

NEUTRAL ENZYME ASSISTED DEINKING OF XEROGRAPHIC OFFICE WASTE WITH A CELLULASE/AMYLASE MIXTURE

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ABSTRACT

This paper presents the results of a laboratory investigation exploring the benefits of neutral enzyme-enhanced deinking of xerographic office waste. Four different non ionic surfactants were preliminarily tested in a cellulase assisted deinking. A commercial α -amylase was also employed to optimize the cellulase-assisted deinking process of xerographic office waste. Using a selected surfactant along with a cellulase/amylase mixture the area coverage of the residual toner particles, measured by image analysis, was reduced up to 96%. The enzyme/surfactant deinking process did not significantly affect the brightness and the sheet strength properties whereas the Canadian standard freeness was slightly improved with respect to reference treatment.

Application:

In an high efficiency enzyme-assisted deinking process, in terms of toner particle removing, taking advantage from the synergistic action of cellulase and amylase enzymes.

KEYWORDS

Amylase, cellulase, deinking, enzyme, flotation, image analysis, ink, recycling, toner, xero copy paper.

INTRODUCTION

The increasing use of recycled pulp along with the increasing fraction of office waste paper has generated a need of more efficient deinking processes. Due to the substantial waste produced in these processes papermakers would benefit from environmentally friendly technologies. It is

well known that the removal of laser and xerographic toners by conventional deinking methods is difficult and therefore to overcome this problem in the last few years enzyme assisted deinking has been proposed as potential alternative to conventional approaches (1). Several research groups have demonstrated that hydrolytic enzymes, mainly cellulases, are the most suitable enzymes to facilitate toner detachment and its removal by subsequent flotation and washing steps (2,3,4). Because non ionic surfactants interact with cellulases to improve their action, they have often been used to enhance enzyme assisted deinking (5,6). Mill scale trials have confirmed laboratory investigations showing that enzyme enhanced deinking can be pursued as short term objective to improve sorted postconsumer paper (7). Nevertheless, the enzymatic deinking process still needs to be optimized to meet industrial applications of unsorted mixed office waste. Recently, Zollner and Schroeder (8) reported the use of an α -amylase to deink white office papers. They obtained a substantial increase in toner removal and showed that new enzymatic approaches can be useful. Since starch is widely present in mixed office waste, being used both as surface-sizing agent and wet-end additive, its degradation is very likely to aid cellulase assisted deinking. Another key factor is represented by the pH of the process. In deinking plants alkaline chemistry is the most widely used, nonetheless most mills would probably prefer running deinking processes under neutral conditions. Pieroni et al. (9) have shown that in a tissue deinking mill the utilization of a carefully selected non ionic surfactants allowed to shift from alkaline deinking to neutral deinking without decreasing brightness values. In their study neutral conditions allowed also a better runnability of papermachine and a significant reduction of antistickies chemicals.

In order to produce higher papergrade, neutral enzyme/surfactant chemistry could be one of the best choices for deinking. By adapting enzyme mixtures and surfactant structure it is possible to improve pulp quality from different waste paper furnishes. The aim of our work was to evaluate at laboratory scale the efficiency of a cellulase/amylase enzyme blend in order to optimize a neutral deinking process of xerographic office waste paper.

EXPERIMENTAL

Paper furnish

The commercial neutral paper Repro 80 (210 x 297 mm, 80 g/m², Cartiere Burgo) was printed with a standard pattern by using a Sharp SF - 8570 copy machine and Sharp SF - 880ST1 black toner. The paper stock was homogenized, aged prior to use and characterized to determine the chemical composition. TAPPI Method T264 was used to determine extractives content, except that the ethanol-benzene mixture was replaced with ethanol-cyclohexane. The TAPPI Methods T222, T250 and T223 were applied for the determination of acid-insoluble lignin, acid soluble lignin and pentosans content, respectively. TAPPI Method T249 for preparation of holocellulose was employed with the modification suggested by Maekawa and Koshijima (10). Ash content in the paper was determined at 525°C according to TAPPI Method T211. Quality of fillers was investigated in paper and in its ash by using a X-ray Siemens D-500 Diffractometer (Cu, K α radiation).

Surfactants and Enzymes

Four non-ionic surfactants supplied by Hercules incorporated were used in the pulping stage of the deinking treatments. The surfactants differed on chemical structure and hydrophilic lipophilic balance value (HLB). A shake cylinder test was carried out to determine the foaming of 5 µl of surfactants in 50 mL water (hardness 10°f) at 38°C. In **Table I** the experimental names and their main features are reported.

The enzymes, supplied by Novo Nordisk, used in the experiments were: Novozyme 342 (NZ 342), consisting mainly of cellulase and xylanase activities, and BAN 240, a commercial α -amylase preparation. Cellulase and amylase activities were determined on each batches utilized by measuring the reducing sugars produced at neutral pH, 50°C, using 1% carboxymethylcellulose (CMC) and potato starch as substrates, respectively (11). The Nelson-Somogyi method was used for reducing sugar determination.

Surfactant	Fatty chain	HLB value	Foam (mL)
F1	ethoxylated alcohol	5.2	4
F2	ethoxylated alcohol	7.8	10
F3	ethoxylated fatty acid	11.4	3
F4	ethoxylated alcohol	14.5	32

Table I. Surfactant properties.

Pulping and Enzymatic Treatments

For all pulping trials 100 g o.d. shredded paper was soaked overnight at 5°C in 500 mL of deionized water. Prior to the pulping stage 1400 mL of water containing a selected amount of surfactants were added (5% pulp consistency). In the pulping stage the paper was slushed in a laboratory disintegrator (Toniolo Milano-Italy) at 3000 rpm for 10 min. at 50°C. Following this step enzymes diluted in 100 mL of sodium phosphate buffer pH 7.0 were added in the pulper continuing fiberization for 30 min. For surfactant only trials the same amount of buffer was added to meet the condition used in the enzymatic treatments. A reference treatment was also carried out slushing the paper in the condition described above, except that neither surfactant nor enzyme were added in the pulper.

Flotation

The flotation was performed in a 20 L laboratory flotation cell (Cattana e Carossino, GE, Italy) at a consistency of 0.5% in neutral pH condition. The treatments were carried out for 10 min. at 30°C, employing 0.15% of F2 surfactant as flotation aid and mixing the suspension with an air flow of 0.5 L/min.

Handsheet preparation and testing

Handsheets of 80 g/m² of the pulp samples were prepared according to TAPPI Method T205. Physical testing was done according to TAPPI Method T 220. The freeness was determined using the TAPPI Method T227 whereas brightness values of the handsheets were obtained according to TAPPI Method T 452.

Image analysis

Image analysis was carried out employing a Rainbow TV Zoom Lens H6x8-II and a TK 1280E JCV scanner to digitize the images of toner particles on handsheets. A Kontron Imaging System KS 300 software version 1.2 by Kontron Elektronik GmbH was used to count toner particles. The minimum diameter value of counted toner particle was set at 80 µm.

The ink area coverage data as parts per million (ppm) was the mean value of a series of 15 dirt counts on each of 5 handsheets. ***This number of replicates was found sufficient to obtain a standard error within 10%.*** The ink particle size distribution was also determined. The results were expressed as mm² / m² of surface, i.e., ppm.

RESULTS AND DISCUSSION

Paper furnish characterization

The paper furnish was characterized with respect to its chemical composition (**Table II**). The ash content was 19% mainly composed of calcium sulfate as determined by X-ray diffraction. The calcium sulfate was originally present in the paper as dihydrate salt. The presence of calcium sulfate resulted in neutral pH condition after slushing the paper and, as a consequence, there was no need to adjust pH before adding the enzymes in the pulper. Starch content was 4.2 % and, as stated by supplier, was potato starch modified by oxidation and esterification, added as surface sizing.

Component	Percentage, %
Cellulose	47.5
Hemicellulose	18.4
Starch	4.2
Acid insoluble lignin	3.6
Acid soluble lignin	0.7
Extractives	1.6
Ash	19.0

Table II. Chemical composition.

Chemi-enzymatic deinking treatments.

Preliminary experiments carried out with four different non ionic surfactants showed that, in our system, the optimum surfactant dosage in the pulper ranged from 0.05% to 0.15%, based on dried fibers (12). With the aim of improving the enzymatic deinking these surfactants were used to study the interaction with cellulase. **Figure 1** illustrates the results obtained using 0.1% of various non ionic surfactants in combination with 0.025 % of cellulase NZ 342. As can be observed, the surfactants assisted cellulase action to different extents. Surfactant F3 was the most effective showing the greatest ink count reduction with respect to reference run, where neither surfactant nor enzyme were added to the pulper. This surfactant, as reported in Table I, has a medium hydrophilic lipophilic balance value along with a low foaming level allowing a good system runnability. In our cellulase/surfactant system we have observed an optimum response in deinking efficiency versus enzyme dose as it has already been reported by other research groups (6). The optimum ink removal was achieved at 0.05% NZ 342 enzyme concentration using 0.1% surfactant (**Figure 2**).

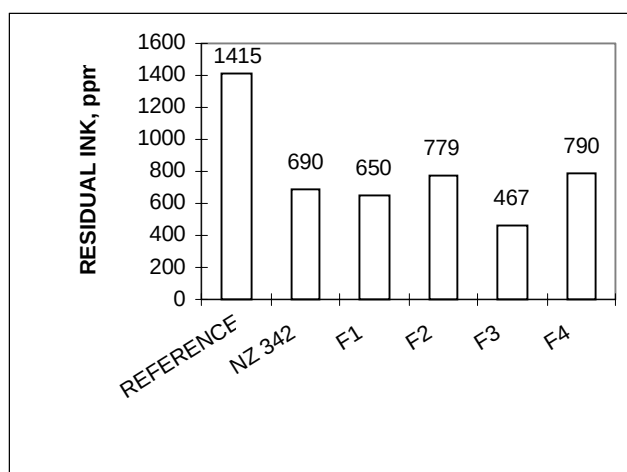


Figure 1. Influence of different surfactants on cellulase assisted deinking.

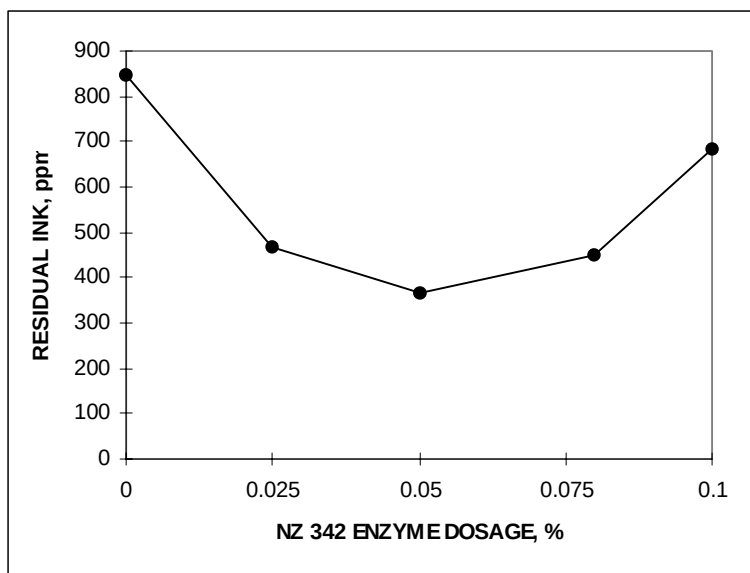


Figure 2. Effect of cellulase NZ 342 dosage on residual ink.

The efficiency of the deinking treatments was calculated as the ratio between the area of ink particles in the treated samples after flotation, and the value of ink particles in the unfloated sample after pulping. In the deinking trials we have always added, before the flotation stage, 0.15% of a flotation aid that we had selected in a previous work (12). As shown in **Figure 3** the reference run, which had no chemicals addition in the pulper, gave 75% efficiency in toner removal. Surfactant only run, which received 0.1% of F3 surfactant in the pulper showed an increase of dirt removal efficiency from 75% to 84%, confirming that better results can be achieved by adding surfactants at the beginning of the pulping process (6). The enzymatic run performed using 0.05% cellulase NZ 342 and 0.1% F3 surfactant increased further the toner removal leading the efficiency up to 93%.

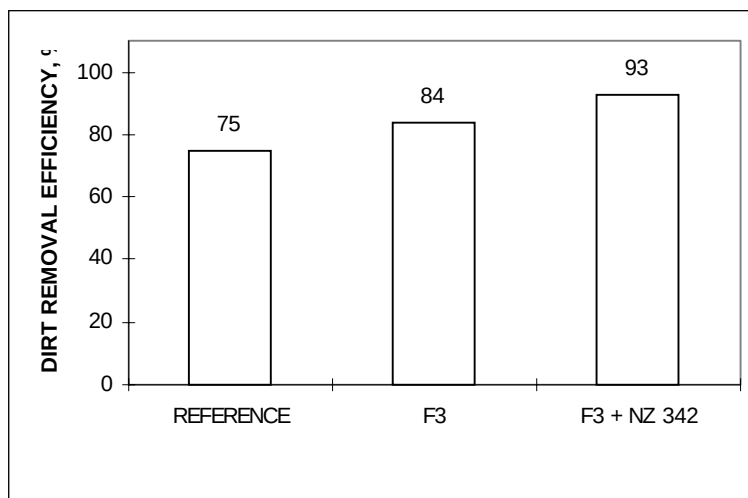


Figure 3. Dirt removal efficiency of different deinking treatments.

With the purpose of optimizing the cellulase assisted deinking process efficiency, we employed BAN 240 α -amylase. In our tests this commercial enzyme preparation showed very little cellulase activity and therefore was suitable to verify the synergism with cellulase NZ 342. In fact, the latter enzyme preparation did not reveal any amylase activity.

Preliminary runs ranging from 0.0005% to 0.002 % of BAN 240 showed a similar improvement in dirt removal efficiency as was observed with cellulase assisted deinking. However, best results were obtained with 0.001% amylase concentration. **Figure 4** shows the efficiency relative to deinking treatments performed using 0.001% amylase BAN 240 alone and combined with 0.05% cellulase NZ 342. The results show that cellulase/amylase blend gave the greatest efficiency (96%) achieved in our experiments obtaining a three point gain compared to cellulase alone treatment (93%). These data indicate that a synergism occurs between the two enzymes in facilitating the removal of ink particles by flotation. The existence of a synergism between the two enzymes is also confirmed by the results obtained using BAN 240 alone. As can be observed in Fig.. 4 the efficiency of a run conducted employing surfactant and 0.001% amylase BAN 240 as enzymatic aid improved deinking efficiency only up to 89%.

Mixed office waste often contain starch and therefore the α -amylase increased the efficiency of the deinking treatment by degrading the starch layer on the surface of the paper. Our results

indicate that by adding amylase enzyme to a cellulase assisted deinking process it is possible to improve significantly the dirt removal by flotation.

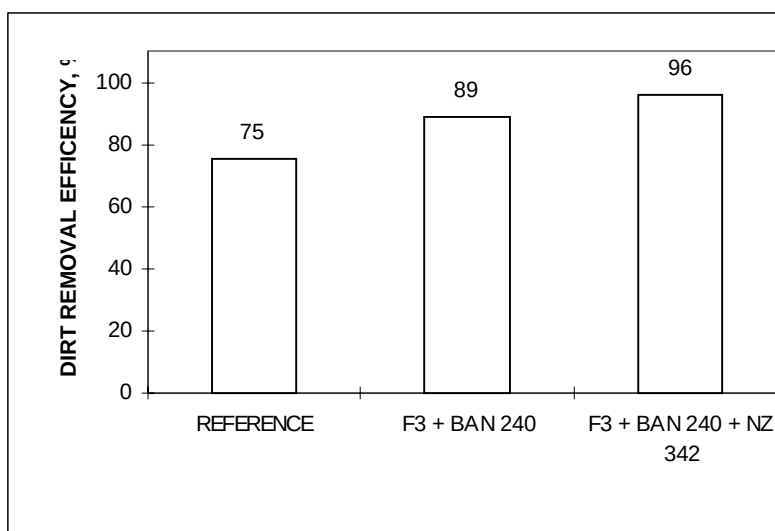


Figure 4. Dirt removal efficiency of different deinking treatments.

Following deinking treatments the particle size profile of the residual dirt present on handsheets was investigated. To simplify the reading of the results we report in **Figure 5** only two classes of ink particles, smaller and bigger than 0.04 mm^2 of equivalent black area. The value of 0.04 mm^2 is the lowest limit of equivalent black area of dirt reported in TAPPI method T213 concerning the dirt visual estimation. Most of the residual ink in the Reference had a size smaller than 0.04 mm^2 ; about the same ratio was also observed in the Unfloated sample. Using the F3 surfactant in the pulping stage, the distribution of the residual ink changed significantly: the amount of the two classes of particles became basically the same. The addition of enzymes produced different patterns of residual dirt. As already previously observed, the amylase alone treatment shows a smaller efficiency compared to cellulase treatment. However, the particle size profile revealed a greater selectivity of this enzyme towards the removal of smaller particles. By comparison to surfactant only chemistry, the cellulase NZ 342 reduced the larger particles to a greater level. Employing both cellulase and amylase enzymes we obtained a significant decrease of smaller particles whereas larger particles did not change significantly with respect to cellulase alone treatment. Therefore the greater efficiency achieved in the deinking process using the enzyme mixture appears to be mainly due to the reduction of the particles smaller than 0.04 mm^2 .

Handsheets and pulp properties.

Brightness was measured on all handsheets prepared following pulping (Unfloated sample) and flotation stages and compared to the brightness of the original commercial paper. The results are reported in **Table III**. In all trials we achieved brightness values similar to that of the original commercial paper. The increasing of brightness compared to the Unfloated sample underline the efficiency of the processes. However, no significant differences were observed among the deinking treatments. In contrast, a slight increase of Canadian standard freeness was observed

particularly when cellulase/amylase mixture was used. Tensile, tear and burst indexes were tested on all samples. The enzymatic treatments did not show any deleterious effect on sheet properties.

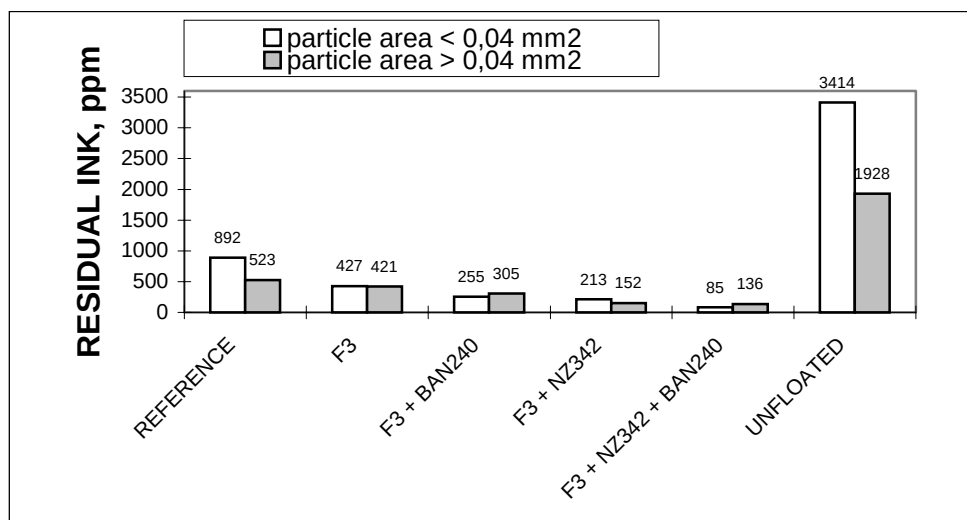


Figure 5. Residual ink particle size distribution following different deinking treatments.

	Commercial paper	Unfloated	Reference	F3	NZ 342	BAN 240	NZ342+BAN 240
Brightness,%	91.6	78.7	90.2	90.4	90.8	89.1	90.5
Freeness, mL	-	-	570	575	620	572	647

Table III. Brightness and Canadian Standard Freeness.

CONCLUSIONS

Neutral cellulase assisted deinking of xerographic office waste can be further improved by adding low levels of amylase in the enzyme mixture. Our data suggest that amylase acts differently than cellulase facilitating a greater removal by flotation of smaller ink particles and showing a great deal of synergism with cellulase. Considering that cellulase alone treatment showed a pretty high efficiency in deinking of our sorted nonimpact white office paper work is in progress to verify if amylase addition would be even more useful in an enzyme assisted deinking of more complex office wastes. We plan to move forward confirming our results with a more heterogeneous mix office waste analyzing also the influence of different type of starches on enzymatic deinking efficiency.

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Received: March 22, 1999

Accepted: April 5, 2000

This paper was accepted for abstracting and publication in the November issue of *TAPPI JOURNAL*.

TAPPI Website: www.tappi.org