlorine in a typical CEH (Chlorination-Extraction-Hypochlorite) or CEHH (Chlorination-Extraction – Hypochlorite - Hypochlorite) bleaching sequence.

Pulp production from straw generates an effluent containing a significant pollution load. In one study, bio-treatments for decolorization of straw-pulping effluents were examined by screening 84 fungal strains in several selection steps, 4 fungi (*Trametes versicolor*, *Gossypium australe*, *Coriolopsis gallica* and *Phanerochaete gigantea*) were chosen for effluent decolorization under agitated culture conditions and two (*Paecilomyces* sp. and *P. chrysosporium)* under stationary conditions. The best decolorization, (close to 90% under stationary conditions) was attained at 28°C and was comparable with the best results reported during fungal treatment of other pulp and paper effluents (Nonwood, 2000).

In wastewater treatment, biological oxygen demand (BOD), aquatic toxicity, organic halides (AOX) and color of water are important factors. In principle the wastewater contains easily degradable components such as sugars, fatty acids and alcohols while lignin an almost non-degradable component is responsible for the color. Moreover, pulping effluents are normally treated biologically for standard parameters such as BOD and chemical oxygen demand (COD) but biological treatment is usually not complete. Parameters unique to these wastes along with the classical ones are color and AOX and are virtually persistent thought the treatment cycle. The color originates from pulping and pulp bleaching processes while AOX originates exclusively from chlorine bleaching (Bergbauer and Eggert, 1992).

The primary objective of the study was to analyze the ability *Penicillium camemberti* which was found to be very effective in treating softwood pulping and bleaching effluents (Taşeli et al., 2004) and chlorinated model compounds like PCP, 2-chlorophenol and trichloroacetic acid (Taşeli and Gökçay, 2005), to degrade hemp-based pulping and bleaching effluents in batch and in up-flow colu-

mn reactor studies.

MATERIALS AND METHODS

Wastewater

Wastewater samples obtained from Turkish State Paper Industries' (SEKA) Kastamonu Pulping and Paper Plant were used for the batch experiments. Afyon Pulp and Paper Plant uses mainly wheat straw fibers for raw material to produce tissue paper. Cooked pulp is bleached in the following sequence: Chlorination (C), alkali extraction with caustic soda (E), hypochlorite (H) stages.

Biological tests

The *P. camemberti* used in this study has been isolated from chlorination-stage acidic effluents of SEKA-Kastamonu Pulp and Paper Plant in Turkey. The isolated fungus was identified through elaborated biochemical tests (Pitt, 1993). During experiments straw-based pulping effluents were supplemented with 2 g/l of acetate and basal salts medium having the following composition: 2 g/l KH_2PO_4, 0.5 g/l $MgSO_4$, 0.1 g/l $CaCl_2$, 0.12 g/l NH_4Cl and 0.001g/l thiamine. The pH was adjusted to 4.5-5.0, and temperature to 25±2°C. Batch culturing was carried out in 200 ml straw-based bleachery effluent samples placed in 500 ml conical flasks that were incubated on a rotary shaker at 80 rpm.

Chemical analysis

Adsorbable organic halogens (AOX) analyses were carried out according to German DIN 38409 Norm. The soluble organics were first adsorbed onto pure activated carbon particles and then filtered off on polycarbonate filters, washed with a nitrate solution and combusted in the furnace of the Euroglass 500 AOX analyzer. The chloride release was detected and recorded by the instrument as mg/l AOX.

Gas chromatography analyses were performed on a Perkin Elmer Autosystem 1020 Plus Gas Chromatograph. Firstly, gas chromatograph was calibrated with standard mix solution including target compounds. The calibration procedure was repeated prior every 5 samples. Secondly, effluent samples were first preconditioned with methanol and then were passed through C18 solid phase extraction columns. Organics retained on the C18 column were eluted with freshly distilled chloroform. The collected chloroform phase was dried by passing through anhydrous Na_2SO_4 and further concentrated down to 0.1 ml in a micro Kuderna Danish concentrator. The concentrated samples were then injected into a gas chromatograph with electron capture detector and CP Sil-5 capillary column (30 m, 0.25 mmID, 0.25 micron film thickness).

Relative color at absorbance of 465 nm was measured using the Pharmacia Biotech Spectrophotometer.

RESULTS AND DISCUSSION

The ability of *P. camemberti* to dechlorinate and decolorize straw based pulping and bleaching effluents was examined in two sets of experiments. In the first set of experiments, each bleaching sequence effluent was inoculated with fungus and treatment efficiency was examined by gas chromatographic (GC) analysis. GC analysis results as chlorination stage, extraction stage and hypochlorite stage are given in Figures 1, 2 and 3, respecti-

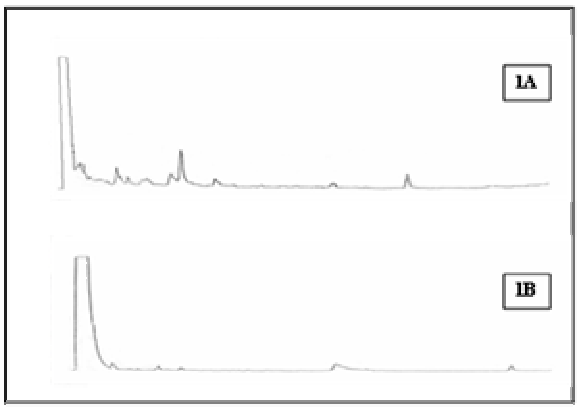

Figure 1. Gas chromatography analysis of chlorination stage before fungal treatment (A) and after fungal treatment under non-shaking conditions (B).

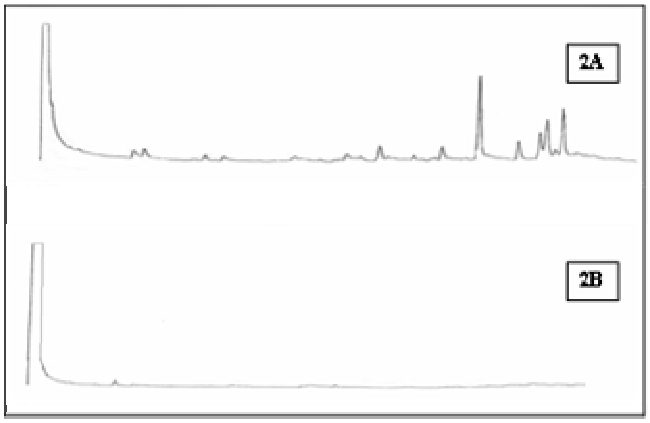

Figure 2. Gas chromatography analysis of extraction stage before fungal treatment (A) and after fungal treatment under non-shaking conditions (B).

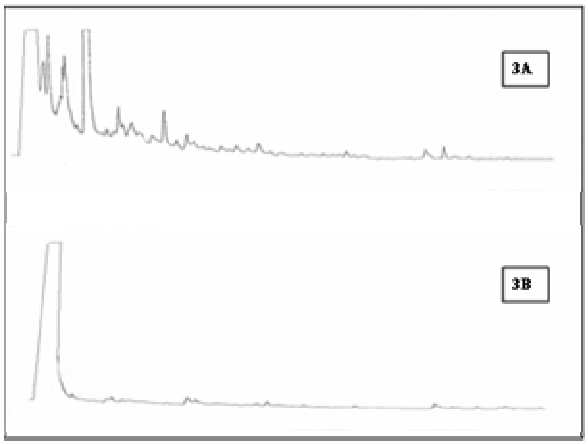

Figure 3. Gas chromatography analysis of hypochlorite stage before fungal treatment (A), and after fungal treatment under non-shaking conditions (B).

Table 1. Efficiency of *Penicillium camemberti* to dechlorinate and decolorize composite bleachery effluent (CEH).

Condition	Shaking[1]	Non-shaking[2]
AOX removal in 10 days	60%	65%
Color removal in 10 days	79%	84%

[1]Wheat straw-based composite bleachery effluent (CEH) + *P. camemberti* + mineral salts + 2 g/l acetate + 0.05 % Tween 80, pH 5, 25°C, shaking (80 rpm).
[2]Wheat straw-based composite bleachery effluent (CEH) + *P. camemberti* + mineral salts + 2 g/l acetate, pH 5, 25°C.

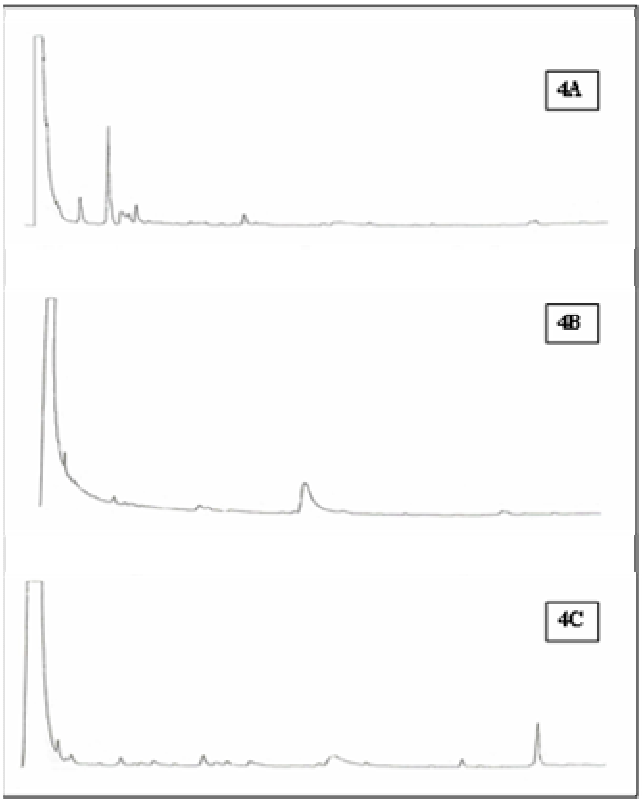

Figure 4. Gas chromatography analysis of composite bleachery effluent (CEH) before fungal treatment (A), after fungal treatment under non-shaking conditions (B) and under shaking conditions (C).

vely. It is clear from these figures that, fungus effectively treats each bleachery sequence.

In order to examine the efficiency of fungus to dechlorinate and decolorize composite bleachery effluent (CEH) and also to confirm the first set of experiments, a second set of experiments were conducted in both shaking and non-shaking batch cultures at 25°C, pH 5 and using acetate as primary carbon source. The flasks were incubated for 10 days and the solutions contained in the flasks were measured on first day and on day 10 of incubation in terms of AOX and color. 10 Days of incubation was chosen since it was proven by the earlier study that 10 Days was the optima for the fungus in batch studies (Taşeli et al., 2004). The results are tabulated in Table 1.

As can be seen from Table 1, the highest removals of 65% AOX and 84% color were obtained with 2 g/l of acetate concentration under non-shaking conditions. However, experiments conducted in shaking flasks resulted in 60% AOX and 79% color removals.

Figure 4 showing the gas chromatograms of straw based composite bleachery effluent (CEH) before and after fungal treatment under non-shaking and shaking conditions confirms that *P. camemberti* is very effective in removing low molecular weight compounds. This result is also in accord with the earlier study in which it was proved that the fungus effectively removed small sized phenolics (MW<1000) presents in the softwood bleachery effluents implying toxicity reduction in the effluents (Taşeli and Gökçay, 2006).

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