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Experimental Results on Enzymatic De-inking of Non-impact Ink Printed Papers

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ABSTRACT

Flotation de-inking is one of the most important processes worldwide for the removal of printed ink from recovered paper. It is also known that use of enzyme (cellulase) improves ink detachment from waste papers. The role of enzyme/substrate (waste paper) ratio and time of enzymatic treatment in the efficiency of flotation columns have been studied in this article. Standard experiments were carried out in a flotation column showed that optimization of the above mentioned parameters improves the overall efficiency of the process considerably. Using optimum enzyme/substrate ratio and enzymatic treatment time may also lower the operating costs of the process.

KEYWORDS

Enzymatic de-inking, Cellulase, Non-impact inks, Flotation column

1. INTRODUCTION

The use of recycling in the paper industry has significantly increased during last 20 years. De-inking of wastepaper in the pulp and paper industry is accomplished primarily by the flotation process. Simple stirred tank reactors with air bubble sparged into recycled pulp slurry are some conventional mechanical flotation devices in use in the de-inking of wastepaper. The air bubbles collect ink particles, which are hydrophobic and rise to the surface of the slurry in a foam or froth. This is drawn off at the top and after the foam collapsed, it is rejected. The clean pulp sinks to the bottom of the cell where it is withdrawn [1]. In the recent years, the use of flotation column (FC) has been suggested as an effective technology for the de-inking of wastepaper [2]. Among the benefits of column flotation are higher selectivity, less floor space, reduced capital costs and lower maintenance and operating costs. Furthermore, power savings up to 80% and reagent savings up to 30% are also reported [3]. Traditional de-inking involves the use of large quantities of chemicals which make the method expensive and causes high damages to envoirment [4]. Enzymatic treatments can favor ink particles detachment from the fibers without discharging of pollutants. Enzymes can remove small fibrils from the surface of the noncontact ink particles thus altering the relative hydrophobicity of the particles, which facilitates their separation in the flotation step [5]. Noncontact inks (toners) contain synthetic binders based on polyester or copolymers of styrene with acrylates, methacrylates, or butadiene. During the printing process, these copolymers physically bond to paper fibers during high temperature curing [6]. Conventional pulping with chemicals does not effectively remove the cured toners from pulp suspension, because the toners have polymerized and fused onto the fibers and placed on a sheet of paper.

An alternative to conventional (chemical) de-inking is biological or enzymatic de-inking. There are two principal approaches to enzymatic de-inking, one employs lipase to hydrolyze ink carriers [7], and the other uses cellulases, xylanases, or pectinases for a limited hydrolysis of outer layers of cellulose fibers to release ink from fiber surfaces [8]. This limitation to outer layers does not affect efficiency of enzymatic treatment, because toners are bound to external surfaces of cellulose fibers.

2. THEORY

Santosh Vyas and Anil Lachke have presented a schematic diagram that indicates the probable mechanism of the enzymatic de-inking process by cellulases (Fig. 1) [9]. During photocopying the toner particles of ink get entangled in microfibrils that are present at the surface of the fiber. This can be observed from a scanning electron microscopic image (Fig. 2). During bio de-inking process, cellulases act in different ways. It is well understood that endoglucanase initiate action on cellulose. The role of endoglucanase in overall process of cellulose degradation is to split the ellulose fibers at several amorphous sites and generates innumerous non-reducing ends of the chain.

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This action leads to loosening of fibers which in turn helps in releasing ink particles from mixed office waste (MOW) paper during flotation de-inking process in the presence of surfactants. Secondly, cellulases act at the frazzled surfaces of cellulose fibers and release short fibers. This capability of releasing short fibers can be assigned to mechano-chemical property of endoglucanase components. It can be interpreted that this short fiber forming activity also removes residual fibers from the toner surfaces[9].

The role of fatty acids as agglomeration and flotation agents, which act to separate the ink particles in the froth flotation de-inking cell, has been clearly established in recent years. In fact, it has been shown from both laboratory de-inking experiments and fundamental surface force measurements that calcium soap particles are produced from the precipitation of these long chain anions with calcium ions. These soap particles then function as collectors by a co-agglomeration process between the soap and ink particle forming larger mixed hydrophobic flocks which become attached to the air bubbles [10]. The mechanisms of flotation de-inking are summarized in Figure 3.

3. Materials and Methods

The Objective of the present work is to optimize the enzymatic conditions during de-inking. We provide an experimental column flotation setup in our laboratory.

A. Sources of Paper

Alkaline paper (80 gsm) printed with toners on a HP laser printer.

B. Sources of Enzyme

The enzyme used was commercial cellulose supplied by Novo Nordisk AS (Denmark): Novozyme 181 (declared activity 17.6 FPU).

C. Chemicals

Sodium hydroxide and calcium soap($Ca(oleate)_2$) were purchased from Merck Chemical Co., Germany.

D. Pulping

Wastepaper was cut into small pieces and immersed into warm water at 70°C for at least 2 hours. These wastepaper feedstocks were pulped and defibrized in a blinder (in 10% consistency based on oven dry weight of pulp) for 2 minutes.

E. Treatment of Chemicals

Pulp suspension diluted to 7% consistency and then NaOH (2% consistency) was added. Chemical treatment was performed for 20 min, during treatment which mixed with a mixer at 200 rpm. The pH was 10.5 and temperature was maintained at 45°C.

F. Enzymatic Treatment

After chemical treatment with NaOH, the pulp was washed with running tap water through a 200-mesh wire. Pulp suspension (7% consistency) was provided and enzymatic treatments with cellulose performed at different enzyme-pulp ratios (0.12, 0.16, 0.2 and 0.24 cc enzyme/gr dry pulp) for various enzymatic treatment times (30, 60, 90 and 120 min). The pH was kept at 5.5 and temperature was 50°C. enzymatic treatment was optimized for enzyme concentration (enzyme-pulp ratio) and treatment time.

G. Flotation

Toners separation and removal from the fiber net was carried out in a flotation column cell. This cell is 1 m tall and 6mm in diameter with an aeration system. An air flowmeter (rotameter) for flow rate control was used. The working flow rate of air was 1.4 l/min. As the enzymatic treatment was accomplished, each sample was diluted to a 0.8% consistency. The pulp was charged into column and floated at 45°C for 15 min in the presence of calcium soap. The froth was collected at the top and after 15 min, the air supply was stopped, the drain was opened and the clean pulp was collected at the bottom. Figure 4 shows a schematic of our laboratory FC.

H. Evaluation of De-inked Pulp

The comparison of the blank handsheet with those from the flotation runs allowed determining the percentage of the toner removed or de-inking efficiency. De-inking effects can be evaluated by measuring brightness [11], residual ink areas and dirt counts [12] of handsheets made from the recycled paper. Decreases in dirt counts and residual ink areas and increases in brightness values indicate an efficient de-inking.

For each experiment, two trials were carried out, and three handsheets (75 gsm) were prepared for each trial according to accepted procedure[13]. Handsheets were scanned with a flatbed scanner using Global Image software for determining residual ink particles concentration. De-inking efficiency can be characterized as follow:

$$E_f = \frac{N_{pp} - N_{dp}}{N_{pp}} \qquad \text{Eq. 1}$$

N_{pp} and N_{dp} are the ink particle concentration for printed paper and de-inked paper. The Image analysis system for determining the above parameters was composed of a magnification lense, illumination device, monochromatic camera and an image analysis device.

4. Results and Discussion

The enhancement in de-inkability of laser printed waste papers by use of enzymatic pretreatment is studied by many researchers [14-16]. Most of these researchers have focused on process conditions like temperature, pH, air flow rate and so on. They have also indicated that use of enzyme improves the de-inking process considerably. But as an engineering and economical view, the use of enzyme will lead to higher process costs. Optimization of the enzyme/substrate ratio and enzymatic treatment time which are neglected in the previous studies is the main subject of this article. The results of enzymatic de-inking of laser printed paper from the batch operation of column flotation are listed in Table 1. The dosage of surfactant (calcium soap) in these experiments was 1% on O.D. (oven dried) weight and flotation time was 15 min. Figure 5 shows the effect of enzymatic de-inking conditions on de-inking efficiency. Mean residual ink area in the handsheets were made from unde-inked pulp was 330.83 (pixel/cm^2) and this quantity was measured after each assay.

The results indicate that with increase in treatment time, the residual ink area decreases therefore de-inking efficiency increases. This was observed that after a certain time residual ink, approximately remains constant. Also, the variation of efficiency versus enzyme-pulp ratio is considerable. The effect of enzyme concentration on efficiency at low concentration (0.12 cc/g) is not obvious. At the higher concentrations, an increase in efficiency, (10-28% depend on treatment time) was obtained. As it was expected, the use of enzyme in de-inking decreased the residual ink concentration, but at high enzyme-pulp ratio (0.24 cc/g) the variation of removal efficiency versus time has been damped. In fact, there is no considerable decrease in ink concentration with enzyme-pulp ratio increasing in high enzyme concentration.

5. Conclusion

This study has shown that the enzymatic treatment can improve ink removal efficiency but for an economical production in large scales the best enzyme to substrate ratio and treatment time must be determined. Optimization of the enzymatic treatment time and enzyme concentration allows elimination of the toner particles and significantly improves the cleanliness of recycled non-impact printed waste papers. Enzymatic treatment time equal to 90 min and enzyme pulp ratio equal to 0.2 cc/g introduced as optimum conditions for de-inking process.

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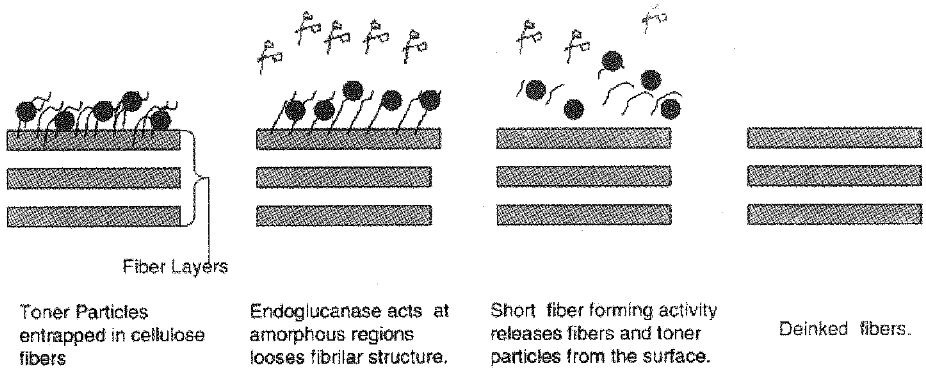

Figure 1: Schematic diagram showing probable mechanism of bio de-inking [9]

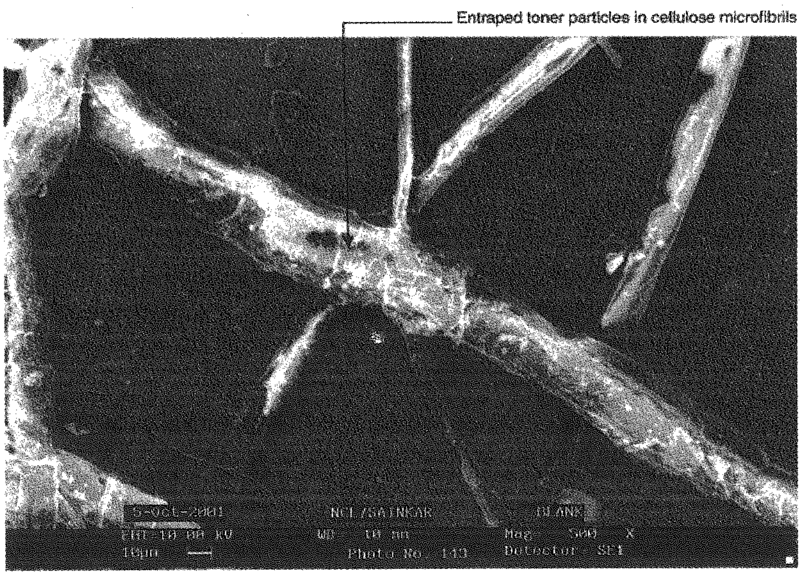

Figure 2: Scanning electron micrograph demonstrating the toner particles of ink entangled in microfibrils [9].

TABLE 1
QUANTIFICATION OF DE-INKING EFFICIENCY AFTER ENZYMATIC TREATMENT.

	Enzymatic treatment time (min)	Enzyme concentration (cm^3/gr dry pulp)			
		0.12	0.16	0.2	0.24
Residual ink (pixel/cm^2)	0	101.67	101.67	101.67	101.67
	30	92.33	78	65.66	62.33
	60	89.67	67.67	53.67	46
	90	88.67	62	45	38
	120	87.66	59.67	39.67	33.33
Efficiency (%)	0	70	70	70	70
	30	72.12	76.37	80.17	81.15
	60	72.94	79.56	83.8	86.07
	90	73.26	81.22	86.41	88.51
	120	73.51	82.03	87.98	89.9

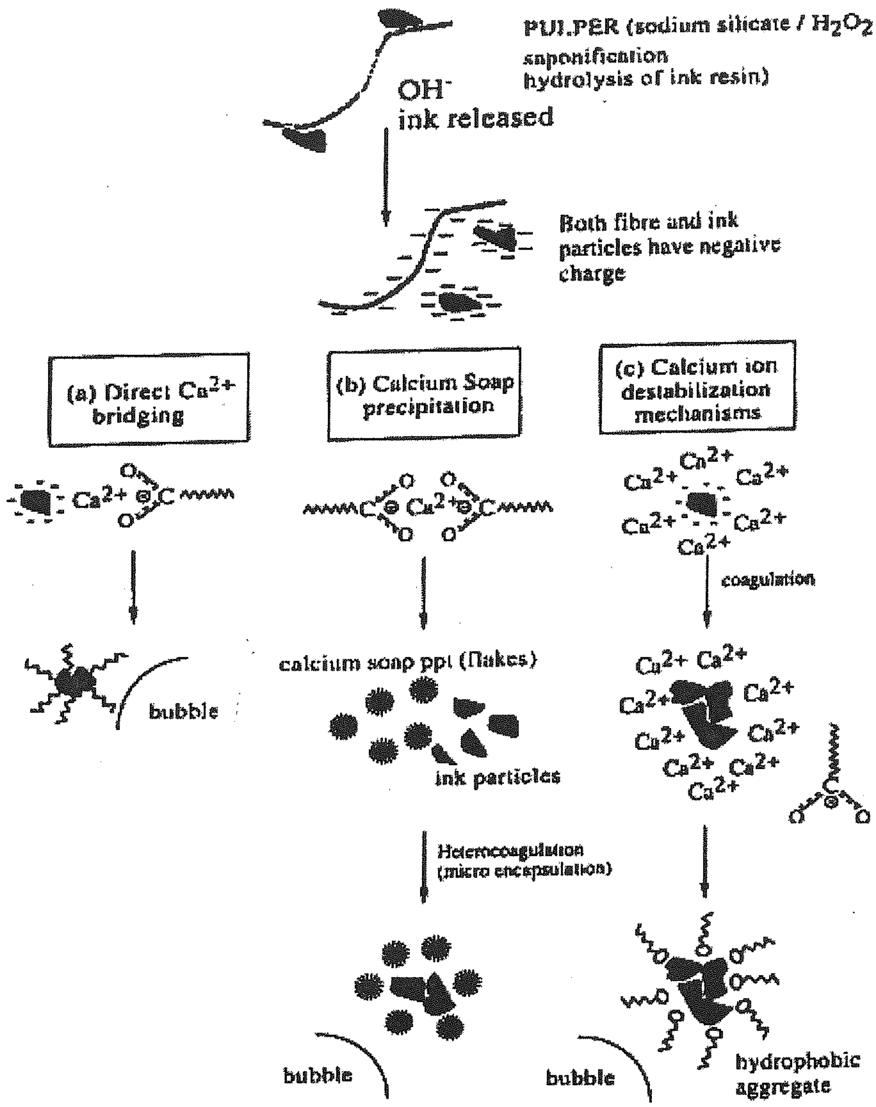

Figure 3: Probable mechanisms of calcium soap flotation de-inking [10].

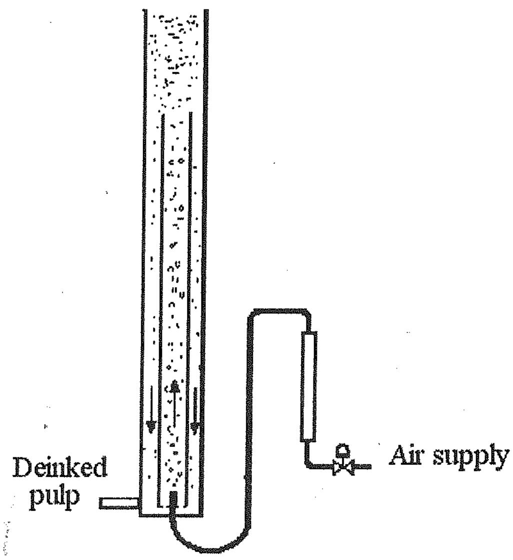

Figure 4: Schematic of flotation column

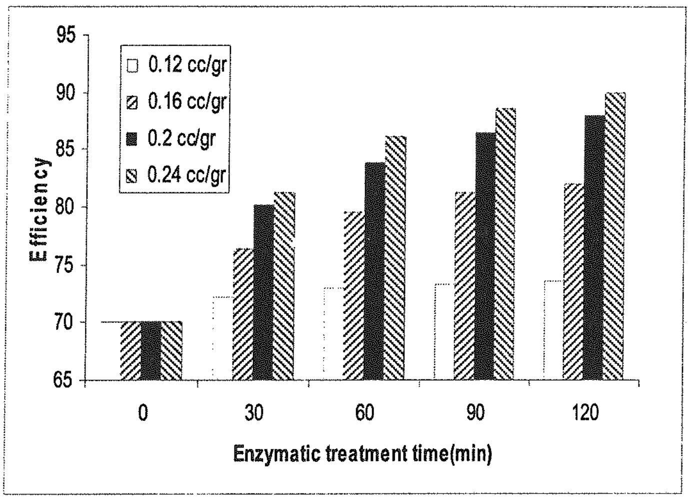

Figure 5: Effects of enzymatic treatment time and enzyme concentration on de-inking efficiency.