Enzymatic Deinking Of Old Newsprints Using Cellulase

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ABSTRACT

Use of enzymes has increased in paper technology in the resent past. Application of enzymes in secondary fiber processing is a relatively new field. The use of secondary fiber has increased substantially over the year world wide. It has been accepted widely that for the manufacture of writing and printing papers, flotation deinking gives better results. The pulping for the same is carried out normally in the presence of sodium hydroxide, hydrogen peroxide, sodium silicate, surfactant and some collector chemicals.P.K.Agnihotri et.al(5) had estimated the optimum conditions for operation with ONP, OMG and their blends. In the present work ONP has been exposed for cellulase enzymes for different dosages of enzymes with different temperature and processing intervals. After 11 trials, it has been estimated that the best dosages for enzyme is 0.4ml/100 gm of ONP, 55°C temperature, 30 minute soaking time and 15 minutes pulping time. It was further observed that if the enzyme is washed out after pulping processes, the properties go on changing with time. It was also observed that with the high dosage of enzyme, ink foam disperses out in the pulp suspension and the sheet formed has uniformly dispersed ink particles with dark color. The deinkability factor for the best run is found 74.35%based on ISO Brightness and 93% based on ERIC 950 value.

KEYWORDS: Deinking chemicals, Deinkabilitys factor, Flotation time, Ink agglomerates,ONP.

INTRODUCTION

The current environment awareness and legislation is leading us for maximum recycling of waste paper. The use of secondary fiber paper has been increasing over the past few years because of the current environmental awareness. The paper industry is the exclusive user of waste paper as a secondary source of raw material. The source of fiber supply is becoming an increasing concern due to the deforestation. Forest preservation and sustainability of the environment, are important burning issues in today's world. An exponential growth in the demand for paper-based products coupled with increased efforts for forest conservation has increased the use of recycled fiber. Without recycling, the fiber supply in the world will not be sufficient to cope up with the demand.

With rapid development in deinking processes, for the reuse of secondary fibers, the recycling process is becoming more and more efficient. The quality of paper made from secondary fibers is virtually approaching that of virgin paper. The process is a lot more eco-friendly than the virgin-paper making process. Deinking has taken lead in today's scenario of increased use of secondary fiber. Only after deinking, one can effectively use the recycled fibers for writing and printing.

The Indian paper industry uses a diverse mix of raw materials, primarily forest based and agro-residues along with secondary fiber .There are many associated problems such as complexity during processing of these fibers. The quality of the end product and environmental issues are the major concerns in encouraging use of these raw materials.

The reuse of the recycle paper fibers for writing and printing papers is essentially dependent on their deinking. Deinking is a sophisticated process for recycling of the paper and for the proper future growth of the paper industry. There is need for the application of effective equipments that will give the best results for recycling of the waste paper. Application of flotation cell is found to be one of the best choices for waste paper recycling.

In the flotation deinking, air bubbles rise through agitating liquid in the tank containing suspended cellulose pulp and contaminant particles. The rising bubbles collect hydrophobic contaminants and ink agglomerates. The attached particles are then transported to a froth layer, from where they are easily removed.

The deinking efficiency of the process has been evaluated by means of brightness measurements, as indicated in TAPPI Standard T452 using an Elrepho 2000 from Data color International, Lawrenceville, N.J, U.S.A.To quantify this deinking efficiency, the brightness of the hand sheets must be compared with a reference. The brightness of the unprinted paper subjected to the same disintegration and flotation condition is considered as a references value. Therefore, the following deinkability factor on the bases of ISO Brightness and ERIC 950 would define global efficiency of the deinking process.

$$D_B = ((B_F - B_P)/(B_{0B} - B_P)) \times 100$$

Where,

D_B=Deinkability factor based on brightness (%)

B_P=Brightness of pulp after pulping (%ISO)

B_F=Brightness of pulp after flotation (%ISO)

B_{0B}=Brightness of unprinted paper subjected to the pulping and flotation stages carried out under the same conditions (%ISO)

$$D_F = ((E_P - E_F)/(E_P - E_{0B})) \times 100$$

Where,

D_F=Deinkability factor based on ERIC 950(%)

E_P=ERIC value of the sample sheet after pulping before ink removed in flotation cell

E_F=ERIC value after flotation deinking

E_{0B}=ERIC value without the presence of ink particles (blank)

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EXPERIMENTAL METHODOLOGY

The waste paper used was offset printed old newspapers. Old newsprint (ONP) came from batches of recently printed offset newspapers (e.g. The Times Of India).The fiber distribution of the ONP as raw materials was determined by quantitative fiber analysis by Indian Standard IS: 5285 1969 (Method Of Tests For Fiber Analysis Of Paper And Board).The fiber analysis of ONP contained a blend of softwood chemicals and mechanical fiber with some hardwood chemical fiber, approximately 30% chemical pulp and 70% mechanical pulp.

The quantities of the chemicals charged in the deinking formulations were calculated as a percentage of the oven dry weight of paper fed to the pulper.Sodiumhydroxide and Hydrogen peroxide were from Qualigens Fine Chemicals. Sodium Silicate, DTPA from Thomas Baker Chemicals Ltd.Triton X-100 from Central Drug House (P) Limited.

ONP was slushed in a hydrapulper and its subsequent flotation was carried out in a flotation cell, to remove the separate ink in the form of foam. All repulping experiments were carried out in a laboratory hydrapulper, which has provisions for controlling temperature and rotor speed.

Conventional deinking is a chemical intensive process and required extensive waste water treatments, which is expensive and becoming highly regulated. Enzymatic deinking offers a potential means for the reduction of chemical use in the deinking process. Thus reducing the load on the wastewater treatment systems. In chemical deinking pulp displays less drainage and posses inferior physical properties, lower ISO brightness and higher ERIC 950.the most promising implication of high deinking efficiency from enhanced deinking is that the dewatering and dispersion steps, as well as subsequent reflotation and washing, may not be essential. This should save capital expenses in constructing a deinking plant as well as reducing electrical energy consumption by the dewatering and dispersion. This should reduce the chemical usage means lower waste treatment cost and less impact on the environment. When the conventional deinking is used, it should increase the chemical usage means higher waste treatment cost and high impact on the environment. (1)

Different enzymes useful for deinking include lipases, pectinases, and hemicellulases, cellulases, and xylanases enzymes. Deinking involves dislodging ink particles from fiber surface and separating dispersed ink from fiber suspensions by washing or flotation. Enzymatic approaches involve attracting either the ink or fiber surface. Lipases and esterase can degrade vegetable-oil-based inks.Pectinases, hemicellulases, and cellulases, remove the ink particles from the fiber surface. According to Korean researchers, the enzymes treatment weakens the bonds, probably by increasing fibrillation or removing surface layers of individual fibers. The suggestion that enzymatic treatment could be sufficient to remove the ink particles from the surface at the low dosages and short reaction times is commonly employed. (2)

Enzymatic treatment and flotation removed the water-based ink with ease, resulting in brightness levels well above those obtained with conventional deinking as shown in Table 1, 4 & 5.Run E1 and E2 are with chemicals only and E3 to E11 are with cellulose Enzyme.

Korean researchers have also reported that presoaking with enzymes for 10-30min before pulping appeared beneficial. It was speculated that longer presoaking time allowed finely dispersed ink particles to separate to the fiber surface or to penetrate into porous parts of fiber, thereby limiting effectiveness of flotation. Soaking after pulping but before flotation adversely affected deinking due to the separation of ink particles to fibers.

In the **Chemical Deinking**, ONP was individually cut into 6-8 cm squares. Pulping was carried out using 250grams oven dry mass with 10% moisture content. Pulping conditions for all the experiments are given in Table1.After the required temperature was achieved, wastepaper was torn and added to the pulping solution. After all the paper had been added to the pulper, the rotor speed was increased. Chemicals (Fatty acid/surfactant, DTPA, Sodium hydroxide, Sodium Silicate, Hydrogen peroxide) were added in the hydrapulper prior to the addition of the waste paper.

In the **Enzymatic Deinking**, ONP was individually cut into 6-8 cm squares. Pulping was carried out using 250grams oven dry mass with 10% moisture content. Pulping conditions for all the experiments are given in Table1.After the required temperature was achieved, wastepaper was torn and added to the pulper.After all the paper and enzyme had been added to the pulper, the presoaking time with enzymes for 15to30 min has adjusted. After that the rotor speed was increased and Chemicals (Fatty acid/surfactant, DTPA, Sodium hydroxide, Sodium Silicate, Hydrogen peroxide) were added in the hydrapulper.

In the flotation stage, about 100 gm oven dry repulped stock from the hydrapulper was diluted to 1% consistency and about 10lit. diluted stock was sent to the batch flotation cell. The flotation was performed in the Lamort type flotation cell. The rotor speed was fixed at 1400rpm.The reason for taking a reasonably high agitation speed was that the air was sucked in through the tube and air bubbles went out through the annular holes from the nozzle plate in the bottom of this tube. The flow of the air is proportional to the speed and thus adequate flow rate was maintained for good flotation. Proper ink particles size and air bubbles ratio is important for good flotation.Szatkowki and Freyberg(3) have proposed that the optimum bubbles size is approximately

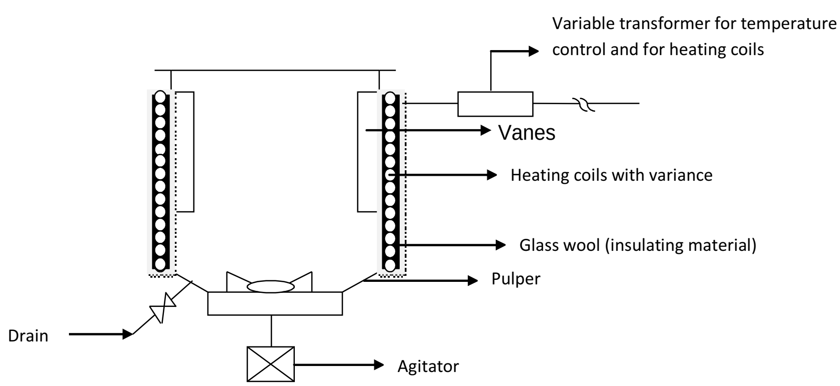


Fig 1: Hydrapulper (6)

five times the size of ink particles agglomerates to be removed. Similarly flotation time of 10 minutes is adopted because further increase in flotation time produces minimal variation in efficiency. Proper flotation time ensures that all the particles had sufficient time to float, and further time shall only use power with no additional advantages in flotation efficiency (4, 5). In both pulping and flotation stages, tap water was used as it contain some salts of calcium and magnesium, which helps in the flotation process.

The optical property was measured on sheets with a basis weight of around 60g/m², prepared before and after flotation on British standard hand sheet machine.ISO brightness is measured on both sides of the sheet, is reported as an average of the two.ISO brightness and ERIC 950 measurements have been done by Technibrite ERIC 950, Technibrite corporation (New Albany, in) USA.

RESULTS AND DISCUSSION:

Some blank runs were carried out to estimate the ISO brightness and ERIC 950 (without the presence of ink particles) were carried out and the results are shown in Table2.

Eleven runs were carried out with different pulping time cellulose enzymes dosages and temperature to observe the effects of pulping time, enzymes dosages and temperature. Run E1 and E2 are with chemicals only and E3 to E11 are with cellulase Enzyme.

The results are given in Table 4. From the table it is observed that experiment no.8 shows the best results in view of deinkability factor based on brightness and ERIC 950.This shows that 1mole commercial cellulase in 250gm o.d ONP, 10% moisture at 55ºC with 30 min pulping time gives the best results. The sample sheets of runs E3, E8, E9, and E11are attached and the effect of enzyme dosage is clearly visible in them.

At 2ml dosages of cellulose the ink foam disappears and the whole ink dispersed back in the system. At 0.5 ml dosage the foam started separating out but the results are not good. At 1.5ml dosage, the separation of foam has been effective but the results are inferior to 1ml. Thus, based on these results, it can be stated that the best results are obtained in 1ml dosage at 30min pulping time and 55ºC temperature. When these results are compared with blanks deinkability run with chemicals only (no enzyme).the results in brief are as below.

Table 3: Deinkability factor based on ISO brightness and ERIC 950 using chemicals and enzyme only. In this table, it shows that when we using the chemical deinking, the deinkability factor on the bases of ISO brightness and ERIC 950 decreases .while using the enzymatic deinking, it should increases.

The results of blank run with (chemicals only) are inferior to any other run with 0.5 to 1.5ml dosages while the 2ml dosage is too high effecting the foam breakage leading to dispersion of ink into the suspension. It was observed that with the increase in dosages from 1 to 1.5 ml the color of pulp suspension has changed after

Table 1: Pulping conditions and chemicals specifications

Conditions	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11
Temperature	60°C	60°C	55°C	50°C	45°C	55°C	50°C	55°C	50°C	55°C	50°C
Enzyme Doses(ml)	-	-	0.5 ml	0.5 ml	0.5 ml	1 ml	1 ml	1 ml	1.5 ml	1.5 ml	2 ml
Soaking time	15 mins.	15 mins.	30 mins.	30 mins.	15 mins.	15 mins.	30 mins.	30 mins.	15 mins.	30 mins.	15 mins.

The following conditions are maintained in all the experiments, which are given as below:

Pulping condition		Chemicals added	
Hydrapulper time	15 min.	Sodium hydroxide	2.0%
Hydrapulper consistency	6%	Sodium silicate	2.5%
Rpm in hydrapulper	1400	Hydrogen peroxide	1.0%
Flotation time	10 mins.	Triton x-100	1.2%
Flotation consistency	1%	DTPA	0.5%
Rpm in flotation cell	2000		

Table 2: ISO Brightness and ERIC 950 of unprinted portion of waste paper.

Specification of material	ISO brightness (%)	Eric 950 (ppm)
Cutting of unprinted portion of waste paper taken for the study were pulped with same. Chemical composition used for deinking of printed paper and after flotation the results are shown	56	210

Table:-3

Deinkability factor based on	Chemicals only	1ml dosage
ISO brightness (%)	27%	74.35%
Eric 950(ppm)	61%	93%

Table 4: Results after Pulping show that the best results were obtained in exp.no.8.

Properties	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11
Brightness (%)	47.87	49.92	52.00	50.10	51.00	51.72	50.10	50.23	50.44	51.32	49.00
ERIC950(ppm)	689.51	434.19	420.15	510.16	656.45	410.32	516.12	542.61	561.00	469.14	691.12
Opacity (%)	99.27	96.73	95.09	97.10	98.00	98.00	98.12	98.21	98.32	97.91	99.92

Table 5: Results after Flotation show that results of enzymatic deinking gives good results than chemical deinking. The best results were found in Exp.no.8, where the ISO Brightness has increased and ERIC 950 has decreased.

Properties	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11
Brightness (%)	50.14	52.48	53.39	53.20	53.33	53.85	53.66	54.52	52.00	55.16	50.17
ERIC950(ppm)	398.34	350.00	317.49	335.16	370.08	335.37	344.17	231.84	420.12	242.87	686.62
Opacity (%)	98.62	98.38	96.88	96.16	96.81	98.20	98.05	97.81	97.14	97.10	98.77

Table 6: Deinkability Factor on the bases ISO Brightness (%) and ERIC 950(ppm) .It shows that the best results are found in Exp.8, in both the cases i.e ISO Brighgtness and ERIC 950

Deinkability Factor (%)	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11
ISO Brightness (%)	27%	42%	34%	52.54%	46.6%	49.76%	60.33%	74.35%	28.06%	60.68%	16.7%
Eric 950(ppm)	61%	38%	49%	58%	64%	37%	56%	93%	40%	87%	31%

Table 7: Results of enzyme before and after of seven days period. From the Table 7, it appears that the property change after the pulp has been left with enzyme without washing it thoroughly, this shows that the enzyme activity continue and the properties have improved in almost all the cases.

Physical properties	After pulping		After flotation	
	Fresh results	Observation for 7 days	Fresh results	Observation for 7 days
GSM	60	63.07	50	58
Tensile strength	38.76	63.07	19.6	34.91
Tear strength	6.2	6.78	5.88	6.08
Bust index	2.61	1.31	1.37	1.56
Brightness (%)	50.32	52.00	53.33	58.39
Eric 950(ppm)	656.45	420.15	370.08	317.49
Opacity (%)	98.58	95.09	96.81	96.88

flotation due to effect of enzyme on foam. When it was further increased to 2ml, the total foam disappears due to severe attack of excess enzyme and whole foam disperses back into the pulp suspension leading to low deinkability factor, based on ISO brightness and ERIC 950 as given in table 3 experiment no.11.The sheet of E11 is having densely distributed ink particles while the sheet of E8 is not having the dispersed ink particles leading to higher brightness and lower ERIC 950 with good appearance. The sample sheets of runs E3, E8, E9, and E11are attached and the effect of enzyme dosage is clearly visible in them.

CONCLUSION:

Considering the importance of enzymes, its application in secondary fiber processing is increasing with time. Studies have been carried out to observe the effect of different operating variables such as temperature, cellulase dosages, soaking time, and pulping time etc.11 runs were conducted with varying conditions as given in Table1. From the Table1, it is evident that the optimum conditions are 0.4ml cellulase/100 gmof ONP, 55°C temperature, 30 minutes soaking time, 15 min pulping time. At high dosages (Exp .11), it was observed that the ink foam disappears in the flotation cell and the whole ink disperses back in the pulp suspension causing dark brown color of the pulp suspension. The sheet made from this pulp suspension also has dispersed ink particles, has dark brown color with lower brightness .The sheet of E8 run which gives best values, is not having dispersed ink particles has good brightness and is good in appearance. At lower dosages the foam separation takes place but the sheet properties are not the best.

Sample Sheets After Pulping and After Flotation for Different Runs Using Cellulase Enzyme

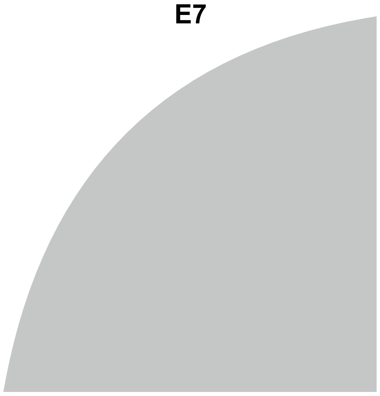
After Pulping | **Conditions** | **After Flotation**

Enzyme Dosage=0.5ml
Temperature=55°C
Soaking Time=15

E3

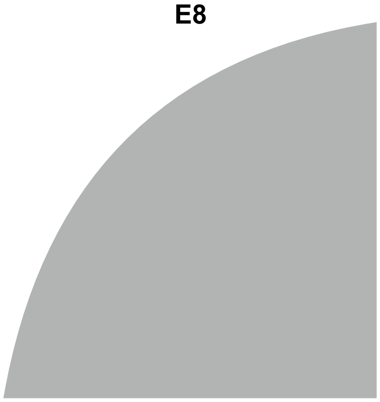
Enzyme Dosage=1ml
Temperature=50°C
Soaking Time=15

E7



Enzyme Dosage=1.5ml
Temperature=55°C
Soaking Time=15

E8



Enzyme Dosage=2ml
Temperature=50°C
Soaking Time=15

E11

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