Enzymatic Deinking of Recycled Paper - An Overview

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ABSTRACT

Mixed office waste present technical and economic challenge to the recycler and of the wide variety of fibre and contaminants present in the paper stock, toner and other non contact polymer ink from laser printing process, is one of the most difficult to deal with. Toner and laser printing ink are synthetic polymers with embedded carbon blocks, they don't disperse readily during conventional repulping processes. Moreover, these are not readily recovered during floatation or washing. Because of these problems recycled papers contaminated with toner have a relatively low value. Most of the deinking chemicals and highenergy dispersion steps employed in current deinking technology are tedious, cost prohibitive and some times leads to loss in pulp yield. The enzymatic deinking process employing suitable enzymes cocktail effective in deinking of laser and xerographic waste paper show promise in Indian paper industry. The present article discuss an overview of enzymatic deinking technology for nonimpact printed toners covering the mechanism & factors influencing the enzyme deinking of waste fibres.

INTRODUCTION

Forest based pulps has continuously lost its share of the total pulp and paper furnish in the global paper industry. This is likely to continue but at significantly reduced pace. As per estimate the share of wood pulp out of the world furnish mix will be 44% by 2014 as against 52% in 1998 and 70% in year 1980. Recycling of fibre is a rapidly growing segment of the paper industry and will continue to gain share of the fibre furnish world wide. The major driving force for increased use of the recycled fibre has been the environmental concern form the pollution control authorities as well as the customers perference for the environmentally benign products which demand highest quality of DIP because of the high brightness level of the final product.

The main quality issues of paper products using recycled fibres have been runnability and printability that have been limiting the use of the furnish. These are normally related to the instability and cleanliness of the raw materials and strength properties. filler contents and average fibre length of the furnishes. The recovered furnish is actually a

Central Pulp & Paper Research Institute Post Box No. 174, Paper Mill Road, Saharanpur (U.P.) mixture in which the different material contents can vary uncontrolled based on the type and quality of collected and mixed paper and boards. These running and printing problems have been solved by developing better deinking processes, machinery, screening and sorting technology, than can help in achieving better quality of DIP and will also allow to use more quality of recycled paper and even unsorted materials in near future.

Though the recycled source of fiber, noncoated printed which includes xerographic and laser printed papers are the fast growing sources due to the increased usage of office photocopier and computer print outs. However due to the difficulties in deinking of these waste paper by conventional deinking methods, the volume of recycling for this high quality fibre is in less use. In order to effectively utilise larger volume of recovered noncontact printed laser papers there is a need to introduce an effective and efficient technology that will deink non contact ink to an acceptable residual ink count in an economically and environmentally acceptable manner. New deinking mills establish in response to these projected needs are already competing for the cleanest and most homogeneous post consumer paper sources e.g. sorted white ledger and soon will have to dip deeper in to the post consumer stream of unsorted mixed office waste (MOW) to remain competitive.

Current deinking technology is being stretched to accommodate both the hard to remove toner ink. Stickies and the coloured dyes and unbleached fibre present in unsorted MOW. Additional chemicals, multiple floatation steps and dispersion alleviate some of the limitation of the heterogeneous paper stocks. While pulp cleanliness resulting from this sequence is good enough, however the process is capital and energy intensive and sometime loss in pulp yield also occur. More over they are not readily removed during floatation or washing. Because of these problems, recycled paper contaminated tonners have a relatively low value.

CPPRI having created its vast infrastructural facilities in the area of biotechnology is actively engaged in promotion of biotechnological application in Pulp & Paper Industry. Among various biotechnological applications, enzymatic prebleaching of pulp, biopulping & Slime control & enzymatic deinking of waste paper are the major areas of interest where thrust has been laid upon evaluation of various enzymes available & being developed indigenously on pulps so that suitable enzymes are made available to the Industry which could be effectively utilised under existing mills conditions.

Recently the use of enzymes to deink recycle fibres has been proposed & being studied intensely in developed countries where in thrust has been laid upon evaluation of the various deinking enzymes available on different papers & inks. But there continues to be a lack of understanding of how these enzymes functions during deinking of papers. The present article highlights an overview of enzymatic deinking process how to remove toner inks from MOW covering the details of the process conditions underwhat conditions enzymes work efficiently while performing its specific tasks.

DISCUSSIONS

ENZYME DEINKING

Laser & Xerographic printed paper are the major components of office paper & their use has increased day to day. Laser & Xerographic printing use thermo plastic toners that fuse on to fibre surfaces during high temperature non contact printing. These oven dispensable inks refuse special chemicals, thermal and mechanical action to detach the ink from fibres so that the inks can be removed by flotation - a deinking process step that separates hydrophobic ink particles from hydrophilic pulp fibres. However costly dewatering & dispersion steps in addition to additional flotation & washing are necessary to improve the deinking of these types of waste paper. Microbial enzymes have also been shown to enhance the release of toners from office waste. Cellulases & Xylanases when applied to Xerographic printed papers in a medium consistency mixer are reported release toner particles and facilitated subsequent flotation & washing steps.

DEINKING PRINCIPLES AND CURRENT DEINKING PRACTICES

The common technique used for ink removal from laser and Xerox printing waste are washing and floatation. These kind of paper use thermoplastic



toner that fuse on to the fibre surfaces during high temperature non-contact printing. These nondispersing inks require special chemicals, thermal and mechanical actions to detach the inks from the fibre so that the ink can be removed by floatation and washings. Floatation is a step in deinking process that separates hydrophobic particles from the hydrophilic fibres as shown in fig-1. Floatation removes particles that are too small to be removed by screens and cleaners and yet are too big to remove by washing.

Washing is most efficient at removing the smallest particles of the ink. The objectives in washings are to keep the ink particles finally disperse and agglomerations. Washing requires the ink particles to be rendered hydrophilic so that they remain in the aqueous phase as shown fig-2. Both of the process normally operates at high pH (10-11) with the use of conventional alkaline deinking agents





such as sodium hydroxide. sodium carbonate. sodium silicate and hydrogen peroxide. In this environment the paper structure collapses rapidly and release the ink particles in to the suspension. A dispersant is added to stabilize the colloidal suspensions of ink particles in washing processes.

The dispersion is replaced with a collector soap in floatation deinking. The optimum size range for the different unit operation are shown in fig-3.

LIMITATIONS AND PROBLEMS IN CURRENT DEINKING TECHNOLOGY

As discussed laser and xerographic inks are thermoplastic which are copolymer of styrene and acrylate designed to be non tacky at room temperature but it melt at temperature of $70-120^{\circ}$ C. During the fusion stage of the copolymer process at high temperature (100° C). These thermoplastic resin binder set to form the printed film by cross linking.

These hard cross linked strongly bond system will only be fragmented to minimum size by strong mechanical forces, which in term leads to fibre degradation. Conventional chemical treatment is not effective in reducing particle size further and particles are visible as dirt in the finished product.

Due to this special treatment of laser and xerographic inks some modified deinking processes

have been tried, among which washing/floatation, two stage floatation and agglomeration and disintegration with subsequent removal of screening and cleaning are prominent are to mention. These requires some chemicals and the equipments but the process are capital and energy intensive too.

ENZYMATIC DEINKING

Predominant enzymes used for deinking of waste paper is mainly the cellulases and hemicellulases. Cellulases could work in several ways to enhance deinking. These reduce the hydrodynamic drag to increase the filtration and floatation rate. As cellulases are known to enhance drainage rates they can enhance any separation process such as filtration or floatation. Deinking with enzymes involves dislodging ink particles from fibre surfaces and then separating the disposed ink from the fibre suspension by washing and/ or floatation.

MECHANISMS OF ENZYMATIC DEINKING

Deinking can be devided in to five different operations occur in partly consecutively and partly overlapping stages. These stages ar

Disintegration, precleaning, chemical or enzyme treatment, floatation and/or washing and finally bleaching.

During enzymatic treatment, the process is preceded by disintegration and followed by a cleaning operation, which makes it very difficult to determine the exact role of the enzyme. Cellulases action may also increase the specific surface areas of the fibres and they reduce interaction with contaminants. That is to say that there might be microfibrils on the surface of these very frazzled, recycled fibres which could be trapping the ink particles, and by giving the fibre a haircut then reduce their adhesion. A model of enzymatic deinking is shown in Fig-4.

However the studies have shown that the most important fraction with respect to toner removal is the increased floatation efficiency imparted by cellulase enzyme activities and the increased removal of toner has been observed during floatation stage.



During floatation air bubbles rise to the surface of the floatation tank through a relatively dilute pulp stock, approximately a 1% consistency. The surface of air bubbles being relatively hydrophobic, they carry the tonner particle to the loop where they are removed by a skimming action. The operating principle of floatation deinking is shown in Fig-5.

PROCESS CONDITIONS DURING ENZYMATIC DEINKING

DEINKING ENZYMES AND THE ORDER OF ITS ADDITION

The perferable enzyme used for deinking wastepaper are commonly a mixture of cellulase and hemicellulase. The order for addition of material is to first added the proper amount of waste and waster in order to achieve desired consistency followed by the diluted solution of enzyme.



TABLE- 1 EFFECT OF PULPING CONSISTENCY IN INK REMOVAL*

Particulars	Residual ink at various levels of consistencies (ppm)		
	12%	16%	
Control pulp	681	343	
Enzyme treated pulp	329	220	

a: Residual ink on hand sheets counted in 10-2000 μ range

Access of cellulase enzyme to cellulase fibre is essential for achieving maximum activity of enzyme. Proper mixing of the enzyme at consistency 11-16% helps in dislodging toner particles from fibre and presence of surfactants help the enzyme penetrate through the paper additives. The increased cellulase available for cellulose attachment. Smoothing of fibre increase pulp freeness. which prevents toner particles from becoming trapped in the repulped fibre network.

Enzyme dosing point has been of great significant to achieve maximum enzyme efficiency. Enzyme activity being site specific. distribution of enzyme throughout the pulp is essential to achieve maximum enzyme efficiency. Addition of the enzyme after proper dilution at pulper near the beginning of the repulping process has been desirable. This allows the enzyme to react with waste furnish at higer consistency while under getting optimum mechanical agitation.

PULP CONSISTENCY

Results shown in the figure-5 cearly indicate that pulping at medium consistency. 12% is advantageous for recovering toner through the combined effect of enzyme and mechanical action. However from the results shown in table-1 clearly indicate that increasing the consistency to as high as 16% increase deinking efficiency. However at higher

deinking pulping consistencies and extended pulping time the effect of mechanical action predominant with only little additional benefit from the enzyme.

SURFACTANTS

Addition of surfactants during enzymatic deinking process play an important role for separation of ink from pulp fibre during floatation. Surfactant make the cellulose more accessible to cellulase enzymes and facilitate enzyme dispersion, thus making the enzyme available to attach to cellulose sites. Under appropriate conditions. Surfactants increase cellulose effectiveness. The use of non-ionic surfactants to the paper prior to addition of enzymes has been preferred to achieve better deinking efficiency is indicated from the results shown in Table-II

Certain anionic surfactants containing sulphates or sulphonated functionally can reduce the efficiency of the enzyme to hydrolyze cellulase and in tern reduce the deinking efficiency of the enzyme.

Moreover there should always be synergy of enzyme with a particular surfactant which leads to be evaluated for an ideal enzyme preparation. Results of effectiveness of two of the identified enzymes and their synergy with the available surfactants in shown in Table-III.

TABLE- II EFFECT OF ADDING SURFACTANT VIA FLOATATION CELL O	R PULPER.
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Specimen	Residual ink (ppm)	
	Floatation cell	Pulper
Control	326	231
Enzyme treated	278	168

Variables	Residual ink (ppm)	
Control	368	
Enzyme A, Surfactant A	242	
Enzyme A, Surfactant B	303	
Enzyme B Surfactant A	278	
Enzyme B, Surfactant B	214	

Table-III Enzyme / surfactant synergy

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The commercial cellulase enzyme preparation selected for deinking most active nearly to neutral pH range and around 6.5 to 7.5 increasing the waste paper stream containing alkali additional place some office waste paper repulped waste at the upper end of pH range of approximately 8.5-8.9, however better deinking efficiency have been obtained by adjusting the pH to 7.0- Results of the effect of pH on ink removal are shown in Table-IV

Depending on the mill performance sulphuric or phosphoric acids can be used to maintained proper pH. Relative Enzyme activity at various pH levels is shown in Fig.-5

TEMPERATURE

The optimum temperature range for an conventional cellulase based enzyme has been 45- 55° C. Having realized that the toner-based inks might began to fuse and reattach at higher temperature, the temperature below 65° C is always preferable. The schematic of the proposed process flow sheet of the enzymatic deinking is shown in fig.-6.



TABLE- IV Effect of pH on Ink Removal

Particulars	pH	Residual Ink (ppm)
Control pulp		139
Enzyme treated pulp	8.6	64
Enzyme treated pulp	7.0	47

CONCLUSION

- 1. Enzymatic deinking of laser and xerographic waste paper appears to promising technology for deinking of hard to remove toner inks.
- 2. Medium consistency pulping conditions of 11-13% appeared to be more effective than low consistency and pulping condidtions for toner removal.
- 3. Higher consistency and washing remove laser and xerographic toner from mixed office waste more effectively with a suitable blend of cellulase and xylanase.
- 4. Selection of an enzyme with optimum activity in the range of the pulped paper stock would minimize pH adjustment in the pulper and therefore simplifies the process and lowers the process cost.
- 5. Efforts are required to develop and evaluate enzymes preparation suitable for the kind of waste paper utilized by the Indian paper industry to make the technology technoeconomically viable

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