Near infrared monitoring of recycled paper biodegradation

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Introduction

Over 67 million tons of packaging waste is generated annually in the European Union (EU). There are two ways to utilise such a large amount of paper: recycling or composting. Recycling is the most common but re-pulping causes the recovered fibres to have poorer mechanical properties. It is commonly accepted that fibres can be utilised five to seven times before they become too short. Usually some additives (new fibres or fillers) are necessary to enrich pulp in order to avoid a loss of mechanical properties. Until recently, 90% of paper pulp was made of wood but economic pressures have resulted in supplementation with non-wood fibrous materials such as marine algae, fruits or fast growing plants.[1]

An alternative pulp supplement might be cereal bran. Advanced technologies in the food industry are capable of removing all nutrients from bran, even if 15 years ago bran was a constituent of bakery products and animal feed. Moreover, the disposal of a large amount of waste has become a problem (medium size companies generate up to 150 tons of waste each day). By linking the problem of bran waste together with paper pulp costs, we have developed the idea of using bran fibres as additives for waste paper. Bran might be used as filler in the manufacturing of extruded paper, pots or pulp containers which are extensively used for horticulture. Recyclable paper containers recently became ecologically acceptable and more popular. Moreover, biodegradable packing materials with natural additives are an interesting alternative to traditional plastics since they may be biodegraded through composting. Additionally, such containers help to reduce labour costs; seedling and pot can be planted quickly, avoiding root disturbance and any interruption to growth.

The aims of this study include examining the influence of wheat and rye bran additions on the colonisation rate of selected *Ascomycetes* sp. fungi. The other goal was to investigate the suitability of near infrared (NIR) spectroscopy as a new method for rapidly estimating the biodegradation rate of recycled paper.

Materials and Methods

Samples

Sheets of paper weighing 100±5 g.m^{-2} were produced with a Rapid-Köthen apparatus from type D recycled pulp (cardboard, paper, grey bags, corrugated board) and used as experimental samples. Papers were made of pulp with a 0, 3, 5 or 10% addition of wheat and rye bran. Mycological tests[2] were performed for *Chaetomium globosum* and on a mixture containing *Aspergillus niger*, *Penicillium funiculosum* and *Trichoderma viride*. The fungal growth rates were estimated after 4, 7, 10, 14 and 21 days according to the four point scale. Determination of paper resistance (breaking length) was performed according to the standard PN-EN ISO 1924-1:1998. Further, waste paper samples with 0, 3 and 5% cereal bran were selected for degradation tests in various soils. Three different types of soils were selected for monitoring the speed of paper decomposition. Sandy soil is characterised by being free draining (holding water very poorly) due to a very low organic content. Forest soil is generally rich with cones and needles but poor in nutrients. Agricultural soil, which consists of highly decomposed matter deeply mixed with mineral soil, has a neutral pH and a carbon to nitrogen ratio of approximately 10. Samples were exposed to degradation for two months and monitored at weeks 1, 4 and 8 during the experiment.

Near infrared spectroscopy

Experimental samples were measured using a VECTOR 22-N (Bruker Optics GmbH, Ettlingen, Germany). Each sample was represented by an averaged spectrum from five strips of paper, each measured at three different points (15 spectra were averaged per sample). All measurements were made in an air-conditioned room (20±2°C and 65±2% relative humidity) in order to minimise the effect of temperature and moisture variations. Vector normalisation and computation of second derivative spectra (Savitzky-Golay algorithm) were applied as spectra pre-processing. Principal component analysis (PCA), partial least squares regression (PLS) and 2D spectral correlation[3] were used for data analysis and mining. The interpretation of spectra was

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based on literature research.[4] Numerical analyses were performed in OPUS 6.5 (Bruker Optics GmbH, Ettlingen, Germany).

Results and Discussion

Degradation of the samples without cereal bran was generally less intensive. As presented in Figure 1, spectra of recycled paper without the addition of *Ascomycetes* fungi are nearly the same after two weeks of infestation. Additions of bran to pulp, especially wheat and rye (3%, 10%), increased fungal growth to the extent where mycelium covered the surface after 4 days of exposure.

Recycled paper was more susceptible to growth by *C. globosum*, which grew more steadily. Consequently, a perfect separation of the various degradation stages was obtained (PCA algorithm).

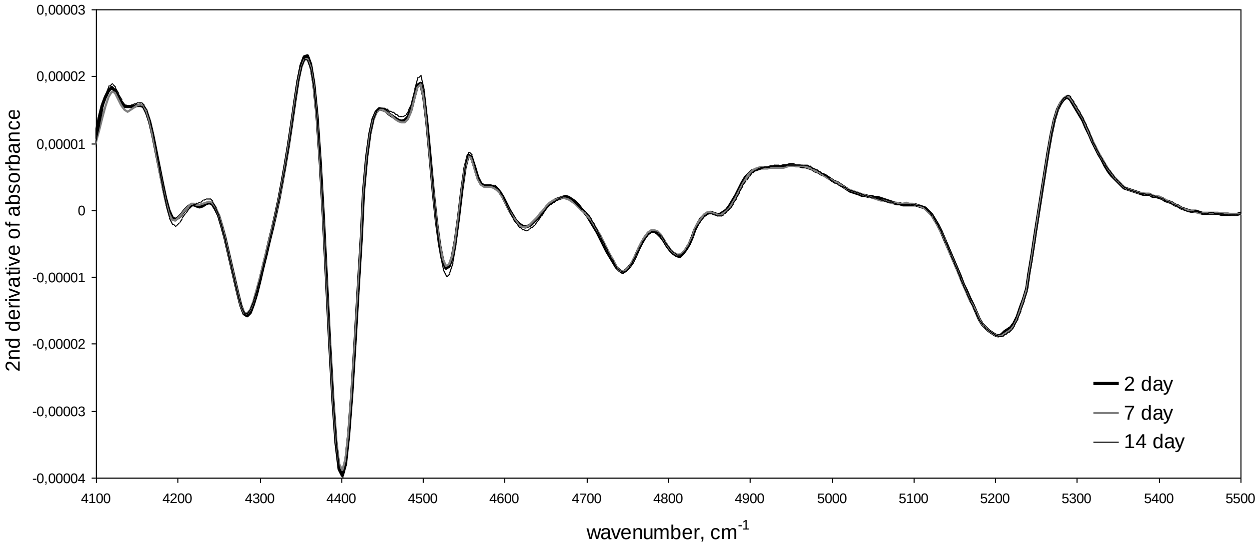

Figure 1. Effect of time on the biodegradation of the recycled paper without additions of *A. Niger, T. viride* and *P. funiculosum*.

As presented in Figure 2, the most affected spectral regions were 4280 cm^{-1} and 4404 cm^{-1} (CH and CH_2 of cellulose), 5219 cm^{-1} (OH groups associated with water) and 4620–4890 cm^{-1} (OH and CH groups of cellulose).[4] No significant changes were noticed around 5464 cm^{-1}, which is associated with vibrations of OH and CH groups of crystalline (and semi-crystalline) cellulose.[4] Such small variations can be explained by the fact that fungi growing on the paper surface are not capable of metabolising crystalline regions of linear polymer carbohydrates (such as crystalline cellulose).

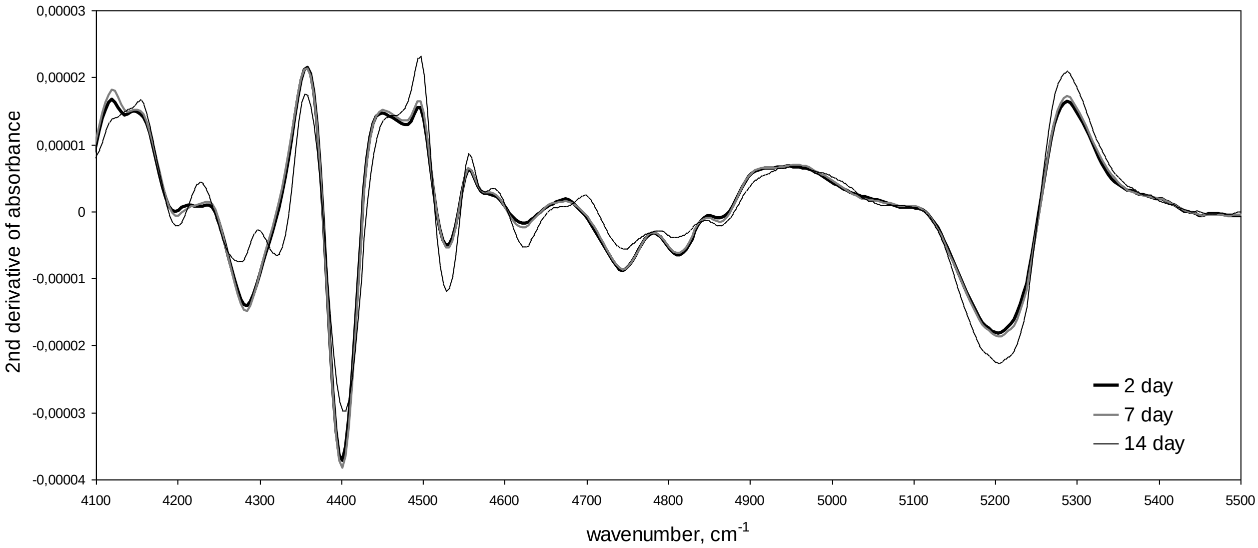

Figure 2. Effect of time on the biodegradation of the recycled paper with addition of 10% rye bran and exposed to *Chaeotomium globosum*.

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In such cases, all the crystalline regions must be converted into an amorphous form before digestion. Even if holocellulose is the favourable nutrient for fungi, its impact on spectra is minor. Relatively moderate differences around 4198 cm^{-1} are a consequence of the fact that quantities of holocellulose are rather limited in the paper products. Therefore it can be stated that enzymatic activity of *Ascomycetes* fungi caused shortening of cellulose chains, lowering of microfibril bonds and breaking of fibres.

Changes in the mechanical properties of degraded papers were estimated in conjunction with the mycological tests. Mechanical properties (breaking length) of recycled paper increased with the addition of cereal bran (up to 10%). The highest strength was noticed for paper samples with rye bran additions, especially in the first test period. Mechanical properties of most paper samples without bran additions were not affected by fungal infestation in the first 14 days after exposure. The resistance of paper samples exposed to *C. globosum* was relatively weak compared to the resistance of samples exposed to the mixture of *A. niger*, *T. viride*, *P. funiculosum*.

The partial least squares algorithm allows correlation of the reference data (breaking length) with near infrared spectra. Application of the optimisation process allows selection of the proper spectral pre-treatment. Averaged model spectra in the regions of 12000–7500 cm^{-1} and 6100–4100 cm^{-1}, after vector normalisation and cross-validation, were used for constructing the PLS model. The determination coefficient (r^2) reached 0.68 and the average error of cross-validation (RMSECV) was 0.413 km after the training process. The use of FT-NIR for prediction of mechanical properties is one of the most promising practical applications of this technique. It may become possible (after creation of appropriate models) to quickly and accurately estimate selected material properties, such as chemical composition, physical properties or others, based only on their near infrared spectra. However, it must be mentioned that to build reliable, flexible and generalised models, large databases of precise reference values are indispensable.

2D spectral correlation was applied to data analysis in order to quantify in detail the effect of the fungal degradation on spectra and for monitoring of biodegradation kinetics. The method developed by Noda and Ozaki[3] is based on computation of auto-correlation and/or cross-correlation between several spectra-recordings, so called “disturbances”. These might include changes in temperature, moisture or concentration etc. In this research, however, experiment time (linked to degradation level) has been considered as a disturbing factor. The resulting chart of 2D synchronous spectral correlation of paper with 10% additions of wheat infected by *Chaetomium* is presented in Figure 3. It is clear that the major changes to the spectra as an effect of fungal degradation (dark colour) are associated with the 4280 cm^{-1}, 4404 cm^{-1}, 4620-4890 cm^{-1} and 5219 cm^{-1} spectral regions, which is in agreement with previous discussion.

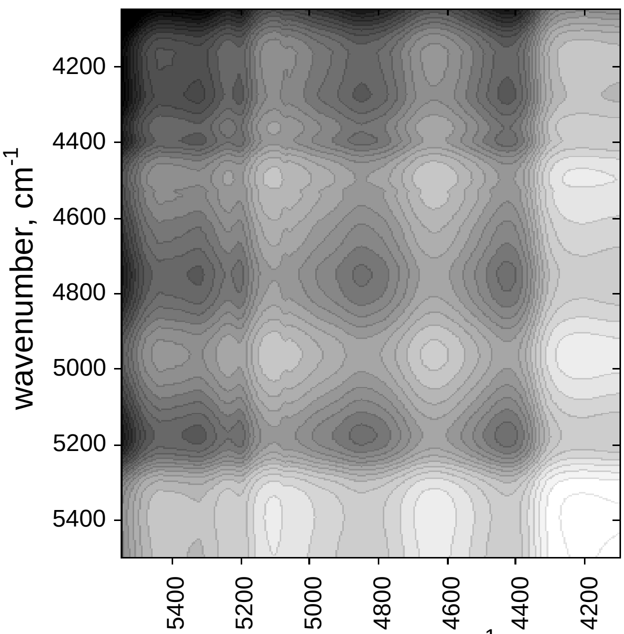

Figure 3. 2D spectral correlation of paper with the addition 10% wheat bran at different degradation stages.

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The effect of soil type on the biodegradation of recycled paper is presented in Figure 4, which focuses on waste paper with 5% wheat bran. All previously mentioned spectral regions (with the exception of 5464 cm^{-1}) were affected by degradation. Spectra of paper placed in sandy soil appeared the most similar to control samples (not degraded). It proved that the sandy soil containing the lowest organic content and persistent low humidity has the least impact on the speed of degradation. In contrast, agricultural and forest soils accelerated the speed of degradation.

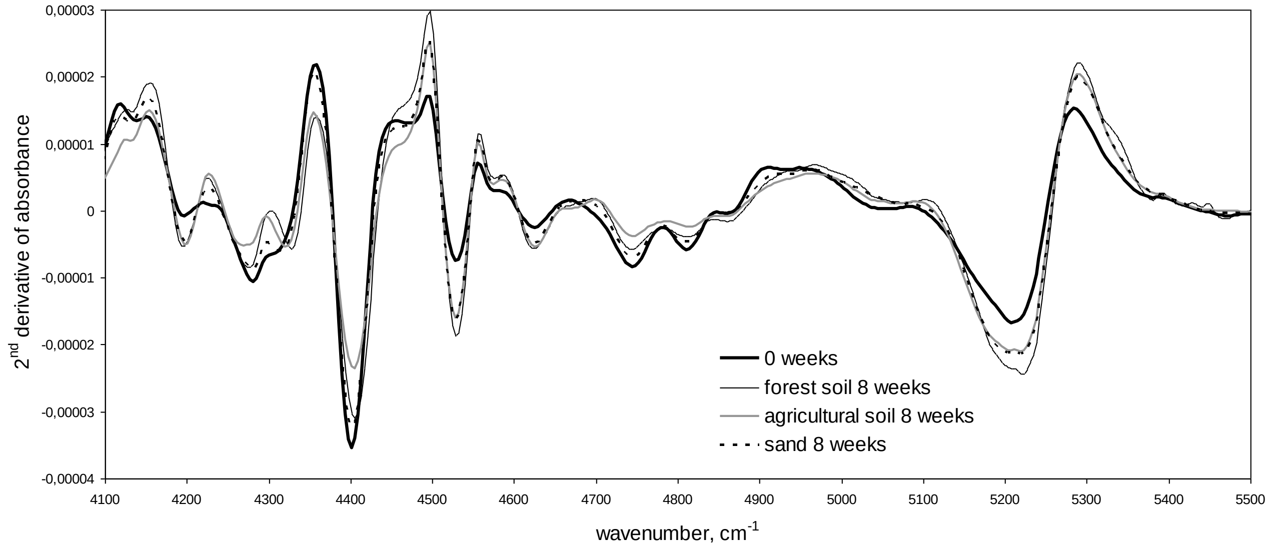

Figure 4. Effect of soil type on the biodegradation of recycled paper with 5% wheat bran.

The effect of exposure time on paper degradation can be observed in Figure 5, where spectra of waste paper with 5% wheat bran placed in forest soil showed fast degradation. Spectra collected after one week of exposure were noticeably different to those spectra collected from the control sample (not exposed to degradation) and were generally similar to spectra collected after 8 weeks of exposure. NIR data consequently show that degradation began quickly in forest soil (and also in agricultural soil) .

Bran addition generally reduced the speed of degradation when compared with commercially-available pots containing 20% peat. The commercially-available pot material readily absorbs water and promotes decomposition. By comparing the rates of biodegradable pots containing different organic additives, it can be concluded that pots made of paper with rye bran degraded the fastest.

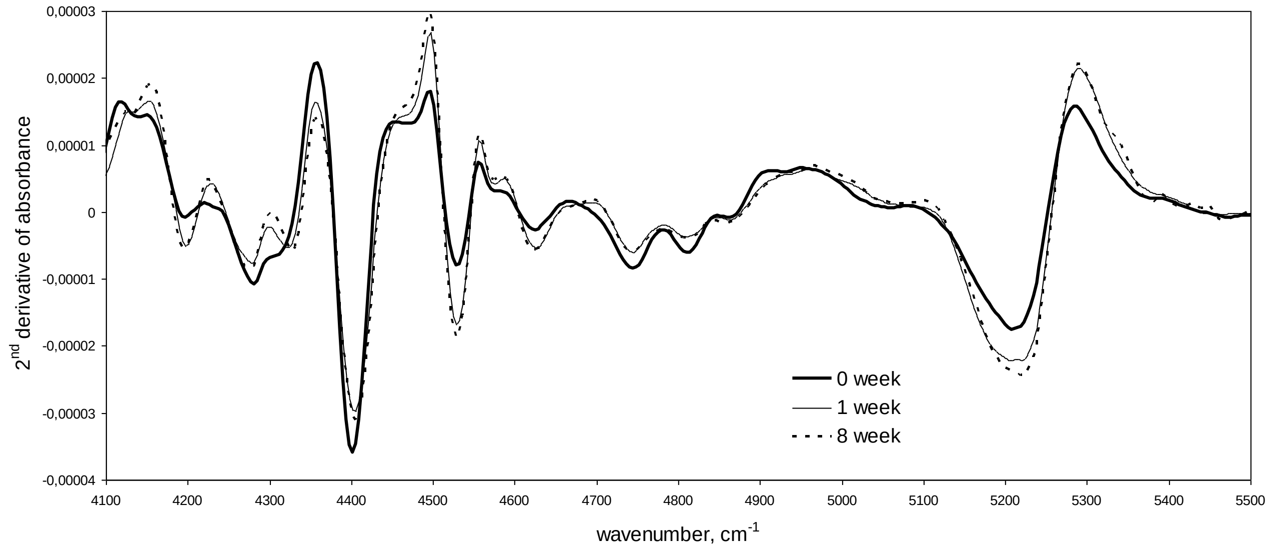

Figure 5. Effect of time on the biodegradation of recycled paper with 5% wheat bran (in forest soil).

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Conclusion

The addition of wheat and rye bran as fillers to recycled paper increased the susceptibility to mycelium colonisation in comparison to samples without additions. Mechanical properties (breaking length) of recycled paper increased with the addition of cereal bran (up to 10%). However, the addition of rye bran improved breaking length more than the addition of wheat bran. The drop of mechanical properties (breaking length) along the biodegradation progress was related to the loss of certain chemical components and/or changes in their properties compared to the original material. It was observed that biodegradation of waste paper infected by *C. globosum* was the quickest and showed a tendency towards better separation of individual stages of biodegradation.

FT-NIR spectra analysis and 2D spectral correlation confirmed that the spectral regions most affected by *Ascomycetes* fungi could be attributed to cellulose, especially CH (4280 cm^{-1}), CH_2 (4404 cm^{-1}) and OH groups (stretching vibration in the region 4620–4890 cm^{-1}).

FT-NIR demonstrated that agricultural and forest soils accelerated the degradation speed of paper samples while sandy soil (i.e. poor in organic matter) had the lowest impact on degradation. By observing the degradation speed of investigated papers in various types of soils, it was possible to select a product with the optimal composition for a specific purpose (i.e. pots used in horticulture or for a forest nursery).

Near infrared spectroscopy proved its potential in the characterisation of biodegradation of ligno-cellulosic materials. Some possible applications of the near infrared spectroscopy include classification of recycled papers, determination of the degradation stage and estimation of chemical composition or physical properties.

Acknowledgements

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