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# PRELIMINARY STUDIES ON ENZYMATIC DEINKING

Pala, H.; Gama, F.M.; Mota, M.

Dept. Engenharia Biológica, Instituto de Biotecnologia e Química Fina, Universidade do Minho, Campus de Gualtar, 4709 Braga Codex, Portugal

## ABSTRACT

Results on enzymatic deinking of paper pulps are shown. The process includes paper pulping, with an enzymatic cocktail, followed by flotation and dewatering. Three different wastepaper samples were used and tested. The deinking of the pulp was monitored by image analysis. Physical, mechanical and optical properties of pulp and paper were also determined. The obtained data revealed the effectiveness of the assayed enzyme preparation. However, enzyme use needs further optimisation as paper strength properties suffered important alteration.

## INTRODUCTION

Wastepaper recycling is nowadays mandatory, because of the world-wide lack of virgin fibre, and in order to reduce the cellulosic residues produced in developed societies. The incorporation of secondary fibres in paper production became an accepted reality, and research on recycling technologies, namely for effectively removal of pulp contaminants (deinking) is necessary.

Traditional processes use expensive, potentially environmental damaging chemicals. An alternative to these methods are biological treatments, which use enzymes to peel away cellulose fibrils, thus removing attached ink particles which are then removed by flotation [1]. Enzymatic technology is also known as specially advantageous to deink mixed office waste (MOW), the best quality wastepaper. The reuse of MOW is usually limited by its high content of noncontact inks, which are very difficult to remove by application of current methodologies [2]. So far, a satisfactory theory describing the way the enzymes act removing the ink particles from the fibres surface has not been presented. The main purpose of this work was to develop an efficient experimental methodology to study the enzymatic deinking methods. Further work will follow, with the aim of analysing the fundamentals of the process, both in terms of the enzymes surface activity and reactivity.

## METHODS AND MATERIALS

The experimental sequence used in the enzymatic deinking is shown in Figure 1. Chemical deinking sequence was similar. In order to conveniently estimate the enzymatic action, a blank and a control were made parallel to the enzymatic assays. The blank refers to the starting pulp (no treatment was performed). Control pulps were processed in a similar manner as those given the enzymatic treatment described above, except that no enzyme was added.

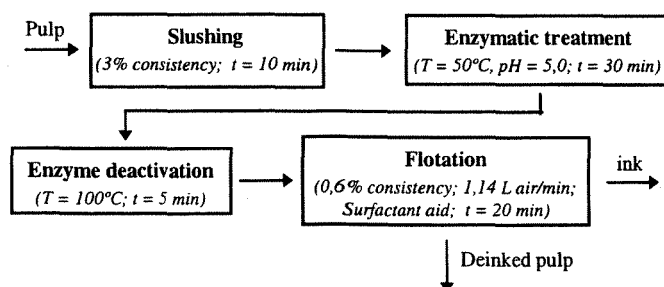


Figure 1: Experimental sequence

## Enzymatic Preparation

The enzymatic cocktail used was a commercial preparation kindly supplied by Buckman Laboratories. Its relevant activities are presented in Table I. Assay procedures used to determine enzymatic activities are the following:

### Carboxymethylcellulase (CMCase)

0,5 mL of the diluted enzyme was incubated in 0,5 mL of carboxymethylcellulose solution 1% (sodium citrate buffer, 0,05 M, pH = 5,0). The enzymatic reaction took place at 50°C, during 30 min. Released sugars were measured by DNS method, using glucose as the standard.

### Filter paper activity (FPase)

0,5 mL of diluted enzyme was added to 1 mL of sodium citrate buffer containing 50 mg of Whatman n°1 filter paper. After incubating for 60 min at T= 50°C, released sugars were measured by DNS method, using glucose as the standard.

### Xylanase activity

0,5 mL of diluted enzyme was incubated in 1,5 mL of oat spelt xylan solution 1% (sodium citrate buffer, 0,05 M, pH = 5,0). After incubating for 30 min at T= 65°C, released sugars were measured by DNS method, using glucose as the standard.

TABLE I: ENZYMATIC ACTIVITIES

Activity	Activity (U/mL)	Dosage (U/g OD pulp)
CMCase	6	1,2
FPase	3	0,6
Xylanase	29	5,8

## Paper Furnish

The current work aims to study the potential of enzymes in the deinking of three different wastepaper samples: (i) photocopy printed paper; (ii) a chemical pulp; (iii) a mechanical pulp. The last two samples were kindly supplied by Renova and the first one was prepared at U.M. laboratory by soaking photocopy printed paper in warm water and disintegrating for about 30 minutes.

## Enzymatic Pulping

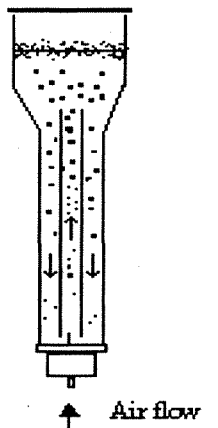
After a 10 minutes fiberization step with sodium citrate buffer 0,05 M, pH 5,0, the enzyme was added to the mixer and was allowed to react with the pulp during 30 minutes at 3% consistency. To finish up the trial, the enzyme was deactivate by heating the pulp at 100°C and boiling for approximately 5 minutes. After this, the pulp was floated.

## Chemical Pulping

After a 10 minutes fiberization step with water, deinking chemicals were added and pulping continued for another 30 minutes (pH = 11,0), followed by immediate floating of the pulp. The chemicals used were 0,7% NaOH, 15% sodium silicate and 0,6% hydrogen peroxide based on OD weight of pulp. Pulp consistency was 6%.

## Flotation

A laboratory flotation unit was developed and optimised at the U.M. laboratories in order to separate fibres from ink particles. It actually consists on an airlift reactor (Figure 2) which operates with 4,5L sludge (0,6% consistency) during 20 minutes at room temperature and an air flow of 1,14 L/min. During the flotation process a surfactant is added.



This kind of reactor is characterised by liquid and solid phases cyclic flow. The circulation in the reactor is established by the difference between fluids densities in the downcomer (descending tube) and in the riser (ascending tube). This variation arises from the injection of air through the reactor's bottom. At the top of the reactor there is a degaseification zone, where the gas used in the impulsion is released and the formed foam and retained ink are collected.

Figure 2: Airlift reactor

## Dewatering and Handsheet Preparation

The floated samples were recovered and dewatered on a vacuum filter. Handsheets were made according to the usual standard TAPPI procedures.

## Physical, Mechanical and Optical Properties

Properties of pulp and paper were determined according to the standard TAPPI procedures. Parameters as drainage rate, burst, tensile, tear and brightness were measured.

## Image Analysis

The image analysis system is composed of a magnification lens, charge-coupled device (CCD) camera, image displayer and computer. All the images were acquired with the same magnification and lightning in order for comparable results to

be obtained [3]. A 4x objective was chosen, as a reasonable compromise between image enlargement and analysed area. Several authors have already demonstrate that the two sides of the same handsheet can lead to different results as contaminants tend to accumulate differently on either side [3,4]. Therefore, all the handsheets were analysed in the same side. Particle counts, shapes and sizes were examined using a commercial available software (Globalab Image). To ensure image analysis results reproducibility a suitable threshold value was selected to identify the contaminants and maintained in all performed analysis with the same kind of pulp [3]. For each handsheet 40 images were retained and treated.

## Image Analysis Calibration

A calibration of the image analysis system was done as follows: Six handsheets were made, using different proportions of deinked and non-deinked chemical pulps. The predicted ink concentration, calculated on the basis of the particles concentration in each of the two "pure" pulps, was compared with the obtained one. Brightness values were also determined.

## RESULTS AND DISCUSSION

### Image analysis calibration

The smallest spot which could be distinguished, under the operation conditions, had a surface area of 299  $\mu\text{m}^2$ . The average analysed area was 355  $\text{mm}^2$ . Figure 3 shows the correlation between real ink concentration and the predicted one, demonstrating the applicability of the technique. The effect of random sampling errors was calculated for the coverage and particle areas using the correlations suggested by Zayer et al [3]. The greatest confidence interval (%CI) for a confidence level of 95% is 9%.

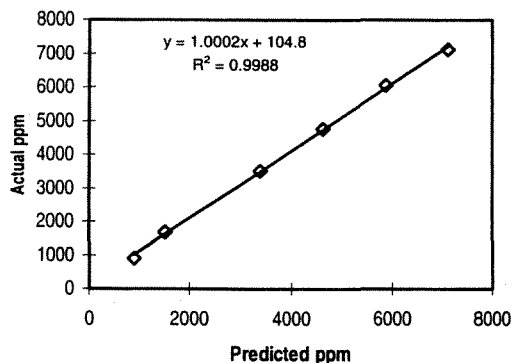


Figure 3: Actual ink concentration versus predicted ink concentration

A good correlation between brightness and ink particle concentration was found, which cannot be attributed to the ink particles concentration. The effect of ink particles on brightness values has been shown to be a complex one.

Darker particles contribute more heavily to the decrease in brightness values than do lighter particles of the same size [6] and smaller particles sizes cause brightness to decline more rapidly [6].

## Evaluation of enzymatic deinking performance

Figures 4 and 5 summarise image analysis results. The analysed area was the same in each case. The obtained information demonstrate enzymatic treatment efficiency on ink removal from secondary fibre. Mechanical pulp deinking seems to be less effective.

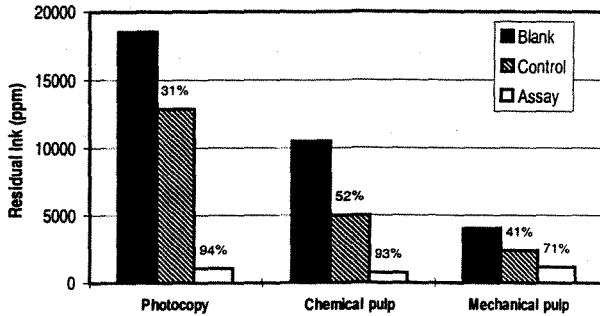


Figure 4: Enzymatic deinking efficiency

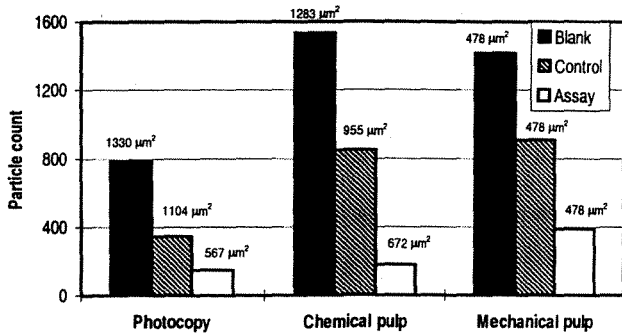


Figure 5: Particle count and ink particle size median variation

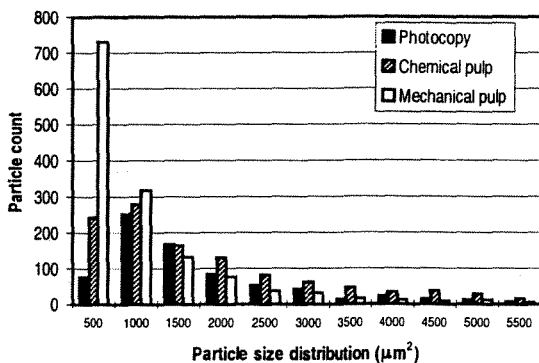


Figure 6: Particle size distribution for the different non treated pulp samples

The enzymatic improvement on deinking has been justified by the peeling effect that enzymes perform on fibre surface, which could facilitate the ink detachment [7,8]. However, as the detached ink is usually removed by flotation, the efficiency of the overall process depends not only on the detachment of the

ink particles but also on the size of the detached particles, because that is one of the critical factors of the flotation process. The smaller particles are the most difficult to remove, and every deinking process has to be optimised so that particle size is not excessively reduced [9]. This situation can probably justify the lower deinking efficiency in the case of the mechanical pulp: as shown in Figure 6, the mechanical pulp presents the lowest average ink particle size.

Brightness was also measured. Only the chemical and mechanical pulps had higher values following deinking (Table II). In these cases, brightness increased when either flotation or enzymatic treatment plus flotation were applied. By comparing the obtained brightness values with residual ink concentration, it can be concluded that, when the average particle size is small, traditional brightness measuring techniques do not reflect the relative ink concentration in the paper [5,6,10]. As a matter of fact, the mechanical pulps present lower brightness values, even if chemical pulp is the one that presents the higher residual ink concentration.

TABLE II: BRIGHTNESS (%)

	Chemical Pulp	Mechanical Pulp
Assay	91,3	78,8
Control	85,9	74,6
Blank	84,5	72,9

The enzymatic treatment changed also significantly the ink size distribution profile. Figure 7 presents particle size distributions of treated and untreated chemical pulps. Photocopy paper and mechanical pulp exhibited profiles similar to this one. Median values of ink particle size for the several pulps are shown in Figure 5. As suggested by Prasad *et al.* [4], the larger particles have apparently either been removed from the pulp, or reduced in size after the enzymatic treatment and flotation.

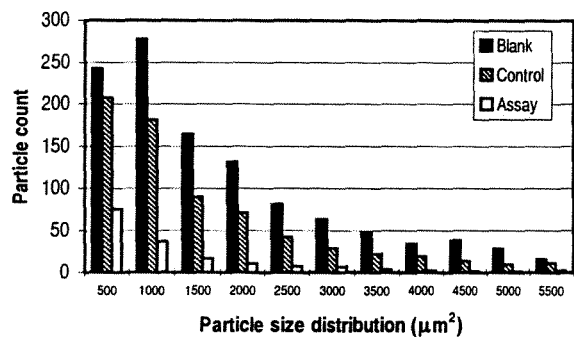


Figure 7: Particle size distribution for different samples of chemical pulp

Finally, physical and mechanical properties of pulp and paper were determined. The obtained results are presented on Table III. Burst, tensile and tear indexes were reduced, and surprisingly, only the photocopy paper exhibited a slight improvement in drainability.

A high enzyme concentration in the pulping process may reduce the overall hydrogen bonding potential of the fibres, and therefore the paper mechanical resistance [11]. This is probably the reason why the mechanical indexes registered in this work were significantly lower after the enzymatic treatment. Work remains to be done regarding the optimisation of the process, conveniently optimising the enzyme concentration for efficient ink removal, and at the same time not affecting the paper mechanical properties [8,9].

TABLE III: ENZYMATIC ACTION ON PULP AND PAPER PROPERTIES

Sample	Drainability (°SR)	Burst Index (KPa.m <sup>2</sup> /g)	Tensile Index (N.m/g)	Tear Index (mN.m <sup>2</sup> /g)
<b>Photocopy</b>				
Assay	32,5	2,5	44,8	4,0
Control	41,8	3,6	54,3	10,1
Blank	35,5	3,8	55,6	10,1
<b>Chemical</b>				
Assay	49,5	1,4	30,8	3,1
Control	45,5	2,6	40,5	8,9
Blank	33,5	2,5	37,7	9,2
<b>Mechanical</b>				
Assay	67,3	1,5	32,3	3,1
Control	64,0	2,7	41,7	8,9
Blank	47,5	2,2	35,7	9,0

#### Evaluation of chemical versus deinking performance

This study compares enzyme and chemical deinking of a chemical pulp. It was verified that the enzyme facilitated deinking to a greater extent than chemicals (Figure 8). The used chemical preparation did not affect significantly the paper mechanical properties, and it even allowed for a slight increase in resistance; on the other hand, the pulp drainage rate was lowered. This can be explained as the effect of alkaline pH, which causes fibre to swell, increasing its surface area and intensifying fibre bonding. Also the chemical deinking allowed for a brightness improvement of the paper sheets, but lower than the one resulting from the enzymatic treatment.

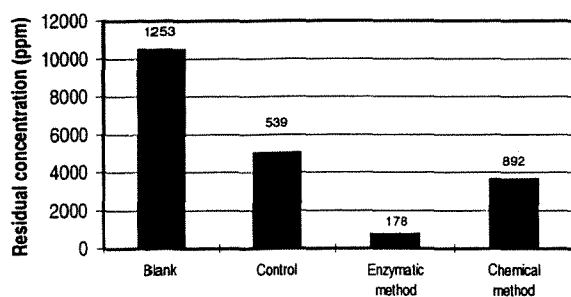


Figure 8: Deinking efficiency and particle count

#### CONCLUSIONS

The present work confirms the efficiency of cellulase/xylanase cocktails on paper pulps deinking, although considerable loss of the paper physical properties resulted under the used

experimental conditions. The main objective of this work, at this stage, was to establish all the necessary techniques for future enzyme testing and selection: a very effective flotation device, different from those described in the literature, has been used, and standard procedures for image analysis of paper sheets have been defined. The tested enzyme preparation proved to be more effective on ink removal than a conventional chemical methodology. Optimisation of the process will follow. Pulping time, consistency, pH, enzyme concentration and the presence of surfactants are factors that will be analysed in order to improve the enzymatic performance. The mechanism of the deinking process will also be analysed in future work.

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