A Study on the Removal of Fluorescent Whitening Agents from Recycled Fibers

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ABSTRACT

Virgin bleached kraft pulp, CPO (computer printout) and white ledgers are main raw materials used in tissue mills. The utilization rate of recycled fibers and virgin pulp in South Korea tissue industry are 90% and 10%, respectively. To improve brightness of printing grades the use of 'fluorescent whitening agents (FWAs)' or 'optical brightening agents (OBAs)' has been increased. When recycling these papers for tissue production, it is unavoidable that FWAs contained in recycled papers flow into tissue production lines and remain in the products. And this draws great attention from the public. This study was carried out to develop a technology for the removal of fluorescent whitening agents from recycled fibers. Enzymatic removal of FWAs was evaluated as a method to remove FWAs from the recycled fiber. The α-amylase that degrades starched used for surface sizing of fine papers and contained substantial amount of FWAs showed high efficiency in FWA removal. The pH of pulp suspension affecting the solubility and affinity of FWA onto fibers was one of the critical factors in FWA removal. It was found to keep pH in alkaline condition is needed to prevent the re-adsorption of FWAs on fibers. The temperature of pulp suspension was another important factor affecting on FWA removal. The higher the temperature, the greater the efficiency of removing FWAs was obtained. Optimum pH and temperature for the effective removal of FWAs were suggested to be pH 8.5 and 65°C, respectively. The enzymatic removal of FWAs showed a great synergistic effect when proper control in pH and temperature was made.

INTRODUCTION

Recycled fibers have become an important source of raw materials for pulp and paper industry. There are many challenges, however, to use recycled fibers for the production of highly value-added products [1]. Today a large number of end products are being produced with the use of recycled fibers. These include printing and writing papers, newsprint, coated paper and board, and tissue papers. The utilization rate of the recycled fibers as raw materials depends upon the grades. In the case of tissue products, the utilization rate of recycled fibers and virgin pulp are 90% and 10%, respectively, according to the statistics of Korea Paper Manufacture's Association.

One of the major problems in using recycled fibers for paper production is that they contain contaminants. Among many contaminants encountered with recycled fibers, FWAs contained in CPO and white ledgers have drawn public attention. When tissue products are made with these recycled fibers, it is unavoidable for them to have FWAs. Even though it has not been verified whether FWA is carcinogenic, FWAs contained in tissue products have drawn great attention from the public. Public concern asks the domestic tissue industry to develop a technology to remove residual FWAs coming to the production line with the recycled fibers. Not many research efforts or technological approaches to solve the problem associated with the contamination of tissue products with recycled FWAs have been made [2-4].

It was suggested that use of strong oxidizing agents that destroy the molecular structure of FWAs can be used to eliminate the FWA problems in tissue mills. However, the utilization of these agents was reported to be impractical and marginally effective for the removal of FWAs.

In pulp and paper industry, enzymes, which are known as environmentally friendly additive, have been widely used in pulp bleaching and deinking. In this study, the effect of several enzymes on removing residual FWAs from recycled fibers was examined. The main idea is that enzymes can detach FWAs present on paper surface with surface sizing agents, such as oxidized starch or polyvinyl alcohol. After the detachment, the detached FWAs present in process water can be removed by the flocculation or breakdown with chemicals.

The applicability of enzymes on FWA removal was estimated by applying them into pulp suspensions prepared with commercial fine papers. And the optimum conditions for the effective removal of FWA were investigated.

Experimental

Materials

Two commercial fine papers with grammages of 80 g/m^2 (FP1) and 75 g/m^2 (FP2) were used as model recycled fibers.

Three types of enzymes, LTAA, Fibrezyme and Multifect, with the specifications provided by suppliers shown in Table 1 were used.

Hydrochloric acid and sodium hydroxide were used to control pH of pulp suspensions and FWA solutions.

Table 1. Optical properties of the commercial fine papers

Grammage (g/m^2)	CIE whiteness $FI_{whiteness}$ (%)	ISO brightness $FI_{brightness}$ (%)	FE (457 nm)
80	116.33 43.55	89.49 7.07	553.6
75	152.10 64.71	94.15 11.06	972.9

Table 2. specifications of enzymes

Commercial name	Composition	Activity (unit)
LTAA	α-amylase	2,000 (WU/ml)
Fibrezyme	Cellulase Hemicellulase	8,400 (CMCase/g)
Multifect	Cellulase Hemicellulase	2,200 (IU/g)

Methods

Applicability of enzymatic removal of FWAs

Commercial fine paper (FP1) was used as a raw material for estimating the applicability of enzymatic removal of FWAs. Commercial fine paper (FP1) was disintegrated in a laboratory disintegrator at 3.0% consistency for 50,000 rev. and then dilution was made to 1.0% consistency.

Three types of enzymes including LTAA, Fibrezyme and Multifect were applied to the stock. Application conditions are shown in Table 2. Different application conditions were employed for three enzymes since enzymes had different activities depending on conditions of use such as pH and temperature. After the enzyme treatment, handsheets with the grammage of 80 g/m^2 were made and conditioned at 23°C and 50% RH. Fluorescence emission of the handsheets was measured using image restoration microscope. To determine the amount of extracted starch and FWAs, COD of the supernatant of pulp suspension was measured. The supernatant of pulp suspension was obtained after centrifugal separation at 500 G for 30 minutes.

Table 3. Conditions of enzyme treatments

Enzyme	pH	Temperature (℃)	Addition (%)	Reaction time (hr)
LTAA	6.0	80	0.10	1
Fibrezyme	7.5	50	0.10	1
Multifect	6.5	50	0.10	1

Optimum conditions for the removal of FWAs and enzyme treatment

Commercial fine paper (FP2) was disintegrated at 3.5% consistency for 50,000 rev. using a laboratory disintegrator. Pulp suspensions were diluted to 1.0% consistency and FWA was added.

To investigate the effect of pH of pulp suspension on the removal of FWAs, pHs of pulp were controlled at 6.5, 7.5 and 8.5 with either HCl or NaOH solutions while stirring them at 600 rpm for an hour. To examine the effect of the temperature of pulp suspension on FWA removal, the temperature of pulps were controlled to 25, 65 and 80°C in a constant water bath. Through these investigations, optimum conditions of pH and temperature of pulp suspension for the removal of FWAs were determined.

Enzyme treatment was carried out at the optimum pH and temperature conditions for the removal of FWAs. In addition, the effect of enzyme addition on the removal of FWAs was also investigated.

To determine the removal of FWAs, handsheets with the grammage of 80 g/m^2 were made according to TAPPI Test Method T205 sp-02. After conditioned at 23°C and 50% RH, fluorescence index were measured using Elrepho spectrophotometer [2]. And the supernatant of pulp suspension was obtained by centrifugal separation at 500 G for 30 minutes. Fluorescence emission of the supernatant was measured using QuantaMaster spectrofluorometer. Excitation and emission wavelengths were 337 nm and 438 nm, respectively. Other chemical analysis which included measurements of starch concentration and COD was also carried out.

Results and Discussion

Applicability of enzymatic removal of FWAs

Three types of enzymes were applied to remove FWAs from commercial fine paper (FP1). Enzymes used were LTAA (α-amylase), Fibrezyme and Multifect. These enzymes are widely used in the paper industry for deinking and process optimization [5-8].

The bacterial α-amylase is obtained from a controlled fermentation of *bacilius subtilis*. It is an endo-amylase that randomly hydrolyzes the predominating α-D-(1-4) glucosidic linkages of starch. Fibrezyme is a mixture of cellulase and hemicellulase. It acts on the surface of fibers and removes small particles present in pulp suspension. It is usually used in the enzymatic deinking. Multifect is consisted of diverse enzymes including cellulase, hemicellulase, xylanase and mannanase. The main components of Multifect, however, are cellulase and hemicellulase. It is derived from controlled fermentation of *Tricoderma reesei*. Multifect acts on the surface of fibers, and it is known to improve the drainage in papermaking process as well as the physical properties of products.

Table 4 shows fluorescence emission of the paper determined using image restoration microscopy technique. Fluorescence emission of commercial fine paper (FP1) was about 553. After disintegration of FP1, fluorescence emission reduced and this indicated the removal of FWAs from fine papers by the mechanical action of disintegration. Treatment with α-amylase decreased fluorescence emission of handsheet further. Treatment with Fibrezyme and Multifect, however, did not show any synergic effect for the removal of FWAs in fine papers. This shows that there were differences in enzyme effects. It is known that α-amylase degrades starches, while Fibrezyme and Multifect act on the surface of fibers. In other words, α-amylase detaches starches on paper surface by degrading α-D-(1-4) glucosidic linkage of starch [9]. Zollner *et al.* [16] also reported that α-amylase degraded the starch used for surface sizing agents and wet end additive. However, Fibrezyme and Multifect appeared to attack fiber surfaces not starches since they are mainly consisted of cellulase [10]. This fact could be confirmed from COD data shown in Table 4. Treatment with α-amylase increased COD by 25.2%, but other enzymes increased COD of the supernatant only by 3~4%. Since dissolved starch increases COD of the supernatant of pulp suspension [19], increases in COD indicates the increase of the amount of degraded starch in supernatant. In other word, the result of COD shows that α-amylase degraded the starch present on the papers which ends up COD in the supernatant.

Table 4. Fluorescence emission of handsheet treated with enzymes (Fluorescence excitation = 360 nm)

	Fluorescence emission of handsheet	COD of supernatant (ppm)
FP 1	553.6	-
Disintegration	490.2	662.5
LTAA	355.2	885.5
Fibrezyme	479.7	691.0
Multifect	484.9	689.0

Therefore, it can be concluded that α-amylase increases detachment or dissolution of surface sized starch in recycled fibers. This action of α-amylase would increase the removal of FWAs from recycled fibers if FWAs contained in the starch film detaches from paper surface along with starch. To maximize the FWA removal with this enzyme, optimum conditions of enzymatic treatment should be established and applied.

Investigation of optimum conditions for enzymatic removal of FWAs

pH of pulp suspension

Pulp suspension was prepared with commercial fine papers (FP2) using a laboratory disintegrator and diluted to 1.0% consistency. Initial pH of pulp suspension was approximately 8.5 because the fine paper contained calcium carbonate fillers. The pH of pulp suspension was controlled to 6.5, 7.5 and 8.5.

Fluorescence indices of handsheets, fluorescence emission and starch concentration of the supernatant of pulp suspension were shown in Table 5. As the pH of pulp suspension decreased toward acidic conditions, fluorescence indices of handsheets increased. This indicated that FWAs which was detached from fine papers re-adsorbed on fibers in acidic conditions. Increases in re-adsorption of FWAs on fibers at low pH results in a reduction of FWA concentration in the supernatant of pulp suspension. However, the starch concentration in the supernatant of pulp suspension did not change significantly irrespective of the pH of pulp suspension. This indicates that detached FWAs would re-adsorb on fibers under acidic conditions.

This 'redyeing' phenomenon seems to originate from the change of FWA solubility with pH [11]. Because acidic condition increases the affinity of T-FWA to fibers, detached FWAs readsorbed on the fibers.

Table 5. Effect of pH on the removal of FWAs from recycled fibers at room temperature

pH	Fluorescence index (%)	Fluorescence emission	Starch concentration (mg/g)
6.5	57.5	32,219	60.7
7.5	53.8	38,899	62.7
8.5	45.7	53,722	63.0

Temperature of pulp suspension

To investigate the effect of the temperature of pulp suspension on FWA removal papermaking stock was prepared with fine papers (FP2). While stirring the stock for an hour the temperatures of the stocks were adjusted to 25, 65 and 80˚C and their pH conditions were controlled to either 8.5 or 6.5.

Table 6 shows the effect of the temperature of pulp suspension on the removal of FWAs at pH 8.5. As the temperature of pulp suspension increased, fluorescence indices substantially decreased indicating that the removal of FWAs increased. Increases in FWA concentration, starch concentration and COD in the supernatant of pulp suspension also showed that FWA dissolution increased at high temperature. Especially, increases in the starch concentration caused an increase in FWA concentration. This indicates that starch dissolution is the prime cause of the increase in FWAs in solution. In other word, starch dissolution that increased with temperature resulted in FWA concentration in the supernatant of pulp suspension.

Table 7 shows the effect of the temperature of pulp suspension on the removal of FWAs at pH 6.5. The removal of FWAs in pulp suspension at pH 6.5 also increased as the temperature increased. FWA concentration, starch concentration and COD of the supernatant of pulp suspension also supported the results of fluorescence indices as shown in Table 7.

However, fluorescence indices of handsheets at pH 6.5 were higher than those at pH 8.5 even though the heat treatments were carried out. This was because the initial fluorescence indices of handsheet at pH 6.5 were higher than those at pH 8.5. Especially, it should be noticed that even though the initial starch concentrations at pH 6.5 and 8.5 were the same, the increase of starch concentration at pH 8.5 was greater than that at pH 6.5. This indicated that the temperature was also very important factor for the removal of FWAs. The higher the temperature of pulp suspension, the more starch and FWAs can be removed. And this is more so in alkaline condition.

Increasing the stock temperature to 80˚C would be impractical to apply in the mill. It is rather common the temperature of stock reaches to 60~65˚C especially during summer season. It was found that when pulp suspension is alkaline, the effect of high temperature is more beneficial for the removal of FWAs.

Table 6. Effect of pH on the removal of FWAs from recycled fibers at pH 8.5

pH	Fluorescence index (%)	Fluorescence emission	Starch concentration (mg/g)
25	45.7	55,157	60.7
65	37.6	61,306	76.9
80	30.4	65,091	94.8

Table 7. Effect of pH on the removal of FWAs from recycled fibers at pH 6.5

pH	Fluorescence index (%)	Fluorescence emission	Starch concentration (mg/g)
25	57.5	32,219	60.6
65	53.8	38,131	65.3
80	45.7	40,349	70.0

Enzymatic removal of FWAs from recycled fibers

The α-amylase was applied to stock prepared with commercial fine papers (FP2). Papers were disintegrated at 3.5% consistency for 50,000 revolution and diluted to 1.0% consistency.

Table 8 shows fluorescence indices of handsheets treated with α-amylase. Here, control means handsheet which was made only after disintegration at room temperature and 0.0 means handsheet which was made after treatment at pH 8.5 and 65˚C without α-amylase. At the addition of 0.0 WU, fluorescence indices reduced significantly because pH and temperature of pulp suspension was adjusted to optimum conditions. As α-amylase addition increased from 4.6 to 9.2 WU, fluorescence indices decreased further. However, after the addition of α-amylase increased from 9.2 to 18.4 WU, fluorescence indices of handsheets did not show significant reduction. This indicated that the addition of 9.2 WU was the optimum addition level. Highest fluorescence emission and COD of the supernatant of pulp suspension was obtained at the addition of 9.2 WU.

The reason is that α-amylase degrades the starch present with FWAs on fine papers and detached FWAs from recycled fibers. Fluorescence emission and COD of the supernatant of pulp suspension show the same trends. Therefore, the enzymatic removal of FWAs showed a great deal of synergism with the control of pH and temperature.

Table 8. Enzymatic removal of FWAs at pH 8.5 and 65˚C

Enzyme addition (WU)	Fluorescence index (%)	Fluorescence emission
Fine paper	64.7	-
Control	45.7	55,157
0.0	37.6	61,306
4.6	29.4	64,012
9.2	27.8	66,470
18.4	28.3	65,107

Conclusions

The applicability and optimum conditions for the removal of FWAs from recycled fibers were explored.

Three enzymes were applied, but α-amylase showed the highest efficiency for the removal of FWAs. This was because of the ability of α-amylase to degrade the starch.

Optimum conditions for the enzymatic removal of FWAs were investigated. The pH of pulp suspension was very important as it altered FWAs' solubility in solution and affinity to fibers, and it should be kept under alkaline condition to prevent the re-adsorption of FWAs on fibers. The temperature of pulp suspension was also important factor affecting on the removal. The removal of FWAs was in proportion to the temperature. Optimum pH and temperature was suggested to be pH 8.5 and 65°C in the mills for the effective removal of FWAs. Enzymatic removal of FWAs with α-amylase showed a great deal of synergism with the control of pH and temperature.

ACKNOWLEDGEMENT

This work was supported by Korea Institute of Environmental Science and Technology, Ministry of Environment. And it was partially supported by Brain Korea 21 project, Korea Research Foundation.

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