ENVIRONMENTALLY FRIENDLY DEINKING PROCESS BY ENZYMES

MIJA SEŽUN,[*] GREGOR LAVRIČ[*] and STAŠA MALALAN[**]

[*]*Pulp and Paper Institute, Bogišićeva 8, 1000 Ljubljana, Slovenia*
[**]*Faculty of Natural Sciences and Engineering, Snežniška 5, 1000 Ljubljana*
✉ *Corresponding author: Mija Sežun, mija.sezun@icp-lj.si*

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One of the most relevant challenges of recent years is a concern for the environment. Chemicals used for different industrial purposes have a big environmental impact. Various industries, including paper production, work on reducing their consumption. One of the alternative replacements for the chemicals used in the paper industry are environmentally friendly enzymes. In our study, different deinking processes using specific enzymes (cellulases, lipases and laccases) were compared with the one based on chemicals. We investigated which procedure was more efficient by determining the properties (basic, strength and optical) of the laboratory paper sheets after the treatments. By comparing chemical and enzymatic treatments, it could be concluded that enzymatic treatment improved the mechanical properties of laboratory sheets produced out of recovered paper printed mainly in offset printing. It was also remarked that enzymatic treatment by lipase provided the best results in terms of mechanical properties, while enzymatic treatment by laccase provided the worst results for most mechanical properties. The highest level of brightness was achieved in a sample treated with a mixture of cellulase and laccase. Our study confirms the fact that the use of enzymes in the paper industry enables to upgrade the chemical deinking process. Due to lower chemical consumption, the environmental impact may be reduced and costs lowered.

Keywords: recovered paper, deinking, enzymes, paper properties

INTRODUCTION

The application of sustainable development policies implies the application of green processes that reduce waste and pollution by changing patterns of production. Green processes are based on innovative ideas that generate alternatives to technologies that can negatively affect the environment. Today, enzyme-catalyzed processes are gradually replacing chemical processes in many areas of industry, because they save energy, water and chemicals, help to improve product quality, and furthermore, they give valuable environmental benefits.[1] Recovered paper is the main and most important source of fibres in papermaking all over the world. Lately, different types of prints have posed difficulties in treating by conventional deinking techniques, such as dewashing, dispersion, washing and flotation (for example, electrophotographic and xerographic prints).[2-4] In recent years, the biotechnology in the paper industry witnessed great progress, major attention being dedicated to reducing the impact on the environment. One of the achievements in papermaking technologies is the replacement of chemicals with enzymes in the deinking process. During the last 20 years, several researchers have been developing enzymatic deinking, using a number of enzymes, including cellulase, xylanase, laccase and lipase, due to their potential to reduce environmentally unfriendly chemicals.[5-12] In addition to ink removal, enzymatic deinking can improve paper strength properties due to the removal of fines and the improvement of interfibrillar bonding in paper. Enzymatic deinking of recovered paper is still a topic of keen research interest, as witnessed by several publications from the last few years. Das *et al.*[13] extracted enzyme cocktails, containing cellulases and xylanase, produced by *Aspergillus fumigatus* ABK9 from the wheat bran-rice straw mixed substrate and used them for deinking waste office paper pulp. The cocktail increased the brightness of waste office paper pulp by 82.8% ISO. In the research of Efrati *et al.*,[14] *Trichoderma* cellulase was used on deinked pulp and its effects on fibre morphology, crystallinity and strength of the pulp were studied. The results showed that the enzymatic treatment enhanced the mechanical properties of the treated pulps. Enzymatic treatment was also found effective in the study by Nathan *et al.*[15] It increased the brightness of recovered newspaper paper by up to 10%. A recent study by Vinod Kumar *et al.*[16] concluded that individual treatment of paper pulp with enzymes (cellulase/xylanase) could enhance the paper brightness to about 32.86%, whereas the combinational effect could enhance brightness to only about 28.67%. The results of Akbari *et al.*[17] from a recent study seem to be well-grounded. The effect of pH variations on deinking efficiency of old newspaper by pectinase was investigated in their study. The results showed that more efficient pectinase deinking of old newspaper can be achieved at a pH level of 4-4.5, as indicated by the improved optical and mechanical properties of standard handsheets obtained by enzymatic deinking at pH levels ranging from 4 to 5.

EXPERIMENTAL

Sample

A recovered paper sample was obtained from a Slovenian producer of newsprint and coated graphic papers. The recovered paper was previously evaluated according to the standard EN 643. The mixture of different types of recovered paper contained 60-70% of newspapers and magazines. Most of the recovered paper was offset printed (95%), while the remaining 5% included other printing technologies (flexography, inkjet, electrophotographic *etc.*). For the experiment, we took three different samples of the most commonly used recovered paper. The samples were merged and cut to a size of 2 × 2 cm. We determined dry matter, according to the standard EN 14346: 2007, and the loss on ignition of dry matter according to the standard DIN EN 12879: 2001. Each sample weighed 75 g of absolutely dry matter. The deinking process was carried out by a slightly modified INGEDE 11 method.

Chemical deinking process

During the experiment, we used the following chemicals: sodium hydroxide (NaOH), collector (Nopco flot), sodium silicate (Na_2SiO_3), hydrogen peroxide (H_2O_2). All these chemicals were obtained from the Slovenian paper mill Vipap Videm Krško d.d.

An amount of 100 mL of H_2O_2 was added into the solution of chemicals (400 mL) and the mixture was diluted with water to a volume of 1500 mL. 75 g of sample was added to the mixture of chemicals during constant stirring at 3000 rpm in a thermostated spreader (T = 45 °C, time of mixing = 20 minutes). The temperature was maintained by using a water bath. Once the dissolution was completed, the mixture was stabilized in a water bath for 60 minutes at a constant temperature of 45 °C. Based on the standard, the recommended pH value was set to 9.48. The next step was the flotation of the previously dissolved sample, which took place in a flotation cell in the presence of water (18 L). Substance concentration during flotation was 0.42%. After the flotation process, laboratory paper sheets were prepared.

Enzymatic deinking process

In the study, we used enzymes in addition to chemicals, as well as mixtures of enzymes and chemicals. Optimal conditions for the enzymes' activity, as well as their optimum quantity, were determined on the basis of a literature review and preliminary laboratory tests, which defined the conditions (temperature, time, pH value and quantity) under which each individual enzyme performed best. We used the enzymes described below.

Cellulase

An amount of 75 g of absolutely dry matter was mixed using the spreader in 1400 mL of water. 1.8 µL of cellulase enzyme (Celluclast, Novozymes) was added to the mixture and dissolved for 30 min at an initial temperature of 55 °C and pH value of 5.5, under constant stirring at 3000 rpm.

Lipase

Another enzyme we used was lipase (Resinate, Novozyme). According to the above-mentioned process, 17.1 µL of lipase was added to the mixture of absolutely dry matter and water, and dissolved for 30 minutes at 50 °C and a pH value of 6.5.

Laccase

Laccase (Sigma Aldrich) was prepared in a buffer solution (1 mg/mL) and mixed by a spreader. After 30 minutes of dissolution, as in previous experiments, the same amount of chemicals was added. The pH value was 6 and the temperature was 25 °C.

Enzyme mixture

During the last experiment, ¼ (17.1 µL) cellulase enzyme and ¾ (11.8 µL) of laccase enzyme and the same amount of chemicals as in previous experiments were added to the spreader. The pH value was 6 and the temperature – 50 °C. At the end of the deinking procedure, laboratory paper sheets were prepared. The paper sheets were produced on Rapid-Köthen apparatus, in accordance with ISO 5269-2:2004. All the paper samples were conditioned according to ISO 187:1990 before testing. All tests were carried out at 50% relative humidity, at a temperature of 23 °C.

In accordance with the standards, we determined the following characteristics: grammage (ISO 536:2012), thickness (ISO 534:2011), density (ISO 534:2011), tear index (ISO 1974:2012), burst index (ISO 2758:2014), elongation at break (ISO 1924-2:2008) and tensile index (ISO 1924-2:2008), ISO brightness (ISO 2470-1) and opacity (ISO 2471). The properties of the laboratory paper sheets were determined at the temperature of 23 °C and 50% relative humidity.

RESULTS AND DISCUSSION

The results of basic (Table 1), strength (Table 2) and optical properties (Figs. 1 and 2) of paper after the deinking process are shown and discussed below.

Basic properties of paper after deinking process

Table 1 shows the basic properties (grammage, thickness and density) of the laboratory paper sheets achieved after the deinking process. From the values of these parameters, we can conclude that all the samples achieved similar levels of those properties. This can be explained by the fact that the paper sheets were produced under completely controlled laboratory conditions.

Strength properties of paper after deinking process

The enzymatic treatment, in combination with chemicals, has mostly improved the elongation at break and the tensile index of the samples. The highest tensile index values were obtained by treating the mixture with cellulase. We can conclude that cellulase opened the fibre structure, increased the fibril content and thus contributed to better inter-fibre bonding. All these effects of cellulose treatment have already been proven in one of our preliminary researches on enzymatic fibrillation of cellulose fibres.[18]

Overall, the best results were achieved by the lipase treatment. Most of the recovered paper was printed by the offset printing technique (95%). The composition of the offset printing ink vehicle is based on natural resins and vegetable and mineral oils. Lipase has the ability to degrade the structure of those oils (esters of higher fatty acids). Thus, it can be assumed that the enzymatic treatment with lipase reduced the content of oils in the paper, thereby improving inter-fibre bonds.[19,20] The values of the tear and burst index increased following most of the enzymatic treatments, probably due to the higher content of the fine fraction, conducing to an improvement of inter-fibre bonding. The highest values were obtained after the lipase treatment, while the lowest values were again achieved following the enzymatic treatment by laccase (alone or in combination with cellulase).

Optical properties of paper after deinking process

The highest level of ISO brightness (Fig. 1) was achieved for the sample treated by a mixture of cellulase and laccase. We assume that cellulase caused the opening of the fibre structure, allowing the printing ink to separate from the surface of the cellulose fibers.[15] The treatment with lipase was also effective. It is assumed that lipase removed the oils present in offset printing inks, thus contributing to an improved brightness of the sample.

Table 1
Basic properties of paper

Treatment	Basic properties	$\bar{x}$
Chemicals	Grammage (g m^{-2})	70.9
	Thickness (mm)	0.13
	Density (kg m^{-3})	534
Chem. + cellulases	Grammage (g m^{-2})	58.5
	Thickness (mm)	0.11
	Density (kg m^{-3})	532
Chem. + lipases	Grammage (g m^{-2})	66.2
	Thickness (mm)	0.12
	Density (kg m^{-3})	570
Chem. + laccases	Grammage (g m^{-2})	63.2
	Thickness (mm)	0.11
	Density (kg m^{-3})	565
Chem. + mix of enzymes	Grammage (g m^{-2})	65.1
	Thickness (mm)	0.12
	Density (kg m^{-3})	559

Table 2
Strength properties of paper

Treatment	Strength properties	$\bar{x}$
Chemicals	Elongation at break (%)	2.19
	Tensile index (kNm^2 kg^{-1})	33.15
	Tear index (mNm^2 g^{-1})	5.91
	Burst index (kPam^2 kg^{-1})	2.07
Chem. + cellulases	Elongation at break (%)	2.36
	Tensile index (kNm^2 kg^{-1})	35.78
	Tear index (mNm^2 g^{-1})	6.29
	Burst index (kPam^2 kg^{-1})	2.43
Chem. + lipases	Elongation at break (%)	2.36
	Tensile index (kNm^2 kg^{-1})	38.97
	Tear index (mNm^2 g^{-1})	6.52
	Burst index (kPam^2 kg^{-1})	2.63
Chem. + laccases	Elongation at break (%)	2.34
	Tensile index (kNm^2 kg^{-1})	31.76
	Tear index (mNm^2 g^{-1})	5.63
	Burst index (kPam^2 kg^{-1})	2.18
Chem. + mix of enzymes	Elongation at break (%)	2.10
	Tensile index (kNm^2 kg^{-1})	39.13
	Tear index (mNm^2 g^{-1})	5.93
	Burst index (kPam^2 kg^{-1})	2.39

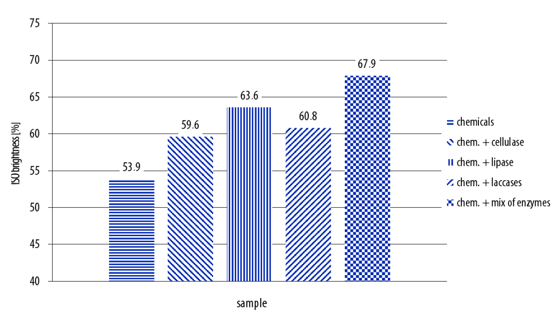

Figure 1: Optical properties of paper – ISO brightness (%)

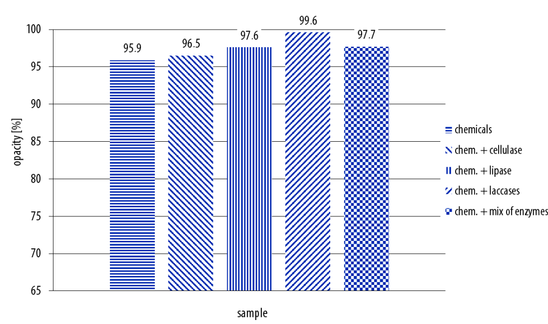

Figure 2: Optical properties of paper – opacity (%)

A similar level of ISO brightness was also achieved by the treatment with laccase. We can conclude that laccase caused the degradation of lignin and other components (impurities) and, in this way, contributed to a higher degree of brightness.[21]

The highest level of paper opacity (Fig. 2) was achieved in a sample deinked using chemicals and laccase. On the basis of Figure 2, we can conclude that the results attained for all the samples are similar.

CONCLUSION

By comparing chemical and enzymatic treatments, it can be concluded that enzymatic treatment improved the mechanical properties of laboratory handsheets. It is also evident that enzymatic treatment using lipase provided the best results in terms of mechanical properties, while enzymatic treatment with laccase provided the worst values for most mechanical properties. The highest level of brightness was achieved for a sample treated with a mixture of cellulase and laccase. Our study confirms the fact that the use of enzymes in the paper industry allows upgrading the process of chemical deinking. Due to lower chemical consumption, the environmental impact may be reduced, and costs lowered. In the literature, there are many examples of enzymatic deinking of different types of recovered paper. Basically, all highlight the idea that the use of appropriate enzymes can improve paper properties. This is also evident in our study, which is one of the few to describe the impact of commercially available individual types of enzymes, as well as their mixtures, on paper properties. In the future, enzymatic deinking will, most probably, be a constant practice for all paper mills that use recovered paper as input material.

The changes on the global print market, where the use of flexo and digital printing has significantly increased in recent years, will also require to alter the deinking processes. Especially, personalized, smaller print runs, printed by different printing techniques, will challenge paper plants to develop universal deinking procedures, combining different chemical and enzyme processes, as shown in our research.

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