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Mechanisms of MOW paper deinking in flotation columns, by enzymatic catalysis using *Trichoderma Sp.*

Jeovani Gonzáluez P., Ramiro Escudero G.

Institute of Research in Metallurgy and Materials.Universidad Michoacana de San Nicolás de Hidalgo. Santiago Tapia 403, C.P. 58000. Morelia, Michoacán, México.
ramiro1963@gmail.com

Abstract. In traditional paper pulp deinking, sodium hydroxide (NaOH) is used as a hydrolysing agent for fibers in concentrations that set the pH of the medium to values greater than 10; however, substantial amounts of solid and liquid waste are created, and their management is problematic and dangerous.
Recently, the implementation of biological treatments, for example, enzymatic deinking, is presented as an option to deink mixed office prints at neutral pH; that is, with the minimum use of chemical reagents and, therefore, better waste management and less environmental impact.
The main objective of this research work is to study the mechanism of hydrolysis, detachment and ink capture in the bubble-enzyme-ink particle system, during the deinking of office paper type MOW (Mixed Office Waste), using a laboratory column flotation. The cellulase enzyme *Trichoderma sp*. was used.
To compare the deinking efficiency of office paper using enzymes, deinking experiments were performed according to the traditional procedure using sodium hydroxide. The quality of the deinked fibers by measuring their optical properties (whiteness, reflectance, opacity, black spots and tonality) was performed in the Laboratory of the Paper Industry Bio Papel Scribe SA de CV, located in the city of Morelia, Michoacán, México.
The operational variables of the flotation column were established through experiments in the water-air system and adding 100 ppm of pine oil as a surfactant (surface tension of the liquid in 56.6 dynes / cm). The superficial air flowrate was set at 1.27 cm / s (6 LPM), whereas the pulp feed flow rate was 0.88 cm / s.
The experimental results show the feasibility of recycling MOW-type office paper by using the enzyme cellulase Endo-β-1,4-D-glucanase and the amino acids Aspartate, Glutamate and Asparagine; the latter, individually and mixed. The optical properties of the sheets of paper formed with the cellulose deinked by this procedure, were better than those evaluated to sheets of paper formed with fibers of recycled and deinked paper by the traditional procedure.
In the case of the combined use of the three amino acids, the ISO whiteness is 90.8%, 303.4 ppm of black spots, reflectance of 47.1% and 89.5 of opacity. By the traditional procedure, the reported whiteness is 80.2%, the reflectance is 57.4%, and the opacity is 99.6%.
Keywords. Paper deinking, flotation column, cellulose *Trichoderma sp*., MOW paper

1. Introduction

Deinking up to now is generally carried out under alkaline conditions and requires the use of chemical reagents such as sodium hydroxide, hydrogen peroxide, sodium silicate, etc., to be more efficient the process and obtain a product with specific optical properties [1-3]. This has a negative impact on the environment, since the generated effluents are difficult to treat due to the presence of contaminants like adhesives, ink pigments, resins, chemicals, organic fines, etc. [4, 5, 6].

The deinking in conditions of neutral pH is of great interest in the development of new technologies for the processing of recycled paper. The main differences with respect to traditional deinking (alkaline medium) are the use of surfactants, enzymes or sodium sulfite instead of the chemical reagents that are conventionally used [5, 6, 7, 8, 9].

Deinking consists in detaching the ink particles from the surface of fibers and then separating the ink by washing or through air bubbles during flotation. Enzyme attacks include two types: attack on the ink particles and attack on the surface of fibers. The enzymes bind to the surface of fibers by modifying them and favoring the ink detachment during the conditioning of the pulp. The hydrolysis of cellulose and its surface degradation are considered important, since that implies the removal of ink from fibers. Enzymes are chemical catalysts, which decrease the activation energy of a reaction, without being consumed by the same reaction. These remain active until denaturation or deactivation by inhibitory molecules. Depending on the type, each enzyme works optimally under specific temperature and pH range [10, 11, 12]. The enzymes most used for enzymatic deinking are cellulases, which attack the structure of the fiber, hydrolyzing the cellulose found in the region of bond between fibers and inks [13, 14, 15], to subsequently capture the ink in the flotation stage. The addition of surfactants improves the role of enzymes [6, 16].

The present work evaluates the feasibility of deinking Mixed Office Waste or MOW type (for its acronym in English) by means of an enzymatic pretreatment and later use of a flotation column, the measurable parameters to evaluate the efficiency of deinking were whiteness (Brightness), Factor of Reflectance, Opacity and Tonality.

2. Materials and Methods

2.1. Enzymatic deinking

Mixed Office Waste (MOW) type paper was used. The sheets were cut and disintegrated in an industrial blender, without chemical reagents. The enzyme Cellulase Trichoderma sp. (Sigma Aldrich) was added as hydrolytic reagent to promote ink detachment. The enzyme was stored at 4°C prior to use.

Figure 1 shows the experimental setup for paper deinking. Capture and separation of detached ink from fibers of cellulose were carried out in a laboratory flotation column (0.1 m in diameter and 2.77 m high), with a gas disperser externally installed to the column. The paper pulp with consistency of 3.0% was conditioned in a tank during 120 min, in this point the chemical reagents were added depending of the deinking method. The temperature of the pulp was kept at 50 °C throughout the experimentation.

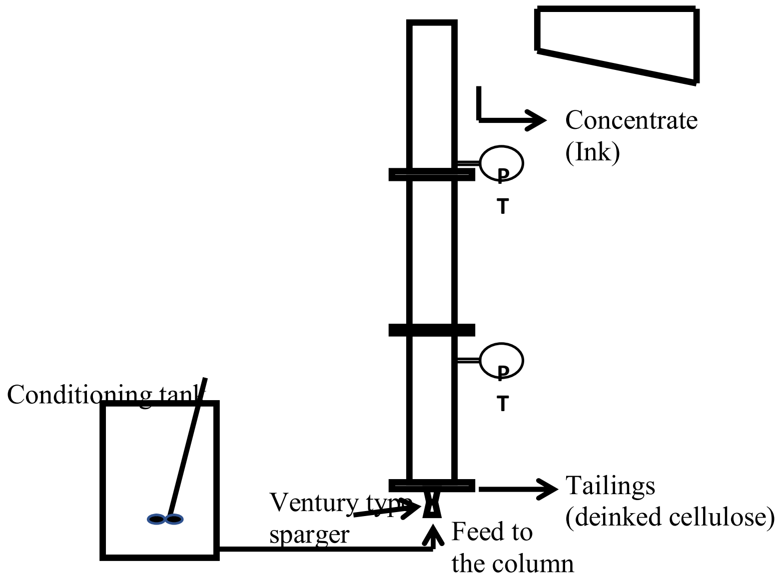

Figure 1.- Experimental setup for deinking of recycled paper. PT means pressure transducer devices.

Flotation deinking was carried out keeping the pulp consistency in 0.15%, in two modalities: traditional deinking by adding sodium hydroxide to the conditioning tank until reaching a pH of 10 with, and deinking by using an enzyme, 0.055% of Cellulase Trichoderma sp., on a dry paper basis at natural pH of 6. In all experiments pine oil was added as surfactant to fix and maintain the surface tension at 0.63 N/m.

The gas holdup in the column was estimated through the pressure drop values from pressure transducers installed in two points along the column. The mean bubble diameter of a swarm was calculated by solving the Drift Flux Analysis model [17].

2.2. Evaluation of deinking

For each deinking procedure samples were collected from the tailings stream (deinked fiber), with standard laboratory sheets, conforming to the standard TAPPI T-205-OM-81, to which the optical properties were determined: ISO whiteness (Brightness), Factor of Reflectance, Opacity and Tonality.

3. RESULTS AND DISCUSION

3.1. Evaluation of deinking in the column.

Samples of the deinked fiber were analyzed by the methods described above; the optical properties measured in the made sheets are shown in Table 1. It is important to note that in the deinking experiments, no bleaching agent was used.

Table 1.- Optical properties of the deinked fibers with sodium hydroxide and the enzyme cellulase.

Property	*Deinked fiber with NaOH*	*Deinked fiber with Enzyme*
Brightness ISO (%)	*80.2*	*75.6*
*L**	*92.86*	*91.08*
*a**	*1.68*	*0.44*
*b**	*0.21*	*3.72*
Reflectance ISO (%)	*57.45*	*49.16*
Opacity (%)	*99.46*	*98.74*

The most relevant characteristic to determine the efficiency of the deinking process is whiteness (Rosencrance et al., 2005), it is determined through the measurement of the Brightness. Brightness ISO is determined using standard sensitivity spectrum centered at a wavelength 457 nm according to ISO 2470 or TAPPI T525 standard and is represented in percentage points. In deinking with enzyme 75.6% of whiteness was achieved, while with NaOH it was 80.2%. Comparing with the results of some other researchers [19, 20], they reported a whiteness of 71.6% for deinking with the enzyme cellulase at 0.05% of the dose with respect to the weight of the processed paper, 3.0% of consistency of the pulp and with the aid of bleaching reagents such as hydrogen peroxide, sodium silicate and a chelating reagent.

Opacity is the measure of the ability of the material to obstruct the passage of light through it; that is, an opaque paper is one that presents difficulties to see through it. This optical property is required on white office papers and on all printing papers. For deinking with NaOH, 99.46% of opacity was achieved, practically the same as for deinking with enzyme, where 98.74% was obtained; the upper limit according to the standard is 100%.

About the reflectance (R), it is defined as the percentage value of reflectance of a stack of papers in relation to a pattern considered as 100%. For the fiber recovered with NaOH, a reflectance of 57.45% was obtained, whereas with the enzyme it was 49.16%. Reflectance spectra in the visible light range show that unbleached pulps absorb more in the blue zone, for this reason they look yellow or brown. Bleached pastes observe high reflectance (close to 100%), and in addition the value is similar throughout the visible spectrum and therefore does not show any color.

The determination or calculation of the tri-stimulus values (X, Y, and Z) of CIE from the spectral reflectance, allows to obtain the color coordinates; for instance, the values L*, a*, and b* in the CIElabcolor space (ISO 5631). The parameter a* measures the dye on the red (+) – green (-) axis, and parameter b* measuresthe dye on the yellow (+) – blue (-) axis. The parameter L* is a tonality referred to the trend from black to white. Absence of color means null values of parameters a* and b*. The results in the deinking with enzyme against NaOH show a L* equal to 91.08 versus 92.86; in other words, 1.78 points with less tendency to white in the deinking with enzyme. In the parameter a* 0.44 was obtained versus 1.68; practically this tonality is zero with the enzyme, whereas with the NaOH tends towards red. The variable b* tends to yellow with the enzyme (3.72), and for the NaOH very close to the absence of this color (0.21).

Conclusions

In the present work, the operating conditions of the laboratory flotation column were established for the maximum airflow and bubble surface area rate for the capture and transport of ink mass detached from Mixed Office Waste (MOW) type paper.

Through the mathematical simulation and analysis of the molecular coupling of the enzyme to cellulose, by the Docking technique, the best coupling between the enzyme-cellulose complex was defined; that is, the pose with better affinity and/or lower binding free energy. Once the best coupling was established, the most important endo-β-1,4-D-glucanase amino-acids were found in this molecular bond, which promotes the hydrolysis of the cellulose and the subsequent release of the ink.

From the paper deinking experiments using the conventional method with NaOH and enzymatic deinking with the help of the commercial enzyme Cellulase Trichoderma sp., it is concluded that the optical and physical properties in the fiber deinked by the conventional method are slightly better to those obtained in the fiber deinked with the enzyme cellulase; however, the weight ratio between the enzyme and the MOW paper should be varied to establish the possibility of improving the optical characteristics of the deinked fibers with this enzyme, until reaching optical properties greater than the deinked with NaOH

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