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EFFECTIVE DEGRADATION OF POLYVINYL ALCOHOL BY COMBINED CHEMICAL AND MICROBIAL PROCESSES

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Chemical pre-treatment of polyvinyl alcohol with Fenton's reagent has been performed in solution prior to inoculation with the white-rot fungus *Pycnoporus cinnabarinus* CBS 101046, which resulted in the degradation of the polyvinyl alcohol. Overall, more than 65% of the polyvinyl alcohol was found to have degraded after the 30 days of combined chemical and biological treatment. A range of low molar mass breakdown products were formed as a result of the initial Fenton's reagent treatment of the polyvinyl alcohol, and these were identified as carboxylic acids, alcohols, ketones, aldehydes and carbon dioxide. The concentration of each of these breakdown products was measured over the 30-day incubation period in the presence of the fungus and the remaining polyvinyl alcohol. It was found that each of these products decreased in concentration during the experiment, suggesting that they were utilized as a carbon source by the fungus. It was also observed that other low molar mass species, i.e., propanoic acid, propanol and pentanone, which were not present immediately after the initial Fenton's reagent treatment, were formed over the incubation period with fungi.

Key words: polyvinyl alcohol, Fenton's reagent, *Pycnoporus cinnabarinus*, fungal degradation, breakdown products.

Polyvinyl alcohol (PVA) is widely used in number of industrial and commercial applications due to its excellent physical properties, such as adhesive and tensile strength, dispersing power, viscosity and resistance to water, oil, grease and solvents [1–4]. The most common applications of PVA are in packaging, preparation of plastic materials and as additives in the paper, wood, paint and textile industry. A recent study indicated that the global production of PVA was close to 1 250 kt in 2007 and it is expected that this utilization will increase annually at a rate of 2.5% [4]. To date, plastic recycling is recognized as the most environmentally responsible method for dealing with plastic waste. Nevertheless, the associated processing costs often mean that a large amount of plastic waste is sent to landfill. Synthetically derived plastics, known to be relatively inert to environmental degradation, can remain relatively unchanged in landfill conditions even after two decades [1, 5–11]. Hence the disposal of plastics, including PVA, can present a significant economic and environmental challenge. This inert behavior is, in part, due to the high molar mass, chemical stability and relatively low surface area to volume ratio, which makes plastics such as PVA resistant to degradation.

A number of methods have been developed to handle plastic waste, including recycling, incineration, landfilling, composting, radiation induced degradation and environmental (biological) degradation. In addition, selected microorganisms have been shown to efficiently utilize PVA as a carbon and energy source in selected environments, such as activated sludge, settling ponds, landfills and, anaerobic digesters. It is likely that PVA may be the only synthetic polymer with an all carbon-carbon backbone that is truly biodegradable [12–17]. The detailed analysis of the biochemical pathways associated with PVA degradation commenced around 30 years ago with the isolation of a PVA-degrading extracellular enzyme (oxidase) from a culture of soil isolated *Pseudomonas* strain was done by Watanabe et al. [18]. Application of this enzyme resulted in the PVA being cleaved into smaller fragments. Kawagoshi and Fujita [13] and Fujita et al.

[19] also reported the secretion of a hydrolase (2,4-pentanedione hydrolase, EC 3.7.1.10) enzyme by *Pseudomonas vesicularis* var. *povalolyticus* PH, which has been associated with the biodegradation of PVA.

Over the years, studies have reported that a number of microorganisms, including bacteria, moulds, yeast and fungi can participate in the degradation of PVA [3, 12, 17, 20–24]. The initial mechanism of PVA biodegradation is believed to be a two step process. Initially random chain cleavage occurs where a two-enzyme catalysed oxidation process cleaves the carbon backbone of the polymer. The first oxidation process converts the 1,3-glycol structure of two adjacent repeating units to a β-diketone by random oxidative dehydrogenation reactions. The second process is the carbon-carbon cleavage reaction that converts one of the ketone groups to a carboxylic acid group, as indicated by the pH drop in the reaction mixture, with an accompanying chain rupture [3, 18]. This mechanism has also been confirmed by study of the degradation behavior of small molecules, such as alcohols and ketones [25], in comparison with the degradation of PVA by *Pseudomonas* sp.

Nevertheless, the biodegradation of PVA is not a straight forward process due to the limited PVA-degrading capacity of most microorganisms and their uncommon presence in environments important for plastic disposal such as soil [2, 4, 15, 26, 27]. Even in well controlled laboratory and composting conditions with selected PVA degraders, the biodegradation of PVA has been reported to be generally slow and the degree of degradation limited [15, 20, 22, 23, 28–30]. The rate and the extent of PVA biodegradability can be successfully increased by addition of a chemical pre-oxidation step in the degradation process which will partially hydrolyze the polymer [15, 23, 31]. Even though combined chemical and biological PVA degradation have been reported, to date, little research has been performed into the products resulting from the combined degradation of PVA.

This study is an extension of our earlier work [23]. Here we aimed to investigate whether PVA can be degraded by the combination of chemical and biological treatment, and whether the microbial degradation of the PVA by the wood rotting fungus *Pycnoporus cinnabarinus* will be enhanced by the initial inclusion of the chemical pre-treatment step. Strains of *P. cinnabarinus* have been previously used in industrial remediation applications [32, 33]. The white-rot fungi are well known as the only microorganisms capable of totally degrading all major wood components, including lignin [34-37]. Strains of *P. cinnabarinus* predominantly produce an extracellular polyphenol oxidase called laccase (EC 1.10.3.2) [35]. Laccase (EC 1.10.3.2) has a number of industrial applications including the treatment of industrial effluents [33, 38], paper pulp delignification [39 41] and decolourisation of dyes [33, 42 45]. Laccase (EC 1.10.3.2) has also been shown to oxidize phenolic groups in lignin model compounds [46 49]. FR has been used as an oxidative pre-treatment for aromatic hydrocarbons [50, 51] and for the decolourisation of dyes in wastewater [52 54]. Larking et al. [23] demonstrated that when used for pre-oxidation treatment of PVA, FR can increase the extent and rate of PVA degradation prior to inoculation with the white-rot fungus *P. cinnabarinus*.

Materials and Methods

Sample preparation. All reagents used to prepare solutions were of analytical reagent quality unless otherwise specified, using distilled water (dH_2O). Low molecular weight PVA is commonly used as a pigment coating adhesive in paper restoration to strengthen decayed papers and therefore the development of its efficient biodegradation procedure may have important biotechnological applications [9, 11, 14]. Powdered PVA was obtained from DuPont (Elvanol 71/30, average degree of polymerisation 180, prepared from the acetate). pH measurements were made using an ORION Research pH meter (Model 420A; Thermo Scientific, USA) calibrated using ORION buffers at pH 4.00 and 7.00. All pH adjustments were made using freshly prepared, carbonate free, 0.1 M NaOH or 0.1 M HCl. FR was prepared by mixing equal volumes of H_2O_2 (2.8 M) with $FeSO_4$ (0.10 M) in the presence of PVA, according to the method described by Martens and Frankenberger [55].

P. cinnabarinus CBS 101046 was isolated from a fallen tree in 1997 in a northern suburb of Melbourne, Australia and identified according to the standard methods as described elsewhere [56]. Stock cultures were stored on 1.5% malt extract agar (MEA, Oxoid) slants under mineral oil at 4 °C. The culture nutrient medium used in the degradation studies was prepared according to the method described elsewhere [57]. *P. cinnabarinus* CBS 101046 was maintained on 2% (w/v) MEA slants until required. This fungus was used to centrally inoculate 2% (w/v) MEA plates and incubated

at 37 °C for a period of 5 days. Of the sub-cultured fungus, 5 mm long plugs were cut from the leading edge of growth, and used in plug inoculation applications.

Quantitative analysis of the degree of PVA breakdown. The total carbon content of the PVA powder was measured using a LECO® CN-2000 (serial no. 3396; LECO Corporation, USA) carbon and nitrogen analyzer. The LECO® standard method 3471 was used to measure the carbon content using a furnace temperature of 1 050 °C, a helium lance flow of 1.0 L min^{-1} and a purge flow of 4.5 L min^{-1}. The total carbon content of the PVA powder was found to be 51.30 ± 0.2%. The concentration of PVA in solution in this study was measured using a modification of this process, a technique previously reported in both [58] and [59].

PVA degradation process. Closed biometer flasks (250 mL) containing solutions of PVA (20.0 mL, 1% w/v) were pre-treated with 0.2 mL of FR and equilibrated for 24 hours. The concentration of carbon dioxide evolved due to chemical degradation of the PVA was measured in both the headspace and in solution. Identical control flasks not treated with FR were prepared to allow for background carbon dioxide levels. The concentration of low molar mass breakdown products (C1 to C5) in solution was then measured. Flasks were supplemented with nutrient medium, the pH adjusted to 5.5, and inoculated with plugs of *P. cinnabarinus* sub-cultured on MEA. Flasks were flushed with pure oxygen and incubated at 37 °C for a period of 30 days in a 95% relative humidity environment. The concentration of breakdown products were measured every 2–3 days throughout the duration of incubation period after adjustment was made for evaporation of water in each case.

Analysis of breakdown products. The concentration of evolved carbon dioxide was measured using a Varian (3400) GC equipped with an Alltech CTR column (Cat. No. 8 700; Varian Inc, USA). The carbon dioxide levels within reactors were measured every 2 to 3 days during initial stages of degradation, thereafter sampling every 6 days was found to be sufficient to capture changes in carbon dioxide concentration. Reactors were flushed with oxygen every 6 to 7 days, following gas analysis to prevent oxygen levels falling, resulting in the formation of an anaerobic environment. The concentrations of methane and nitrogen were also measured using this technique, and if either compound was detected, the experiment was discarded since it was likely in these cases that an anaerobic atmosphere had formed. The concentration of carbon dioxide in solution was measured using an ORION carbon dioxide electrode (Model 95-02; Thermo Scientific, USA) calibrated using ORION solutions and standards. All measurements of carbon dioxide, in closed aerobic reactors, were performed immediately after headspace carbon dioxide analyses.

An isocratic high performance liquid chromatographic (HPLC) analysis was performed to determine the type and concentration of carboxylic acids resulting from the degradation of PVA. This was achieved using a Varian 9010 liquid chromatograph system with a Spherisorb C8 (150×4.2 mm, 5 μm packing) reverse phase column and a Model 9050 UV-visible detector at 210 nm (Varian Inc, USA). Detection and separation of the low molar mass carboxylic acids was conducted at 25 °C using a 0.2 M phosphoric acid mobile phase at a flow rate of 0.8 mL min^{-1}. Samples were analyzed in triplicate and the concentration of each acid was determined against freshly prepared 0.1, 0.01, and 0.001 M methanoic, ethanoic, propanoic, butanoic and pentanoic acid standards. Samples were removed from the incubation medium every 2–3 days and the concentrations of the aforementioned carboxylic acids measured.

Determination of the type and concentration of low molar mass alcohols, aldehydes, and ketones resulting from the degradation of PVA was measured using gas chromatographic analysis (GC). A gradient analysis was performed using a Varian 3400 system with a Carbowax (0.25 mm, 0.25 μm packing) column. The injector temperature used was 200 °C and the breakdown products were detected using a flame ionization detector (FID) at 220 °C. An initial temperature of 45 °C was held for 3 minutes then increased to 150 °C at a rate of 8 °C min^{-1} with a head pressure of 10 psi. Samples were analysed in triplicate and the concentration of each compound determined against freshly prepared standards that included low molar mass alcohols, aldehydes (C1–C5) and ketones (C3–C5) at concentrations 0.1, 0.01 and 0.001 M. Samples were removed from the incubation medium every 2–3 days and the variation in levels determined.

Results and Discussion

Increased levels of degradation of the PVA were achieved over a 30 day period in both the presence and absence of any nutrient source. The greatest extent of degradation was observed in the presence of a nutrient source,

achieving approximately 20% degradation over the 30 day incubation period. The biodegradation of PVA with *P. cinnabarinus* as a function of time in both the presence and absence of nutrients is given in Fig. 1.

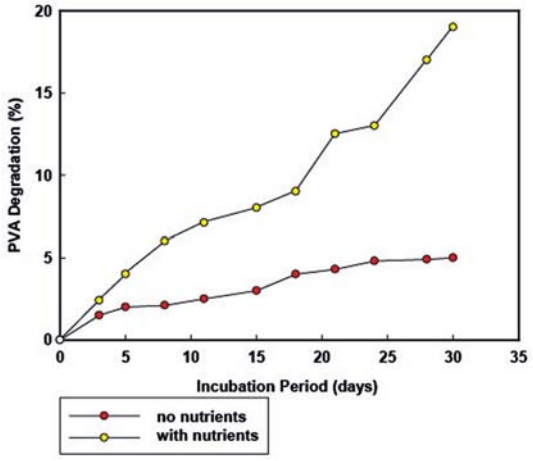

Fig. 1. **Biodegradation of PVA by *P. cinnabarinus* and extracellular oxidase levels in the incubation medium.** All of the data are averages of values from three replicates; the bars indicate standard errors

The extent of PVA degradation in the presence of FR (alone) as a function of time for two volume additions of FR is given in Fig. 2. The results indicate that complete degradation of the PVA in a 200 mL (1% w/v) PVA solution can be achieved by the addition of 1 mL of FR. This treatment method would have significant environmental implications if used in remediation processes, since the FR is a powerful oxidant that has the capacity to kill resident microbial populations in composting environments. Since it was the intention of this study to develop a combined chemical and biological method for the degradation of PVA, FR was used to cause an initial partial breakdown of the polymer, thus assisting and speeding up the subsequent biological degradation in the presence of a white rot fungus. For a volume of 20 mL (1% w/v) PVA, addition of 0.2 mL FR was found to be most effective as it caused approximately 40% PVA degradation without causing any apparent microbial damage. The presence of low molecular weight, acidic by-products after FR treatment was confirmed by the decrease in pH of the PVA containing FR solution (Fig. 3).

The concentration of PVA in solution, after combined chemical and biological oxidation, is given as a function of time in Fig. 4. It can be seen that the original concentration of PVA has decreased by 36% after 24 h of FR pre-treatment. Over the next 30 days, the PVA concentration decreased an additional 20% as a result of the exposure to the *P. cinnabarinus*. Thus approximately 44% PVA remained after the 30 days of combined chemical and biological degradation.

A number of low molecular mass degradation products resulting from the initial chemical pre-oxidation of PVA with FR were detected by assigning all peaks present in the GC and HPLC analyses to the peaks of the comparative standards. The measured solution concentrations of these products, presented in a bar chart format to allow direct comparison, are given in Fig. 5. These results indicate that the FR treatment effectively degraded the PVA to the lower molar mass species listed, and not to other isomeric forms.

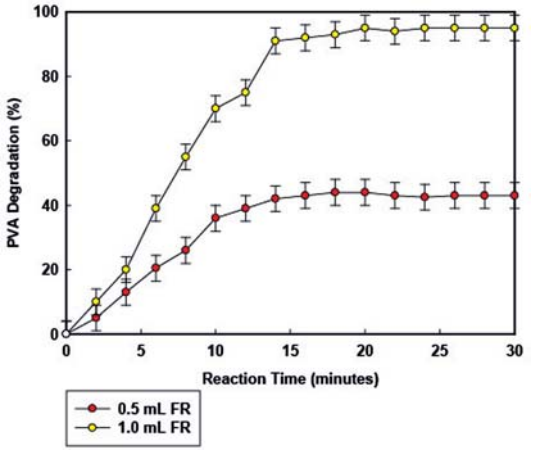

Fig. 2. **Degradation of PVA in solution (200 mL of 1% w/v PVA) after pre treatment with 1.0 and 0.5 mL of FR.** All of the data are averages of values from three replicates; the bars indicate standard errors

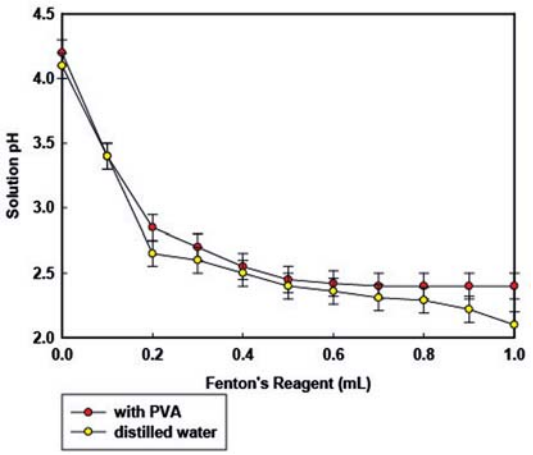

Fig. 3. **Changes in pH of solutions of PVA (200 mL, 1% w/v) following degradation by PVA.** All of the data are averages of values from three replicates; the bars indicate standard errors

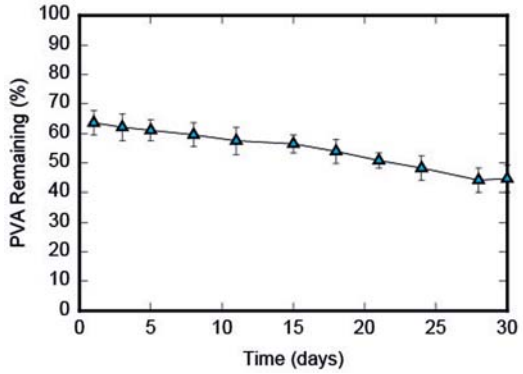

Fig. 4. **Degradation of PVA (20.0 mL, 1% w/v) at an initial pH of 5.5 following pre-oxidation with 0.2 mL FR and plug inoculation with *P. cinnabarinus* (from day 1).** Data are averages of three replicates; the bars indicate standard errors

It can be seen that the dominant breakdown products resulting from the FR treatment were carbon dioxide, methanoic acid, propanone and butanone, the formation of which is consistent with the free radical degradation mechanisms already proposed [3, 12, 18, 29, 60].

The concentration of carboxylic acid, alcohol, ketone and aldehyde breakdown products resulting from both the pre-treatment with FR and biological degradation of PVA using *P. cinnabarinus* were measured as a function of time and compared with controls that were not subjected to either degradative process. Low molar mass breakdown products were identified and quantified at an initial solution pH of 5.5, since this pH has been shown to result in elevated enzyme activities for the *P. cinnabarinus* [23, 61, 62]. Subsequently, changes in concentration of all low molar mass species

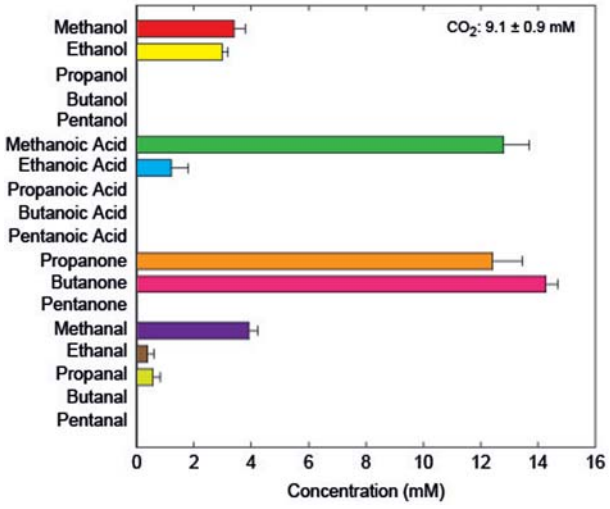

Fig. 5. **Breakdown products of PVA (20.0 mL, 1% w/v) after chemical pre-treatment with 0.2 mL FR.**
Data are the average of three replicates

must have occurred as a direct result of the action of the fungus on either the breakdown products resulting from the FR treatment, or the undegraded PVA remaining in solution. The concentration of the carboxylic acid, alcohol, ketone and aldehydic breakdown products as a function of time is given in Fig. 6, *a, b, c* and *d* respectively.

A progressive reduction in the concentration of methanoic acid was observed until day 23, after which the concentration was found to increase marginally. The ethanoic acid was completely removed from solution by day 11, and propanoic acid, which was not present in solution as a result of the FR treatment, increased in concentration until approximately day 23, after which time the concentration decreased. This decrease occurred at a similar time to the increase in methanoic acid concentration, suggesting that the propanoic acid may have been further degraded to methanoic acid. The concentration of the alcohol breakdown products was also seen to decrease over the incubation period. A rapid reduction in the propanone concentration was observed until approximately day 8, reaching a plateau value of approximately 1.5 mM. The butanone concentration was seen to rapidly decrease until day 11, after which time the concentration increased. A small amount of pentanone was formed from day 11. All aldehydes present resulted from the initial FR treatment. A gradual reduction in the methanal concentration was observed over the incubation period, whereas the concentrations of ethanal and propanal remained relatively constant over the initial stages of incubation, with the concentrations increasing slightly after day 11.

The total concentration of carbon dioxide over the 30 day incubation period is given as a function of time in Fig. 7. After an initially rapid increase in concentration between days 1 and 3, the concentration then more gradually increased over time from day 3. The bar chart presented in Fig. 8 enables a direct comparison of the concentration levels of the breakdown products over the incubation period. The carbon balance associated with the PVA degradation was calculated from both the concentration of breakdown products and the concentration of non-degraded PVA remaining in solution. The results are presented in Table over the 30-day incubation period. In calculating these values, the assumption was made that all carbon in the breakdown products was obtained from the PVA. Whilst it is recognized that other sources of carbon are available from components of the nutrient

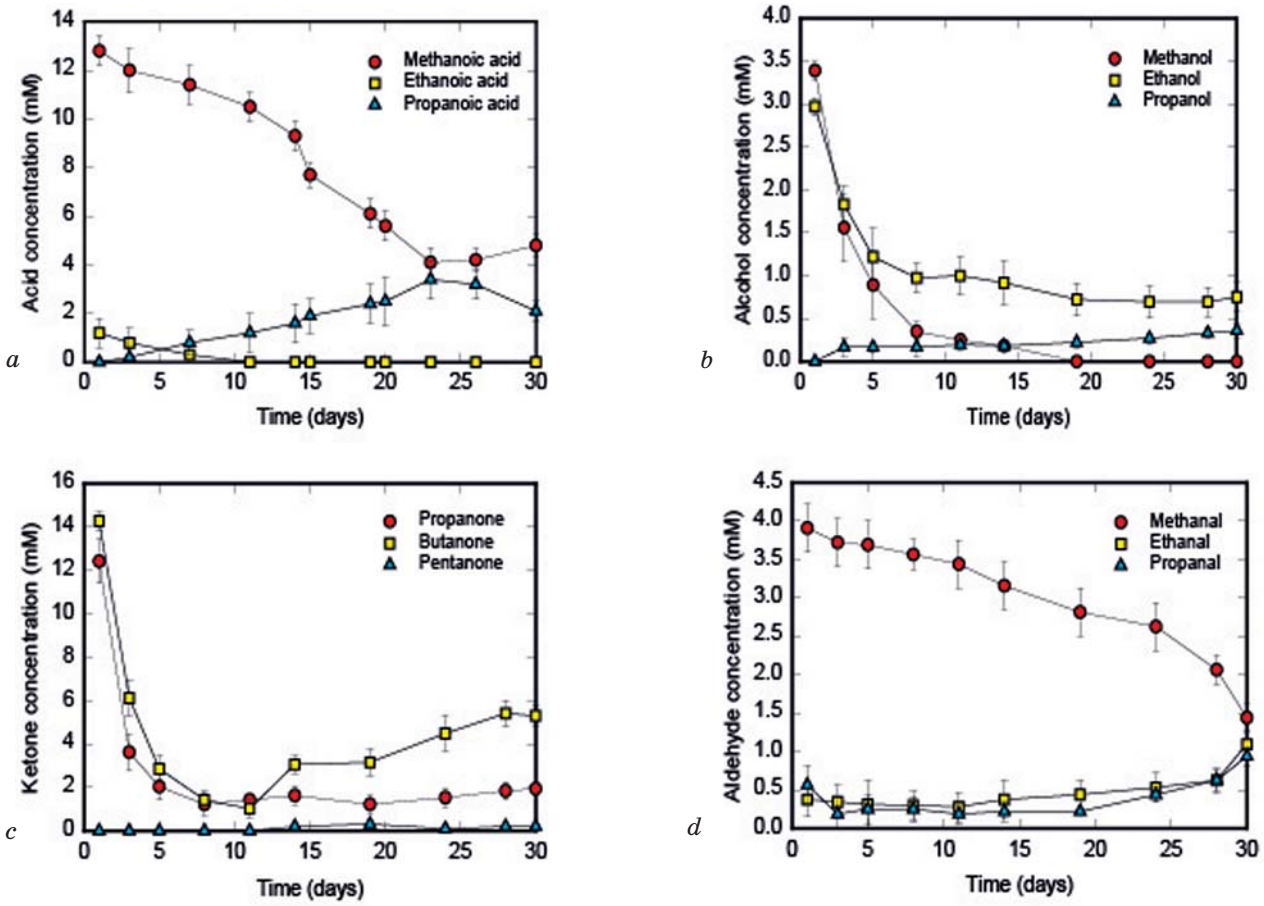

Fig. 6. **Carboxylic acid (*a*), alcohol (*b*), ketone (*c*) and aldehyde (*d*) breakdown products of PVA (20.0 mL, 1% w/v) at an initial pH of 5.5, following pre-oxidation with 0.2 mL FR and plug inoculation with *P. cinnabarinus* (from day 1).** Data are the average of three replicates; the bars indicate standard errors

medium, it has been assumed that these have been incorporated fully into the fungal biomass, so that a carbon balance could be calculated for the PVA degradation process alone. The mass of carbon that was not able to be assigned to either the breakdown products or the non-degraded PVA increased slowly over the incubation period, reaching a maximum of approximately 26% at day 28. It is likely that this unaccounted carbon contributed to the formation of fungal biomass, which was seen to increase over the 30-day incubation period.

The low molar mass degradation products resulting from this combined degradation procedure were identified and quantified, and these provided an insight into the behaviour of the fungus during the degradation process. The degradation of PVA was investigated under three sets of experimental conditions; biological degradation using *P. cinnabarinus* CBS 101046 (a white-rot fungus isolated from Melbourne, Australia), chemical degradation performed with Fenton's reagent (FR) [32] and combined degradation achieved by pre-oxidation of the PVA with FR as a precursor treatment to *P. cinnabarinus* CBS 101046 treatment. The breakdown products of PVA resulting from the combined chemical and biological treatment were monitored, measured and identified over a 30-day incubation period. During this period, an approximately 65% decrease in PVA was observed. Slightly lower PVA biodegradation rates were reported by Huang *et al*. [15]. This group used the white rot basidiomycete *Phanerochaete chrysosporium* ATCC 24725 and was able to achieve an overall degradation of between 58% and 64%, the extent of degradation being dependent on the cultivation conditions. It is also of interest to note that *P. chrysosporium* ATCC 24725 produced manganese peroxidase (EC 1.11.1.13) which was apparently involved in the PVA degradation, while *P. cinnabarinus* in this study produced the enzyme laccase. The PVA-degradation rates of bacterial degraders, mostly belonging to *Gammaproteobacteria* or *Alphaproteobacteria*, were reported to be in the range of 40–50% [4, 26], however, higher

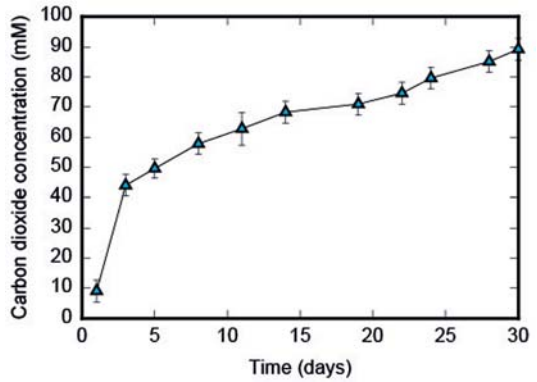

Fig. 7. **Carbon dioxide evolution from solutions of PVA (20.0 mL, 1% w/v) at an initial pH of 5.5, following pre-oxidation with 0.2 mL FR and plug inoculation with *P. cinnabarinus* (from day 1).** Data are the average of three replicates; the bars indicate standard errors

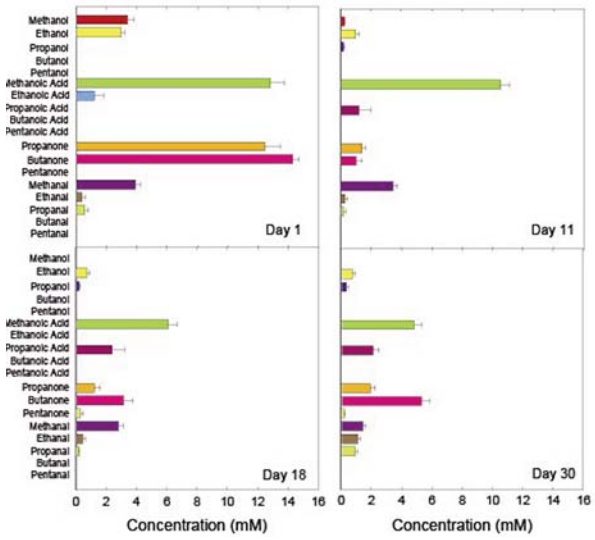

Fig. 8. **Breakdown products of PVA after pre-treatment with 0.2 mL FR and inoculation with *P. cinnabarinus* at days 1, 11, 18 and 30**

PVA degradation efficiencies (up to 80%), were achieved using mixed cultures [26].

Our results have also indicated that the predominant low molar mass breakdown products resulting from FR treatment of PVA were carboxylic acids, alcohols, ketones, aldehydes and carbon dioxide. Methanoic acid, propanone, butanone and carbon dioxide were present in higher concentration that the other compounds detected. They also indicate that the lowest molar mass breakdown products within a class of organic compound (i.e. methanol, methanoic acid, propanone and methanal) are most likely utilized as carbon source by the fungus and tend to decrease in concentration over the incubation period. In general, the concentration of all breakdown products formed from the initial FR treatment were observed to decrease over the incubation period except for carbon dioxide, which was seen to increase with time, probably due to the utilization of both the PVA and the breakdown products as a carbon source by the fungus.

Accompanying this progressive decrease in concentration of the lowest molar mass compounds within each class is a progressive increase in concentration of the higher carbon molar mass compounds (such as propanol, propanoic acid, ethanal and propanal). It is possible that these products are being formed from degradation of PVA fragments by fungal activity. However this also suggests there is probability that the PVA breakdown by the action of the fungus might decline in solutions where multiple carbon sources are present. Overall, more than 65% of the original PVA was found to be degraded after the 30 days of combined chemical and biological treatment.

The work presented here evaluated the effectiveness of combined chemical and biological degradation of polyvinyl alcohol. Degradation in excess 65% of the original PVA polymer was degraded by *P. cinnabarinus* after pre-treatment of the polymer with Fenton's reagent, within 30 days. The pre-treatment step resulted in the formation of numerous low-molecular weight chemical degradation products, the three most abundant of which were methanoic acid, propanone and butanone. Most of these compounds were then subsequently metabolized by *P. cinnabarinus*; propanone and butanone in particular were metabolised very quickly. The rate of polymer degradation was also found to be enhanced when the fungal culture was supplemented with additional nutrients. The combination of chemical treatment and biological degradation has been shown to particularly effective for degradation of PVA polymer.

This work highlights that this novel PVA treatment method achieved significant levels of polymer degradation. It also identified the small molecules formed during the breakdown process and the products formed during the incubation period. This is an important environmental consideration, since a number of polymer breakdown methods have been shown to produce environmental pollutants. The breakdown products reported in this work are able to be utilized as a carbon source by soil bacteria, and therefore do not represent a significant environmental concern.

Carbon mass balance for the combined chemical and biological degradation of PVA (102.6 mg of carbon in 20 mL of nutrient medium) over a 30-day incubation period

	Mass of carbon (mg)								
Compound	Day 1	Day 3	Day 8	Day 11	Day 14	Day 18	Day 24	Day 28	Day 30
Methanoic Acid	3.07 ± 0.22	2.88 ± 0.22	2.64 ± 0.17	2.52 ± 0.14	2.23 ± 0.14	1.47 ± 0.14	0.99 ± 0.14	1.08 ± 0.12	1.15 ± 0.12
Ethanoic Acid	0.58 ± 0.29	0.38 ± 0.29	0.15 ± 0.29	0.00	0.00	0.00	0.00	0.00	0.00
Propanoic Acid	0.00	0.14 ± 0.58	0.65 ± 0.43	0.86 ± 0.58	1.15 ± 0.58	1.73 ± 0.58	2.38 ± 0.50	1.91 ± 0.36	1.51 ± 0.29
Methanol	0.81 ± 0.09	0.37 ± 0.09	0.08 ± 0.03	0.06 ± 0.01	0.04 ± 0.01	0.00	0.00	0.00	0.00
Ethanol	1.43 ± 0.11	0.88 ± 0.11	0.47 ± 0.08	0.48 ± 0.11	0.44 ± 0.12	0.35 ± 0.09	0.33 ± 0.09	0.33 ± 0.08	0.36 ± 0.08
Propanol	0.00	0.12 ± 0.08	0.12 ± 0.08	0.14 ± 0.04	0.13 ± 0.04	0.16 ± 0.04	0.20 ± 0.04	0.24 ± 0.04	0.26 ± 0.06
Propanone	8.95 ± 0.74	2.61 ± 0.59	0.88 ± 0.37	1.03 ± 0.14	1.17 ± 0.30	0.91 ± 0.30	1.10 ± 0.30	1.33 ± 0.30	1.40 ± 0.22
Butanone	13.72 ± 0.39	5.88 ± 0.79	1.37 ± 0.39	0.98 ± 0.39	2.94 ± 0.39	3.01 ± 0.39	4.31 ± 0.79	5.20 ± 0.59	5.09 ± 0.49
Pentanone	0.00	0.00	0.00	0.00	0.24 ± 0.06	0.37 ± 0.24	0.12 ± 0.06	0.24 ± 0.06	0.24 ± 0.06
Methanal	0.94 ± 0.07	0.89 ± 0.07	0.86 ± 0.05	0.83 ± 0.07	0.76 ± 0.07	0.68 ± 0.08	0.63 ± 0.07	0.50 ± 0.05	0.35 ± 0.05
Ethanal	0.18 ± 0.11	0.17 ± 0.11	0.14 ± 0.09	0.14 ± 0.09	0.18 ± 0.12	0.21 ± 0.09	0.26 ± 0.09	0.30 ± 0.06	0.53 ± 0.09
Propanal	0.41 ± 0.18	0.14 ± 0.16	0.18 ± 0.12	0.14 ± 0.09	0.16 ± 0.09	0.16 ± 0.02	0.32 ± 0.06	0.45 ± 0.12	0.68 ± 0.09
Carbon Dioxide	2.19 ± 0.86	10.57 ± 0.91	13.88 ± 0.86	15.08 ± 1.32	16.41 ± 0.86	17.05 ± 0.86	19.12 ± 0.86	20.44 ± 0.86	21.43 ± 0.86
PVA	63.61 ± 4.10	62.07 ± 4.62	59.51 ± 4.10	57.46 ± 4.62	56.94 ± 4.62	53.87 ± 4.10	48.22 ± 4.10	44.12 ± 4.10	44.63 ± 4.62
Total	95.88 ± 6.95	87.11 ± 8.34	80.94 ± 6.89	79.72 ± 7.48	82.80 ± 7.27	79.95 ± 6.80	77.98 ± 6.98	76.13 ± 6.62	77.62 ± 6.92
Carbon from PVA not accounted for in total	6.72	15.49	21.66	22.88	19.80	22.65	24.62	26.47	24.98

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This paper is dedicated to the memory of Professor Greg Lonergan, who died suddenly on 2 September 2006.

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ЕФЕКТИВНА ДЕГРАДАЦІЯ ПОЛІВІНІЛОВОГО СПИРТУ З ВИКОРИСТАННЯМ КОМБІНОВАНИХ ХІМІЧНИХ І МІКРОБІОЛОГІЧНИХ ПРОЦЕСІВ

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Попередня хімічна обробка полівінілового спирту реактивом Фентона в розчині перед посівом з грибом білою гниллю *Pycnoporus cinnabarinus* CBS 101046 спричинювала деградацію полівінілового спирту. Загалом, більше 65% полівінілового спирту деградувало після 30 днів комбінованої хімічної і біологічної обробки. У результаті оброблення реактивом Фентона з початкового полівінілового спирту утворено низку низькомолекулярних продуктів розпаду, які було ідентифіковано як карбонові кислоти, спирти, кетони, альдегіди і діоксид вуглецю. Концентрацію кожного із цих продуктів розпаду було визначено протягом 30-денного інкубаційного періоду в присутності гриба і залишкового полівінілового спирту. Встановлено, що концентрація кожного із цих продуктів під час експерименту знижувалась. Імовірно, вони були використані грибом як джерело вуглецю. Виявлено також, що інші низькомолекулярні сполуки, тобто пропанова кислота, пропанол і пентанон, які не були присутні після первісної обробки реактивом Фентона, утворені протягом інкубаційного періоду з грибами.

Ключові слова: низькомолекулярний полівініловий спирт, реактив Фентона, *Pycnoporus cinnabarinus*, біодеградація грибом, продукти розпаду.

ЭФФЕКТИВНАЯ ДЕГРАДАЦИЯ ПОЛИВИНИЛОВОГО СПИРТА С ИСПОЛЬЗОВАНИЕМ КОМБИНИРОВАННЫХ ХИМИЧЕСКИХ И МИКРОБИОЛОГИЧЕСКИХ ПРОЦЕССОВ

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Предварительная химическая обработка поливинилового спирта реактивом Фентона в растворе перед посевом с грибом белой гнилью *Pycnoporus cinnabarinus* CBS 101046 вызывала деградацию поливинилового спирта. В целом, более 65% поливинилового спирта деградировало после 30 дней комбинированной химической и биологической обработки. В результате обработки реактивом Фентона из начального поливинилового спирта образован ряд низкомолекулярных продуктов распада, и они были идентифицированы как карбоновые кислоты, спирты, кетоны, альдегиды и диоксид углерода. Концентрация каждого из этих продуктов распада была измерена в течение 30-дневного инкубационного периода в присутствии гриба и оставшегося поливинилового спирта. Установлено, что концентрация каждого из этих продуктов во время эксперимента снижалась. Предположительно, они были использованы грибом в качестве источника углерода. Отмечено также, что другие низкомолекулярные соединения, т.е. пропановая кислота, пропанол и пентанон, которые не присутствовали после первоначальной обработки реактивом Фентона, были образованы в течение инкубационного периода с грибами.

Ключевые слова: низкомолекулярный поливиниловый спирт, реактив Фентона, *Pycnoporus cinnabarinus*, биодеградация грибом, продукты распада.