BLEACHABILITY OF RECYCLED FIBERS DEINKED WITH ENZYME PREPARATIONS

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ABSTRACT

The increasing cost of wastepaper is challenging recyclers to dig deeper into the wastepaper stream to remain competitive. The necessity of dealing with a low-quality paper stock has shifted the recycling emphasis from ink removal to color removal. Our research indicates that enzymes can be an important part of the solution for this new challenge. This study explores the influence of commercially available enzyme preparations used for deinking office wastepaper on pulp brightness and bleachability.

INTRODUCTION

The paper stocks that we used for this study were typical 100% post-consumer mixed wastepaper. We selected paper stocks containing several levels of ash, lignin, and colored components. Initially, we screened various cellulases, hemicellulases, and enzyme preparations composed of mixtures of enzymes for deinking these paper stocks. We determined the effectiveness of laboratory-scale deinking trials by counting residual ink and measuring brightness and L*, a*, b* color of the deinked pulp before and after bleaching with alkaline hydrogen peroxide and formamidine sulfinic acid (FAS).

When we used either cellulases or hemicellulases for deinking, the brightness of the deinked stock was two to three points greater than a comparable control pulped with water. This brightness advantage was maintained after peroxide bleaching of pulps deinked with enzyme preparations containing both cellulase and xylanase activities. This brightness matched that achieved by bleaching conventionally deinked pulps that used additional peroxide and caustic for deinking. Reductive bleaching with FAS was uniformly effective and slightly better on pulps deinked with cellulase preparations.

Paired with other demonstrated advantages of using enzymes in repulping wastepaper, improved brightness and bleachability could permit recyclers to successfully utilize less expensive and more abundant mixed wastepapers. Increased bleachability also implies a lower bleach chemical requirement to achieve comparable brightness levels, an economic and environmental plus.

Preliminary investigations on a low-quality mixed paper furnish containing mechanical, unbleached, and dyed fibers confirmed the positive role of enzymatic deinking for significantly upgrading this stock. By changing the conventional deinking sequence and substituting a pressurized peroxide step for conventional peroxide bleaching, we found that the enzyme-deinked pulp not only reached 80% brightness but was substantially cleaner than the control, both in residual ink and unbleached fibers. We believe that this is the first reported study that examines the bleachability of such a heterogeneous paper stock after enzyme deinking.

BACKGROUND

For the removal of toner inks, enzyme preparations are effective substitutes for conventional deinking chemicals. Previously, we demonstrated on high-quality post-consumer printing and writing paper that not only are enzymes more effective than chemicals for ink removal, but fringe benefits include increased freeness, maintained fiber strength, lower effluent oxygen demand, and often an increased pulp brightness (1,2). The mechanism of enzyme deinking has not been clearly defined, but most researchers agree that a combination of mechanical action of medium consistency pulping in the presence of a surfactant is vital for process viability. Although some research (3,4,5) has shown that cellulases are key to toner ink removal, we found that some of the most effective commercial deinking enzyme preparations are combinations of cellulases and hemicellulases.

Our previous studies focused on optimizing ink removal. We also observed a slightly greater brightness level in pulp deinked with several of the enzyme preparations that we compared. This increased brightness was not dramatic on already high brightness sorted office papers. However, when we shifted our research to a more realistic mixed office waste for comparative evaluations, the contrast between

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several added brightness points contributed by enzyme treatment was more apparent. It would be cost effective to select an enzyme preparation for ink removal that would also enhance pulp brightness.

The use of enzymes to enhance pulp brightness has been reported by others. However, the emphasis has been on virgin fiber, using xylanase to reduce the chlorine demand for bleaching kraft pulps. Kim, Ow, and Eom were the first to demonstrate the advantage of enzymes for deinking secondary fibers (3). Newsprint was a logical paper source for initial investigations, because newsprint is a readily available segregated paper source that is compatible with the slightly acidic pH range required by cellulase preparations. Kim et al. demonstrated that newspaper deinked with cellulase was comparable in brightness to conventional alkaline peroxide deinked newsprint. Others observed that brightness increased with increased levels of enzymes applied to deinking newsprint and that optimal mixtures of cellulases and hemicellulases produced even greater brightness gains than were obtained with chemical deinking (6).

Prasad, Heitmann, and Joyce reported that cellulases and hemicellulases could also be effective in deinking and improving the brightness of letterpress and color offset printed newsprint (7). They found that a xylanase preparation produced the highest brightness on letterpress paper, and the best brightness response on offset printed paper was obtained with a mixture of cellulase and hemicellulase. This suggested the need to optimize various paper stocks, printing methods, and inks for the best enzyme preparation for both deinking and brightening.

The study reported here addresses the role of enzymatic deinking in upgrading mixed wastepaper. We examined several grades of unsegregated post-consumer paper containing varying amounts of ash, lignin, and colored components. A dramatic difference between enzymatic deinking of clean, white office paper and a mixed paper stock is that flotation removes most contaminating toners from a sorted stock. However, when an unsorted mixed paper stock is deinked, many contaminants remain with the accepts: dyed and unbleached fibers, ink aggregates, stickies, and water dispersible inks. Even when most toner inks are removed, a major task remains of color stripping and bleaching to upgrade the deinked pulp for use in printing and writing grades.

MATERIALS AND METHODS

Paper Stocks

Two paper stocks were used in this study:

1. Typical mixed office waste – 65% sorted high-quality office paper, high laser printed content, 20% colored/offset printed, 10% newsprint, 5% magazines, Kappa ~ 5, 11% ash.
2. Curbside wastepaper—low quality mixture, high in newsprint, glossy colored content, plus some laser and computer printout (CPO), Kappa ~ 42, 8% ash.

A large batch of each paper stock was shredded, fiberized, and subsequently pulped in 1-kg capacity Hobart mixer with surfactant, with and without various enzymes, following conditions outlined in previous papers (1,2). The batch was floated in a Denver cell, washed and screened, and made into Tappi standard handsheets for speck check analysis for residual ink. The deinked pulp was chelated with 0.2% DTPA and bleached with 2% hydrogen peroxide or 1% FAS. Brightness was read from 3-g handsheets made before (initial) and after bleaching.

Enzyme Preparations

The following indicates enzyme activity:
Enzyme A: cellulase, xylanase, mannanase mixture
Enzyme B: cellulase, (xylanase negligible), used at pH 7
Enzyme C: xylanase (cellulase free), used at pH 7.5
Enzyme D: alkaline xylanase (cellulase free)
Enzyme E: cellulase, xylanase, used at pH 7
Enzyme F: xylanase (cellulase free), used at pH 7.5
Enzyme G: cellulase, xylanase, mannanase mixture

Pulping and Deinking

City water was used for all pulping and deinking processes. Fiberized stocks were pulped at 14% consistency in Hobart mixer for 25 min at 55°C, ambient pH 8.4 to 8.6, except where noted. Pulp was floated at 1% consistency in Denver cell for 4 min and then washed on sidehill screen.

Bleaching Conditions

The following lists the bleaching chemicals and conditions used in this study:

Alkaline hydrogen peroxide
Hydrogen peroxide (2% on ovendried pulp)
Sodium hydroxide (0.8%)
Sodium silicate (3%)
Magnesium sulfate (0.05%)
15% consistency
75°C to 80°C
1-h holding time

Formamidine sulfinic acid (FAS)
1.0% on ovendried pulp
0.25% to 0.5% NaOH to initial pH 10.5
12% consistency
75°C to 80°C
45-min holding time

Pressurized Peroxide (PO)
Peroxide bleaching chemicals were mixed into 500 g (ovendried) of pulp and placed in the holding chamber of a batch pressurized refiner. The reacting chamber was pressurized with oxygen and held for 10 min at 0.2 MPa and passed through refiner plates with a wide gap.
Chemicals: 5% NaOH, 2% H_2O_2, 3% sodium silicate.
Bleach chemicals were mixed into chelated pulp at 25% consistency. Refiner was preheated 30 min with steam; pulp was added and steamed for 2 min before oxygen was added up to 0.2 MPa at 95°C to 100°C.

DISCUSSION OF RESULTS

Two separate mixed paper stocks were used in this study. The first batch contained a high percentage of clean printing and writing paper to which colored paper and newsprint were added. The second batch was curbside wastepaper, with little printing and writing paper included. Descriptions of these stocks are included in the Materials and Methods section.

Results of these deinking and bleaching trials of the first paper stock are summarized in Table 1. Reported brightness values are average of triplicate samples. Brightness of the flotation accepts are denoted by "initial" brightness. As expected, the pulp that was repulped with only surfactant and water had the lowest brightness, 57.8% The highest initial brightness, 61.5%, resulted from conventional chemical deinking using 0.5% hydrogen peroxide and typical stabilizers. Accepts from all enzyme treatments had initial brightness levels between 58.0% and 61.5%. A cellulase, enzyme B, matched the 61.3% brightness of the chemical treatment; a cellulase-free xylanase, enzyme C, matched the 57.8% of the water control of this paper stock.

When bleached with 2% hydrogen peroxide, the brightness increased 7 to 10 points, with almost all enzyme-treated pulps matching or slightly surpassing the brightness of the bleached chemical control, 68.7%. Pulps deinked with enzyme preparation with mixed enzyme activities, enzyme A reached 70.0%, a 10 brightness point increase over the initial deinked brightness. In this oxidative bleach step, enzyme preparations composed of multiple enzyme activities performed slightly better on this pulp stock than preparations displaying only either cellulase or xylanase activity.

Table 1. Bleach Response On Mixed Office Waste

	Brightness (%)		
	Initial	2% H_2O_2	1% FAS
Water control	57.8	67.0	68.8
Enzyme A	60.4	70.0	70.3
Enzyme B	61.3	68.4	68.8
Enzyme C	57.7	67.8	65.5
Enzyme D	59.7	67.4	67.8
Enzyme E	58.0	69.0	67.7
Enzyme F	58.5	67.6	67.7
Enzyme G	58.6	68.9	68.0
Chemical control	61.5	68.7	68.0

High peroxide residuals at 1 h indicate a higher brightness potential at a longer retention time.

Reductive bleaching with 1% FAS resulted in an increase of 8 to 11 brightness points. Here, the enzyme preparations containing high xylanase activity were less responsive than those with cellulase activity. Enzymes A, B, and G matched or surpassed the 68.0% brightness achieved on the chemical control.

Although these results were reproducible on this paper stock, they may not hold true on a paper stock with greater levels of ash or lignin content. Unsegregated wastepaper is more difficult to deink and bleach with conventional deinking and bleaching systems than is sorted newsprint or high-grade ledger paper. Because multiple ink types, paper grades, and color content all have to be addressed to successfully utilize mixed office waste using environmentally responsible methods, ingenuity must replace convention. Cleaning and screening to reduce ash content and contaminants may have to precede pulping to optimize that step. Flotation deinking is needed for toner ink removal, and washing is required for water-dispersible ink removal. Compared with pH and temperature optimum for bleaching virgin fiber, atypical bleaching pH and temperatures are often most effective for brightness development when reductive bleach chemicals are used on secondary fiber.

Using this freedom to explore, we conducted preliminary deinking and bleach trials on a low-grade, mixed paper stock. This material was put together by Superior Recycled Fiber Industries, Inc. from a collection of curbside paper. A large quantity of newsprint, glossy, and colored paper as well as mixed office wastepaper comprised this stock. This paper stock was more complex to deink and bleach than other recycled paper with which we have worked, because it contained large amounts of contaminants, lignin, and ash. The initial brightness of 47.5% was paired with a Kappa number of approximately 42.

We observed art interesting correlation between reduced deinkability and limited response to alkaline peroxide bleaching. Enzyme and peroxide effectiveness appeared to be dependent on the paper stock. It is unclear whether paper additives, such as sizings, fillers, coatings, residual metals from printing inks or process water, or other substances are responsible for this effect. This clarification could impact the design of mill-scale deinking processes for using low-quality paper stock.

Table 2 traces the residual ink, brightness, and bleach response observed after changing the point of the enzyme addition. When cleaned and screened, both the initial brightness of the enzyme deinked pulp and the final bleached brightness reflected the optical advantage of enzyme pulping. High brightness levels were obtained on this pulp by using pressurized peroxide (PO) bleaching. Adding enough pressure to permit the use of higher temperature accelerates the production of the perhydroxyl anion (OOH^-), which is responsible for peroxide bleaching (8, 9). Chemials were applied more appropriate for oxygen bleaching than PO bleaching. The brightness of the enzyme-deinked pulp was 72.8% after the PO stage-almost 6 points brighter than the control. When 1% FAS was applied to the PO bleached pulps, the enzyme-treated pulp reached 80.0% compared with 76.7% for the control.

In addition, oxygen selectively targeted residual contaminants. This step dramatically demonstrated the effectiveness of enzyme deinking compared with a control on final brightness and cleanliness. Both ink and unbleached or colored fibers appeared to be more selectively removed following enzyme deinking in these preliminary trials. Even though this process has not yet been optimized, residual ink on the enzyme-treated pulp approached TAPPI dirt count specifications for acceptability with 35 ppm, considerably cleaner than the control with 128 ppm. These positive preliminary results give optimism to the possibility of increased wastepaper utilization.

Table 2. Bleach Response on Curbside Waste Paper

Process steps	Brightness (%) Initial	Brightness (%) 2% H_2O_2		Dirt Count (ppm)	Detection Level[b]
Pulped "as is"					
Water control	47.5	52.3		420	90
Enzyme A	47.5	52.2		415	
Enzyme A/DTPA[a]	48.0	52.6		367	
Cleaned/Screened					
Water control	55.8	60.4		211	110
Enzyme A	56.2	61.3		162	
Enzyme D	54.0	63.3		149	
Cleaned/Screened/Washed					
Water control	56.7	65.7		96	
Enzyme A	56.2	66.0		124	110
Cleaned/Screened/ Pressurized Peroxide (PO)			**(PO)Y_{FAS}**		
Water control	56	67.1	76.7	128	
Enzyme A	56	72.8	80.0	35	125

[a] 0.2% DTPA was added with Enzyme A in the pulper.
[b] A detection level of 125 should be used for Tappi Dirt Count (0.02 - 5.0 mm^2); lower detection levels were needed because original stock contained too many ink specks to be counted accurately at that level. Lower detection levels give relative ink removal.

CONCLUDING REMARKS

Results published on initial deinking experiments of 100% high quality office paper printed with toner inks were confirmed for various mixed office wastepaper stocks. Even at low enzyme levels (0.04% on ovendried pulp), an increase of several brightness points was observed on pulps treated with either cellulase- or xylanase-containing enzyme preparations. Enzyme treatments for deinking gave varying results on both deinkability and bleachability with different paper stocks. When a heterogeneous paper stock is recycled, this finding impacts process design of deinking mills.

From these preliminary trials, we conclude the following:

- Enzyme preparations used for deinking can add 2 to 3 brightness points to deinked pulp.
- Enzyme deinked pulp is responsive to both oxidative and reductive bleaching.
- Low-grade mixed paper stocks may require modification of deinking processes for optimum ink removal and bleach response.
- Enzyme deinking followed by pressurized peroxide bleaching can substantially upgrade curbside wastepaper.
- Pressurized peroxide bleaching dramatically improves brightness and reduces the number of unbleached kraft and colored fibers.

Optimization of the pressurized peroxide stage is essential. Preliminary results under less than optimum conditions have been encouraging as a way to target unbleached fibers in deinked pulp. Determining what components of wastepaper interfere with enzyme deinking and peroxide bleaching is essential for handling unsegregated paper stocks. We plan to examine paper additives for possible inhibitors so that we might specifically address those materials to improve deinking and bleach response.

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