Fabrication of a laboratory scale flotation cell device for bio-deinking of waste papers

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Fabrication of a cost effective, laboratory scale flotation device that can be used for deinking of various grades of wastepaper has been described. The unit consists of aeration device, sparger, baffles for high air to stock ratios and high shear mixing. The sparger is designed in such a way, that, it gives micro turbulent airflow necessary for removal of smaller ink particles. The deinking experiments using alkaline active cellulases from an alkalotolerant Fusarium sp have been reported. The enzyme preparation showed different cellulolytic and xylanolytic activities. Successful application of cellulases in enzymatic deinking of mixed office waste paper has been described.

Re cycling of waste paper into high-grade writing paper is the new trend in paper industry. The major problem in recycling of waste paper is the removal of contaminants mainly the inks. Normally the ink contains non-polar pigments or dyes and an agent that carries the ink to paper and facilitates in binding. These agents are typically water insoluble oils or polymers as in case of toners. Thus, their removal is not an easy process. Washing and flotation are two most commonly used methods of deinking. Other methods like heat decolourization1, irradiation2, organic solvent-based deinking3, and magnetic deinking4 are still under experimental conditions. The choice of method depends on the type of ink to be removed and the desired quality of pulp. Black newspaper inks are generally removed by washing, while coloured magazines are deinked by flotation. Both the methods use chemicals that are highly toxic. Microbial enzymes can prove to be a valuable alternative in order to reduce the use of these toxic chemicals. Microbial cellulases5,6, hemicellulases7, amylases8,9, lipases10 have shown promising results in increasing brightness of the fibres when used in combination with flotation deinking. The availability of efficient flotation device is always one of the limiting factors in evaluating performance of different enzyme preparations for deinking. In this communication, fabrication of the laboratory scale flotation device is described. The alkaline active cellulase preparation was obtained from the alkalotolerant Fusarium sp and its application in deinking of mixed office waste papers has been explored.

Experimental Procedure

Chemicals
Sodium salt of carboxymethyl cellulose (CMC) and oat spelt xylan were purchased from Sigma Chemical Co., U.S.A. Cellulose-123 was purchased from Carl Schleicher & Schull Company, Germany. Wheat bran, rice bran, corn cob and bagasse pith were obtained locally. All the buffer salts and microbial media components were procured from the standard commercial sources and of highest quality available.

Enzyme production
The fungus, alkalotolerant Fusarium sp strain was grown in M-1 medium11 enzyme production. The M-1 medium supplemented with 0.5% wheat bran was inoculated with vegetative mycelia from 7-day-old sporulating slant on PDA. The culture was grown for 3 days and used as the inoculum. Enzyme production was carried out in 250 mL Erlenmeyer flask containing 50 mL M-1 medium with cellulose powder (1%) as the sole carbon source. The culture was incubated at 30°C on a rotary shaker at 200 rpm. The samples were withdrawn at regular intervals. The mycelium was removed by centrifugation at 7000 rpm at 4°C to obtain a clear crude broth. This preparation was used for the measurement of enzyme activities.

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Results given are the mean of at least two observations.

**Enzyme assays**

The activity of endoglucanase (1,4-β-D-glucan-4-glucanohydrolase, EC 3.2.1.4), xylanase (1,4-β-D-xylanohydrolase, EC 3.2.1.8), filter paper degrading activity (FPase) were measured in terms of release of reducing sugars by 3,5-dinitrosalicylic acid (DNSA) method\(^\text{12}\). The enzyme assays were carried out as described earlier\(^\text{13,14}\).

One IU of enzyme activity was defined as the amount of enzyme that liberates 1μmole glucose/min (for endoglucanase and FPase) or xylose/min (for xylanases) under the standard assay conditions. 1 IU of β-glucosidase and β-xylosidase has been defined as the amount of enzyme, which liberates 1μmole of \(p\)-nitrophenol/min under the standard assay conditions.

**Fabrication of flotation cell device**

The efficiency of flotation depends on physical interaction between ink particles, air bubbles and hydrodynamic characteristics of the suspension\(^\text{15}\). Considering these prerequisites, a simplified flotation cell was designed (Figs 1&2). The working volume of the flotation cell was 10 L, with actual dimensions as \(L=260\) mm, \(B=260\) mm and \(H=220\) mm. The cell was constructed with mild steel with standard thickness of 2.5 mm. Joints were welded with an efficiency of 0.85. A hollow cylinder pipe of diameter 62.5 mm is fitted on the cylindrical sparger having diameter 120 mm. The shaft is introduced with impeller blade diameter of 30 mm in hollow cylinder. This shaft is rotated at 1500 rpm using 1.5 Hp motor. The sparger hole has the diameter of 5 mm. For the removal of the foam containing floated ink particles the outflow is provided as a slope from the top of one side of flotation unit. The flotation efficiencies were tested during enzymatic deinking trials with cellulases, on mixed office waste paper. The enzyme treatments were followed by flotation run at 1% consistencies in the same cell.

**Deinking trials**

The waste paper used was a mixture of photocopier waste papers that were coated with toner and laser printouts. Each of them was cut in to small pieces and immersed in the warm water at 50°C for at least 2 h. This paper was fiberized in medium consistency water jacketed pulper for 10-15 min in the presence of 0.1% (v/v) nonionic surfactant. The temperature during pulping was kept at 55°C and pH was adjusted to 8.5 with 1N NaOH. The suspension was mixed until paper particles were no longer visible. The enzyme treatments were carried out at 10% final consistency at pH 8.0-8.5 at 55°C for 20 min. The enzyme dose was selected as 100 IU CMCase/100g of oven dried pulp. Prior to flotation the pulp samples were disintegrated in universal laboratory disintegrator at 5000 rpm for 5 min. The pulp was diluted to 1% consistency by using distilled water. To separate toner particles from the fibres, all the enzyme treatments were followed by 10 min flotation run in a 10 L capacity laboratory flotation unit at room temperature. At the end of flotation, the deinked fibres were recovered on a laboratory mesh from the drain valve of the flotation cell. Control runs were taken under
identical conditions replacing active enzyme by heat denatured enzyme preparation. After flotation, pulp consistency was determined for each sample. From every sample, 5 handsheets were made. The handsheets were dried at room temperature. Handsheets from enzyme treated pulp, heat denatured control runs and handsheets from the pulp without flotation were compared for different optical properties. The ink specks in visible (220 to 80 μm) range were counted according to Tappi Standard method (TAPPI T 213). Brightness was measured at different places on handsheet according to (TAPPI T 452 om 92) and values are expressed as the average % value. The efficiency of deinking was calculated as per the following formula,

\[
\text{Deinking efficiency} \% = \left( \frac{\text{No. of ink specks in blank sample} - \text{No. of ink specks in test sample}}{\text{No. of ink specks in blank sample}} \right) \times 100
\]

Scanning electron microscopic studies
The sediment of short fibres and ink particles from rejected foam after flotation was resuspended in 1.0 mL of distilled water. 0.1 mL of it, was dried on aluminium foil and coated with thin gold layer. The short cellulose fibres and toner particles released due to the action of endoglucanase was determined using a Leica Stereoscan 440 scanning electron microscope.

Results and Discussion

Enzyme properties
The crude culture filtrate showed different extracellular cellulolytic and xylanolytic activities as shown in Table 1. The refined enzyme preparation is active in a pH range of 4 to 10 with pH optima at 5.0 at 60°C. The enzyme is stable16 in an alkaline pH range of 8-0 at 50°C. The half-life of the enzyme at pH 8.5 at 50°C was found to be 10 h. The enzyme showed maximum activity at 60°C and retained17 80% of the maximum enzyme activity at 70°C. The deinking operations can be well performed under the alkaline conditions. Thus, the enzyme preparation was found to be alkaline active and alkali stable indicating their potential for deinking process.

Flotation cell
The increasing varieties in the characteristics of printing inks make new demands on the function of flotation cell. The flotation cell must be capable of removing ink particles that lie under the visible as well as sub visible particle limits. Collectively they determine the brightness levels and the optical cleanliness18. The flotation cell must provide an environment where ink particles have a high probability of colliding with air bubble. This helps ink particles in attaching to an air bubble that float to cell's top surface and finally leaving the fibres in the pulp suspension. The basic conditions required for this high probability of collision include high air to stock ratios and high shear mixing rates. This was achieved in the fabricated flotation device. During the flotation process the high vacuum is created in hollow cylindrical pipe. High speed of impeller blade ensures high air generation. Impeller blades produce high shear mixing.

High air to stock addition rates ensure that there is large population of air bubbles to allow the ink particles to have a high probability of colliding with air bubble and floating to cell’s surface. Generally, the air introduced is up to 10 times the stock volume19. High shear mixing results in dispersion of large quantity of air into stock. Also, high shear mixes the probability, that, ink particle comes in contact with an air bubble. This prevents ink particle from being trapped in the fibres20. Finally high shear mixing ensures that fibres stay suspended. In order to separate the ink particles from the fibres, the ink particles must be hydrophobic so that they can adhere to the air bubble. This was achieved by using non-cationic surfactant.

Small ink particles (< 200 μm) require a high relative velocity in order to break out if the stream line around the bubble come into contact with bubble itself. Thus, the flotation of small particles, requires a micro turbulent flow that is high enough to supply the necessary contact energy. At the same time, the size of the bubble is determined by the turbulent shear field. Smaller the bubble size, higher the degree of turbulence19. The attachment probability increases as

<table>
<thead>
<tr>
<th>Activity</th>
<th>IU/mL</th>
</tr>
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<tbody>
<tr>
<td>CMCase [Endo (1→4)-β-D-glucan-glucanohydrolase (EC 3.2.1.4)]</td>
<td>8.80</td>
</tr>
<tr>
<td>FPase (Filter paper degrading activity)</td>
<td>0.52</td>
</tr>
<tr>
<td>1,4-β-D-glucan-glucohydrolase (EC 3.2.1.21)</td>
<td>1.31</td>
</tr>
<tr>
<td>β-D-xylanase (EC 3.2.1.8)</td>
<td>0.72</td>
</tr>
<tr>
<td>β-1,4-D-xylan xylanohydrolase (EC 3.2.1.37)</td>
<td>0.32</td>
</tr>
<tr>
<td>Protease</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

N.D. = Not detected

Table 1 — Enzyme activities in culture supernatant
the diameter of air bubble decreases, since the particle can approach the air bubbles more easily. In the present flotation cell the micro turbulent airflow, was achieved by selecting sparger hole diameter of 5 mm. The data on ink counts and size of the ink particles suggested, that, smaller ink particles were removed preferentially than the larger ink particles. This also confirms the generation of microturbulent airflow that resulted in preferential removal of smaller ink particles. This was also observed during flotation of enzyme treated samples (Fig. 3). The effect of ink particles on the brightness of paper has been evaluated by McKinney. Generally, enzyme action breakdown larger fibrils into smaller microfibrils which are easily removed by flotation process. This results in further increase in brightness as well as reduction in ink counts (Table 2). The blockage of air suction device by foam and stock deposit can become a serious problem during flotation process. While fabricating the flotation cell, this was avoided as there are no individual air hoses and the entry of compressed air takes place via a hollow cylindrical pipe that is installed outside the cell tank. The simplified air input device is introduced instead of costly air compressors used in commercial flotation cells. The novel sparger unit is designed to generate microturbulent airflow. Absence of individual air hoses that can result in blockage of air device are the key highlights of fabricated flotation cell over commercially available flotation cells.

Deinking trials

In order to evaluate the performance of the fabricated flotation cell, flotation deinking trials were carried out for the pulp samples. The hand sheets made from treated pulp and control pulp samples were compared with those of blank samples for brightness as well as residual ink particles. The flotation deinking process resulted in an increase in brightness as compared to blank pulp samples that are not processed by flotation. Similarly, improved brightness by 3-4 points was shown by enzyme treated pulp over heat denatured control pulp samples. The increase in brightness points can be attributed to combination of enzymatic action and flotation deinking process that yielded reduction in residual ink specks. The enzyme treatment of mixed office waste paper increased removal of ink in the presence of nonionic surfactant. Enzyme treatment resulted in reduction of ink specks after flotation (Table 2). The smaller ink particles (< 200 μm) were removed more effectively than larger ink particles (> 220 μm). However, the reduction in larger size particles is also observed. It can be possible, that, the larger ink particles might have been broken down into smaller particles due to enzyme action and small particles are effectively removed by flotation. Welt and Dinus have also recorded similar observations. The effect of enzymatic deinking on strength properties of the waste paper pulp has been described previously. The data indicated that there is minimal improvements in burst index and breaking length with reduction in tear index values in enzyme treated handsheets over control.

Efficiency of deinking

The efficiency of deinking was determined as explained under experimental section. The highest
efficiency of flotation was found to be around 80%. The results indicated that the highest efficiency of deinking was possible when enzyme trials were followed by flotation run. During flotation, the air bubble rises to the top carrying hydrophobic toner particles along with them. The large toner particles possess cellulose fibrils entrapped within them. These hairy toner particles affect flotation efficiencies severely by generating hydrodynamic drag on air bubble that is rising to the top. Cellulases separate toner particles from entrapped fibers. Now these non-hairy hydrophobic particles are easily separated by flotation. Thus, the efficiency of flotation increases dramatically by application of cellulases.

Conclusion
Microbial enzymes have shown promising results when used in combination with flotation deinking during recycling of waste paper. The availability of efficient laboratory flotation device is always one of the limiting factors in evaluating performance of different enzyme preparations for deinking. The laboratory scale flotation device described herein is cost effective, and has been found to be efficient in biodeinking of mixed office waste papers. This unit can be used for studies on deinking of various grades of waste paper and also for the evaluation of different enzyme preparations at laboratory scale level.

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