EFFECTS OF pH VARIATION ON EFFICIENCY OF OLD NEWSPAPER DEINKING BY PECTINASE DERIVED FROM *ASPERGILLUS NIGER*

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Enzymes are protein molecules with complex structure that accelerate biochemical reactions. The activity of these chemical compounds is limited to a specific range of pH and temperature. The effect of pH variations on deinking efficiency of old newspaper (ONP) by pectinase was investigated in this study. Old newspaper was repulped in a laboratory disintegrator for 10 minutes at 5% consistency and 26500 rpm. Enzymatic treatment of recycled ONP was carried out for 20 minutes at 0.1% enzyme concentration and 10% consistency, and pH levels of 3.5, 4, 4.5, 5, 5.5 and 6. The results showed that more efficient pectinase deinking of old newspaper can be achieved at 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 of 4 to 5.

Keywords: enzymatic deinking, old newspaper, pectinase, pH treatment

INTRODUCTION

The utilization of waste paper has greatly increased in recent years and secondary fibers have come to hold an important share of the fibers used in the pulp and paper industry.[1,2] Traditional chemical deinking uses large quantities of chemicals, which require costly water treatment systems.[3] In order to overcome these disadvantages, enzymatic deinking has attracted a great deal of attention due to its high efficiency and low environmental impact.[4,5] The application of enzymes for replacing or enhancing traditional deinking chemicals has been reported, indicating that enzymatic deinking can get the same or better deinking results, with minimal impact on the physical properties of final paper products.[6,7] Industrial scale-up experiments with enzymatic deinking have been reported[8] and an enzyme enhanced deinking technology has been developed to be applied on a commercial scale.[7,9] Different enzymes have been used for deinking, including cellulases, hemicellulases, lipases, xylanase, pectinases, laccase, esterases, amylolytic and ligninolytic enzymes.[10-18]

Hemicellulases and cellulases can attack the components of fiber surface.[8,19] These enzymes appear to alter the fiber surface by modifying the chemical bonds in the vicinity of ink particles, thereby freeing ink for its removal by washing or flotation. Starch-based coating can be hydrolyzed by amylolytic enzymes and vegetable oil-based ink binders can be degraded by lipases.[20] Cellulases and hemicellulases have already been routinely applied in many mill practices,[8] but the strength properties of deinked pulp are affected to some extent. Therefore, it is desirable to search for more effective and less damaging enzymes for deinking.

Pectinases, poly-α1-4-galacturonic acids, with variable concentration of methylated residues of carboxylic acids, are a heterogeneous group of enzymes that hydrolyze complex polysaccharides of plant tissues, such as pectic substances, into simpler molecules, like galacturonic acids. The pectic substance is a polymer of chain molecules, consisting of a rhamnogalacturonan backbone that is linked with carbohydrates and other polymers.

In fact, it is a common name used for four types of molecules: pectinic acids, pectins, pectic acids, and protopectin. Protopectin is a kind of water insoluble parent pectin substance found in the middle lamella of plant tissues, which yields soluble pectic substances like pectin or pectinic acid upon restricted hydrolysis.[21,22]

Pectinases constitute 25% of the global sale of industrial enzymes annually. The main commercial application of pectinases is in the food industry for the extraction, clarification, and concentration of fruit juices, the clarification of wines and the extraction of oils, flavors, and pigments from plants. With the development of biotechnology and increased tendency of the paper industry to use microorganisms for biotreatment of waste water, biopulping, biobleaching, biodeinking and biorefinery, the use of enzymes, such as pectinases, has been increased in the pulp and paper mills.[23-25]

Carbohydrates such as pectins have negative effects on the drainage rate of the pulp in papermaking, because anionic pectins, which are known as anionic trash, form complexes with cationic papermaking additives, like cationic retention aids, resulting in less effective retention of fines and fillers in the paper. Enzymatic treatment with pectinases can depolymerize polymers of galacturonic acids and subsequently lower the cationic demand of the system.[26,27]

Ricard and Reid[28] purified pectinase from the commercial enzyme mixture Novozym 863 by affinity chromatography. They stated that the enzyme pectinase reduced the cationic demand of peroxide-bleached mechanical pulp by up to 60% and improved the efficiency of cationic polymers as a retention aid.

Li *et al.*[29] studied the effects of pectinase on the stickies deposition and the dissolved and colloidal substances (DCS) prepared from bleached chemi-thermomechanical pulp (CTMP). They reported that, since polygalacturonic acids, the major component of anionic DCS, can be effectively degraded during pectinase treatment, the efficiency of cationic polymers was improved and they subsequently fixed the destabilized sticky particles on the fibers, which led to a decrease in stickies deposition.

In a research carried out by Ahlawat and Mandhan,[30] the effectiveness of alkaline pectinase produced from *Bacillus subtilis SS* in papermaking was studied. The results showed that the best enzymatic pretreatment was achieved with a pectinase dose of 5 IU/g of oven-dried pulp, at pH 9.5, temperature of 70 °C and treatment time of 150 min, which resulted in an increase of 4.3, 14.8 and 65.3% in the brightness, whiteness and fluorescence, respectively, along with a decrease of 15, 5.85, 6.1% in the yellowness, kappa number and permanganate number, respectively.

Singh *et al.*[31] investigated the efficiency of xylano-pectinolytic enzymes in deinking of school waste paper and reported that enzymatically deinked pulp had a decreased requirement of chemicals to nearly 50%, whereas it resulted in a decrease of 20.15% and 22.64% in BOD and COD values of the effluents and a gain of 10.71, 7.49, 10.52, 6.25% in viscosity, breaking length, burst factor and tear factor, respectively, while exhibiting the same optical properties of the pulp, compared to those of conventional chemically deinked pulp.

In the present study, pectinase derived from *Aspergillus niger* was used for deinking ONP and the effects of varying pH on the efficiency of the deinking process, as well as the physical, optical and strength properties of resulting paper were investigated.

EXPERIMENTAL

Materials

Three-month old newspaper (ONP), from Hamshahri newspaper, Iran, was used in this investigation. The waste newspaper was shredded and dry-mixed before repulping.

Pectinase enzyme derived from *Aspergillus niger* fungi, with an activity of 1.06 Unit per milligram, was received from Novozyme Corp., Sigma Aldrich, Germany. Other chemicals, such as sulfuric acid and hydrogen peroxide, were purchased from Merck Co., Germany. All the compounds were used as received.

Repulping

ONP samples (100 g), after soaking with tap water, were repulped in a PTI laboratory disintegrator at 5% consistency and 26500 rpm. The pH of the repulped ONP suspension was 7.7 and was adjusted to the target enzymatic treatment pH using 1N sulfuric acid solution.

Enzymatic deinking

ONP pulp samples were treated with 0.1% pectinase at about 50 °C and 10% consistency for 20 minutes at different pH levels of 4, 4.5, 5, 5.5 and 6. After enzymatic treatment, residual pectinase was deactivated by 0.05% hydrogen peroxide, based on OD pulp, and has been fully washed with tap water on a 200-mesh screen. The repulped ONP suspension, in the absence of the enzyme, was used as control sample.

Evaluation of deinking

Standard handsheets were made according to TAPPI standard T205 sp-02.[32] To evaluate the efficiency of deinking by pectinase at different treatment pH, the optical and strength properties were measured according to relevant TAPPI standards: brightness and yellowness – T452 om-02,[33] opacity – T425 om-01,[34] physical testing – T220 sp-01,[35] tear and burst – T414 om-04[36] and T403 om-02,[37] respectively. A completely randomized design was used to evaluate the data, including ANOVA for the analysis of variances and the Duncan test for comparing the mean values.

RESULTS AND DISCUSSION

Effects of pectinase deinking on physical properties

The effect of pectinase deinking on the handsheet bulk at different pH, compared to the control sample, is shown in Figure 1. The results showed that bulk values increased when deinking was performed by pectinase, instead of conventional chemical deinking. Different mechanisms for ink removal by the enzymes have been proposed.[15,38-42] The pectinase enzyme decomposes the polysaccharide matrix from the primary wall (where pectin is present), promoting the swelling of this wall, along with higher porosity and loss of compactness (increased bulk), allowing increased accessibility and higher dissolution capacity of the fibers. Ink particles are then dislodged as the fibers separate during washing. However, the effect of pectinase treatment in increasing bulk was higher at pH values from 4 to 4.5.

Effects of pectinase deinking on optical properties

The effects of different pH values in pectinase deinking on handsheet brightness, yellowness and opacity, in comparison with those of conventional chemically deinked pulp, are shown in Figures 2, 3 and 4, respectively.

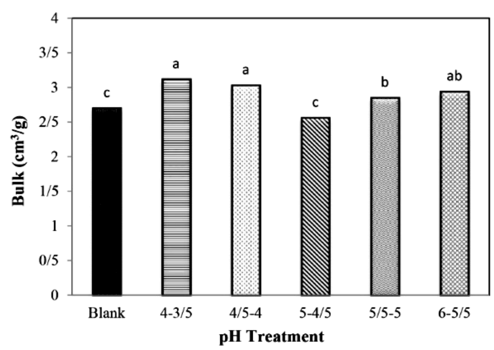

Figure 1: Effect of pH variation in pectinase deinking on the bulk of deinked ONP (mean values compared by the Duncan test; means sharing a letter are not significantly different at 99% confidence level)

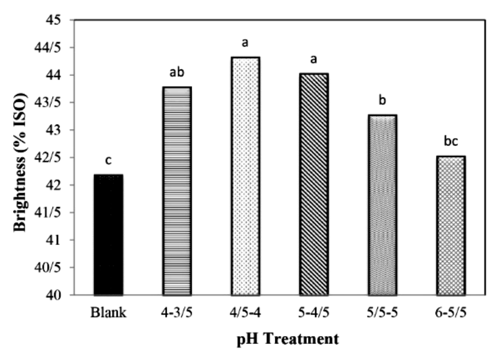

Figure 2: Effect of pH variations in pectinase deinking on the brightness of deinked ONP (mean values compared by the Duncan test; means sharing a letter are not significantly different at 99% confidence level)

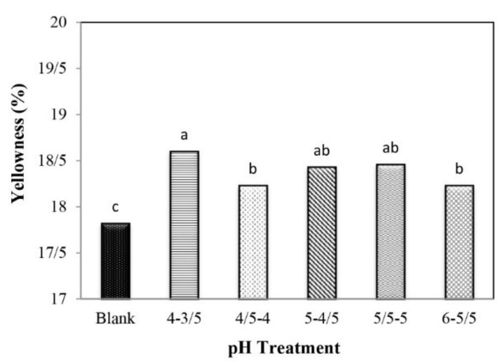

Figure 3: Effect of pH variation in pectinase deinking on the yellowness of deinked ONP (mean values compared by the Duncan test; means sharing a letter are not significantly different at 99% confidence level)

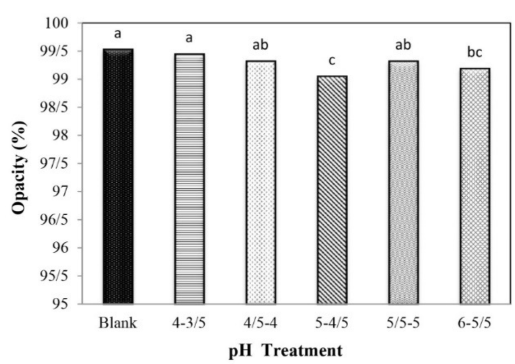

Figure 4: Effect of pH variation in pectinase deinking on the opacity of deinked ONP (mean values compared by the Duncan test; means sharing a letter are not significantly different at 99% confidence level)

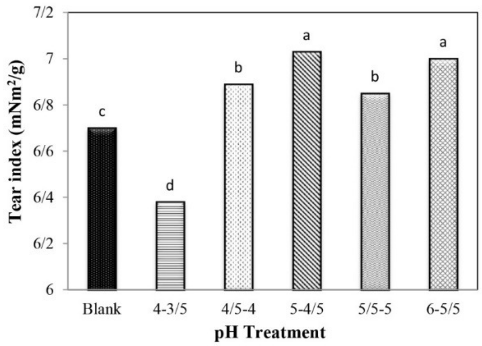

Figure 5: Effect of pH variation in pectinase deinking on the tear strength of deinked ONP (mean values compared by the Duncan test; means sharing a letter are not significantly different at 99% confidence level)

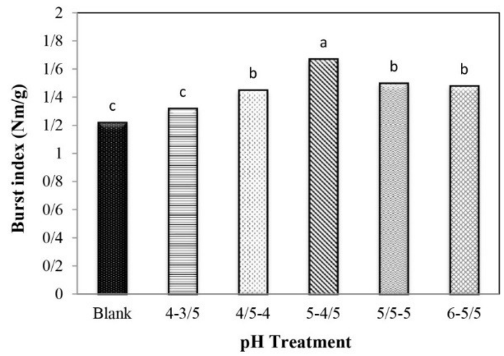

Figure 6: Effect of pH variation in pectinase deinking on the burst strength of deinked ONP (mean values compared by the Duncan test; means sharing a letter are not significantly different at 99% confidence level)

The results indicate that higher brightness at approximately comparable levels of yellowness and opacity can be obtained in deinking ONP by pectinase, compared to the control sample. The brightness improvement can be attributed to higher detachment of ink particles or other colorful compounds.[38,43] Moreover, the pectinase was more efficient at a pH level of 4 to 4.5 in improving the overall optical properties due to higher efficiency of the enzyme in isolating the ink particles and fibers from each other.[38,43]

A higher level of pH in pectinase treatment led to reduced brightness because of the severe impact of the enzyme on the ink particles, converting them to smaller sizes, and probably because of increased deposition of ink onto the fibers[44] or their lumen.[45] However, the positive effect of the detachment of ink particles from the fiber surface in improving brightness is much higher than the negative effect of increasing yellowness.[1]

It is well known that any treatment, either chemical or enzymatic, which causes an increase in brightness, will reduce paper opacity. As a result, the higher brightness gained by pectinase deinking, irrespective of the slightly higher yellowness, may be a reason for the small reduction of opacity.

The effect of different pH levels in enzymatic deinking using pectinase on the strength properties, such as tear and burst indices, compared to the control sample, is shown in Figures 5 and 6, respectively. The results showed that higher strength paper, for both tear and burst, can be obtained in pectinase deinking of ONP. However, more efficient enzymatic deinking in terms of strength development was achieved at pH levels of 4.5 to 5. Fiber fibrillation and detachment of ink particles from the fiber surface improved the fiber-to-fiber bonding[2] and, as a result, increased both the tear and the burst strength of deinked ONP.

CONCLUSION

Enzymatic treatment is a complicated approach, which is affected by various factors. In the present study, the effect of pH variation in pectinase deinking on the efficiency of ONP deinking was investigated and the major findings are as follows. Higher brightness, at almost comparable yellowness and opacity, can be obtained in enzymatic deinking of ONP by pectinase. In this respect, more efficient deinking was achieved at pH levels of 4 to 5. Higher strength of paper, for both tear and burst, can be obtained by pectinase deinking of ONP. However, more efficient enzymatic deinking in terms of strength development was obtained at pH levels of 4.5 to 5.

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