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STUDY OF THE ENZYMATIC/NEUTRAL DEINKING PROCESS OF WASTE PHOTOCOPY PAPER

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ABSTRACT

Enzymatic deinking was performed by mean of common commercial enzymes, whereas the neutral deinking is a process achieved in a chemical environment that provides a pH of about 7.0, and usually with application of only surface tension agents. This work performs the deinking process in neutral conditions, with enzymatic pretreatment of the waste paper pulp, and using ethoxylated fatty acids as surfactant. The enzyme employed in the pretreatment is cellulase or amylase, and the enzymatic activity for these enzymes was evaluated according to IUPAC rules and based on temperature and pH values, as by the supplier. This paper studied the influence of HLB of surfactant in combined processes of enzymatic/neutral deinking. These deinking processes are to cause less environmental impact than the process commonly used in alkaline environment. It studied the process in waste photocopy paper. For comparison, a pulp without enzymatic pretreatment was used. The deinking enzymatic/neutral process is carried out by flotation at a stock consistency of 0.8%, with a 6 minutes flotation phase at 40°C temperature. In the deinking enzymatic/neutral process, the applied enzymes doses are 0.06%, 0.105% and 0.15%, and the ethoxylated fatty acids employed of HLB are 12, 14 and 16. Optical properties were determined as reflection factor at 457 nm (brightness ISO), not eliminating measurement points. For waste photocopy paper the maximum values of brightness ISO is 78.9% and 80.6% when cellulase and amylase are used in enzymatic pretreatment, respectively.

Keywords: Enzymatic deinking, ethoxylated fatty acids, flotation, neutral deinking, HLB value

INTRODUCTION

The deinking is a process for the removal of contaminants from reusable paper fibers. Basically, is carried out in two major phases: the disintegration of printed paper and the separation of ink particles and contaminants from the fibrous suspension by washing or flotation [11]. This process is commonly done in an alkaline medium using chemical substances [7]. In recent years, recycled fiber has acquired importance in the pulp and paper industry. In Europe, the main sources of paper recovery are: 50% from trade and industry, 40% from households and 10% from offices [4]. In Colombia, paper recovery for recycling has had an increase of 7.6% between years 2009 and 2010 [2]. These are low cost fibers for the manufacturing of paper, and through its use forest resources can be preserved, air pollution reduced and savings in both energy and water achieved [5,13]. The enzymatic/neutral deinking is an alternative to counteract the intensive use of chemicals in the conventional process, being a process that reduces the environmental impact, efficient and fast, and with which similar results to what has been achieved in deinking using chemical substances are obtained [6, 9]. Elegir *et al.* [6] performed deinking tests using ethoxylated fatty acids and ethoxylated alcohols in a process assisted by enzymes in neutral environment. It is to note that the surfactant indicating greater ink reduction was an ethoxylated fatty acid with HLB value of 11.4. Theander and Pugh [12] indicate that HLB is an important parameter when using nonionic surfactants, because of their great influence on whiteness and efficiency in washing and flotation processes. Pala *et al.* [10] showed that a good combination of commercial cellulolytic enzymes, as Celluclast 1.5 l and Buzyme 2523, are efficient in pigments extraction. Several enzyme systems consisting of cellulase, lipase and hemicellulase - or their combinations - have been examined by a number of research groups for their potential in deinking of different sort of waste papers [8]. Enzymes improve paper properties such as brightness and resistance compared with paper deinked by chemical methods [3].

MATERIALS AND METHODS

Waste paper

For this work, waste photocopy paper taken from photocopying Medellin's (Colombia) centers was used. This sort of paper was torn into small pieces of approximately 2x2 cm.

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Enzymes

The enzymes used were supplied by CASDIQUIM S.A. company, of the city of Medellin, Colombia. Two types of enzymes: cellulase CAZDIZYME NN and amylase AQUAZYM 250N ULTRA were used.

Determination of the cellulase enzyme activity

Method of FPU filter paper units using membrane (Schleicher & Schuell 100) filter paper as a substrate in quantity of 50 mg per each sample was used. It was valued at three temperatures (55, 40 to 85°C) keeping constant the enzyme action time (60 min.) and pH (7.0). The response variable was the release of glucose by the enzyme action, determined by absorbance readings at 540 nm in a spectrophotometer UV/VIS Schimtz UV-1601PC. The enzyme activity of cellulase NN CAZDIZYME was also determined using as a substrate 0.5 g of pulp from waste photocopy paper, evaluating as variable of interest the enzyme concentration (g enzyme/100 g pulp).

Determination of the amylase enzymatic activity

This determination was performed using the method of hydrolysis of starch with α-amylase applying soluble starch as substrate at a concentration of 0.008 g/mL. The variables of interest were temperature - evaluation at 40, 60 and 85°C - and the reaction time between 0 and 6 minutes. The experimental conditions were 1.56 g enzyme/100 g starch and pH 7.0. The response variable was the release of glucose by the enzyme action, as determined by reading absorbance at 540 nm in a UV/VIS spectrophotometer (Shimadzu UV-1601PC). The enzyme amylase AQUAZYM ULTRA 250N activity was also determined using as substrate 0.5 g of pulp from waste photocopy paper, evaluating as variable of interest the enzyme concentration (g enzyme/100 g pulp).

Surfactant

The surfactants used were ethoxylated fatty acids with 3 different values of HLB: 12, 14 and 16, wherein oleic acid is predominant in the hydrocarbon chain. These products were supplied by the company OXITENO S.A. de CV of the city of Guadalajara, Mexico.

Disintegration

Done during 10 minutes at speed of 3500 rpm and consistency of 2%; conducted in a standard disintegrator such as that described in Appendix A of the TAPPI T 205 sp-02 standard.

Enzymatic pretreatment and reaction

The disintegrated pulp was subjected to heating under constant stirring until the pretreatment temperature; at this time the chelant was added at 1% oven dry, and the pH was brought to neutral by addition of NaOH. Enzyme is added and allowed to act for 20 minutes. The surfactant was added to carry out the curing step during 30 minutes.

Flotation

Stage performed in a 3 L capacity flotation cell during 6 minutes, with airflow of 1 L/min at 21°C, 1 atm. To characterize the process, sheets formation was performed according to TAPPI T205, whiteness ISO measured at 457 nm and specks checked according to TAPPI T452 om-02.

RESULTS AND DISCUSSION

Cellulase enzymatic activity

When determining the enzymatic activity of cellulase as filter paper units, it was found that for the three temperature levels the enzyme concentration required to liberate 2.0 mg of glucose was about 0.047 g enzyme/g paper, which indicates the little temperature effect on the enzymatic hydrolysis of the cellulose.

Table 1 shows the amount of glucose released by the cellulase, where variation in the enzyme concentration is not directly proportional to the amount of glucose released by the enzyme.

Table 1. Glucose released at different enzymatic concentration levels of cellulase CAZDIZYME NN

Enzymatic concentration (g enzyme/100 g pulp)	Absorbance	Glucose released (mg)
0.060	0.269	1.167
0.105	0.298	1.325
0.150	0.283	1.243

Amylase enzymatic activity

The highest amount of glucose released by the enzyme (0161-0254 mg) was achieved at 85°C temperature. **Table 2** shows the amount of glucose released at various amylase concentrations. Hydrolysis of the pulp was higher from 0.105 up to 0.15 (g enzym/100 g pulp) levels. In turn, the enzyme action was higher than that found in experiment with water-soluble starch, despite the use of lower enzyme concentrations.

Table 2. Glucose released at different enzymatic concentration levels of amylase AQUAZYM ULTRA 250N.

Enzymatic concentration (g enzyme/100 g pulp)	Absorbance	Glucose released (mg)
0.060	0.086	0.167
0.105	0.123	0.369
0.150	0.12	0.352

Deinking with enzymatic pretreatment

Statistical analysis was carried out in a Statgraphics Centurion XVI.I, and results were calculated at the 95% significance level.

Waste photocopy paper was disintegrated and pretreated with cellulase and amylase independently. Ethoxylated fatty acids with

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Table 3. Results of brightness ISO and specks for enzymatic/neutral deinking process

			Cellulase		Amylase	
Test	Enzyme doses (%)	HLB	Brightness ISO (%)	Specks (No.)	Brightness ISO (%)	Specks (No.)
1	0.105	14	78.16	169174	76.38	206335
2	0.105	14	76.77	166316	73.37	177230
3	0.105	14	75.77	160339	72.76	187105
4	0.06	12	80.21	153582	78.51	104207
5	0.06	12	79.11	142408	78.16	112523
6	0.06	12	78.1	168395	79.43	123178
7	0.105	14	78.49	196980	80.64	160079
8	0.105	14	78.45	218029	81.02	163457
9	0.105	14	78.38	212312	80.10	175411
10	0.105	14	78.31	141888	77.74	227385
11	0.105	14	77.96	133832	77.95	228684
12	0.105	14	78.03	115122	78.10	206075
13	0.15	12	78.31	160599	76.22	179049
14	0.15	12	78.71	161378	76.35	200618
15	0.15	12	77.43	165016	75.72	209973
16	0.06	16	71.66	150724	79.83	149164
17	0.06	16	72.33	155921	78.79	150464
18	0.06	16	72.33	150464	78.85	149424
19	0.15	16	78.11	115901	81.64	131753
20	0.15	16	78.33	119279	81.49	120579
21	0.15	16	77.01	136951	80.46	134352

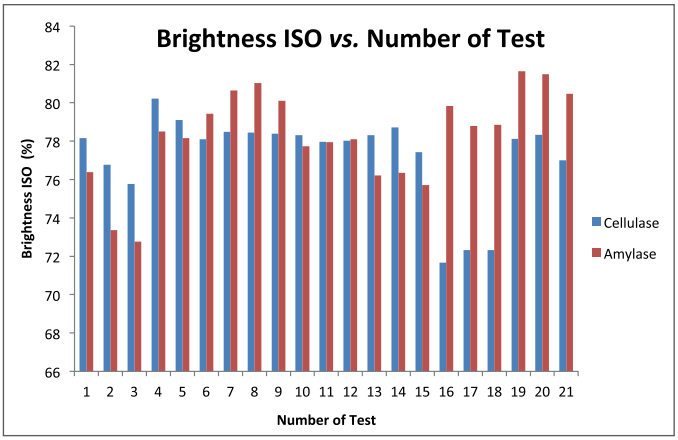

Figure 1. Brightness ISO values for samples treated with cellulase or amylase

12 to 16 HLB values were used in deinking process. **Table 3** shows the results of the experiment design for brightness ISO and for specks per square meter. **Figure 1** shows the brightness results for each type of enzyme. Untreated pulp has 75.41% brightness ISO and 169521 specks per square meter.

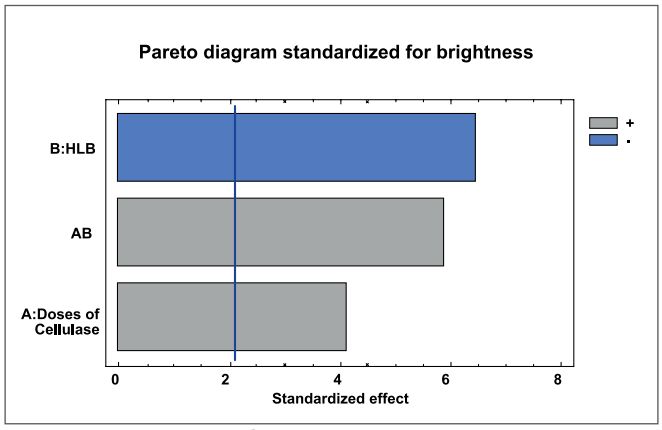

Figure 2. Pareto diagram for brightness ISO using cellulase

Table 3 and Figure 1 show better results of brightness ISO for amylase that for cellulase, which may be due to chances that the used photocopy papers could contain starch, enzyme able to cause mechanical cuts and, thereafter, help to release ink particles to be afterwards removed in the flotation stage [15]. In general terms, the increase for both enzymes was 3 to 6 points in brightness above the control pulp value. Alzate *et al.* [1] found that ethoxylated fatty acids with high HLB used in neutral deinking process produce better optical properties than the conventional alkaline deinking process. **Figures 2** and **6**. Standardized Pareto Chart for brightness ISO using cellulase and amylase, respectively, show that HLB has a statistical significance at the 95% level.

The best results in brightness in pretreatment with cellulase were attained with HLB 12 - as shown in **Figure 3** - in contrast with the best amylase results that came to pass with HLB 16, as shown in **Figure 7.** Theander and Pugh [12] proposed that nonionic surfactants with HLB from 14 to 15.5 give optimal results in deinking mix of newspaper/magazine papers, which result is close to the better HLB found in our work.

Standardized Pareto Chart for brightness shows a combined effect between HLB and enzyme doses, Figures 2 and 6; the better value of brightness was achieved with the lower HLB value and higher enzyme dose (Figure 3). This result is similar to the one found by Elegir *et al.*

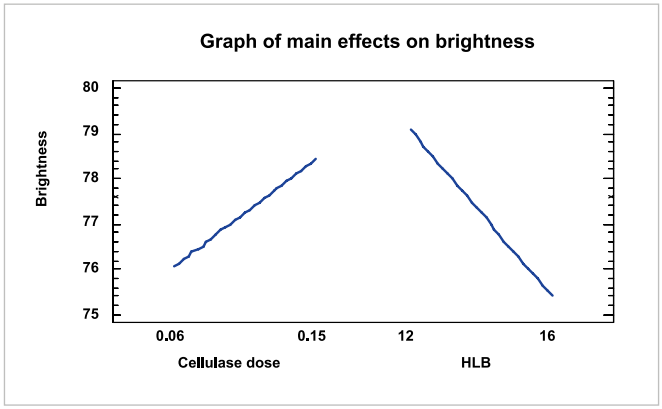

Figure 3. Graph of main effects on brightness with use of cellulase

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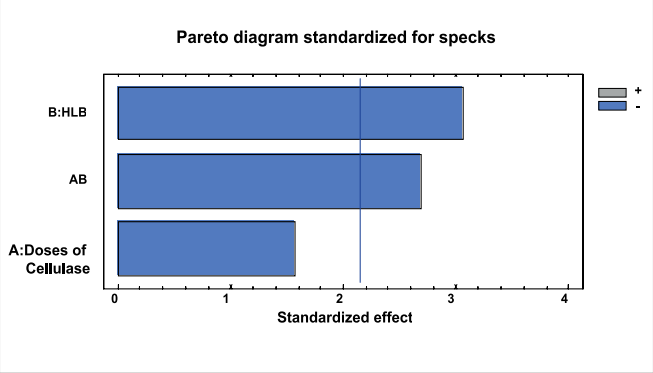

Figure 4. Pareto diagram for specks when using cellulase

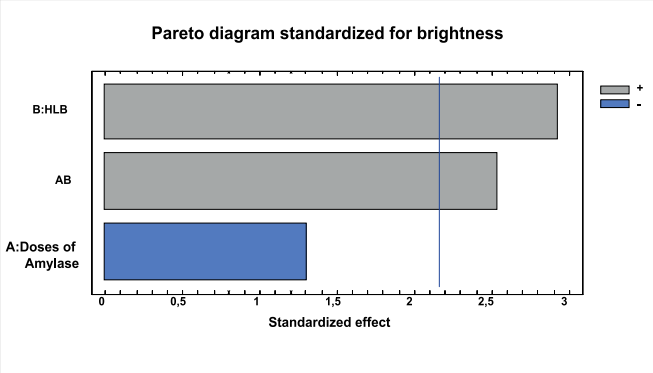

Figure 6. Pareto diagram standardized for brightness ISO using amylase

[6], who used ethoxylated fatty acid with a HLB value close to 12 and assisted by cellulase. They claim the nonionic surfactants interact with the cellulase, improving its effect. According to Zeyer *et al.* [14], the enzymatic hydrolysis of cellulose by cellulase facilitates the deinking process, and depends on pretreatment time, temperature, pH and enzyme dosage. In the evaluation of the enzyme activity, a weak influence of temperature and dosage was observed.

Standardized Pareto Chart for specks using cellulase, **Figure 4**, shows that the main effects are due to the HLB and interaction with the enzymatic dose. According to analysis for brightness, enzyme dose is not of a significant effect; however, it indirectly favors interaction of the HLB and the enzyme dose.

Figure 5 shows the effects of cellulase dose and HLB for specks. Comparing with Figure 3 there is consistency in the effect of enzyme dosage, as it resulted in less amount of black dots with the highest dose. The HLB has no relation about brightness and specks results; a lower HLB produces higher brightness, but not fewer specks. Sometimes a better brightness does not strictly relate to the amount of specks because, in some cases, the increase is due to specks dispersion.

As regards the process using the enzyme amylase, it was observed the use of this enzyme has improved brightness values in pulps deinking processes, as indicates Elegir *et al.* [6], who suggest the deinking of waste photocopy paper treated with cellulase can be improved when mixed with amylase.

Figure 6 shows that only two effects have statistical significance on brightness, HLB and the interaction of enzyme dose with HLB. HLB has an effect opposing to that obtained in the analysis of brightness using cellulase. In the same way, **Figure 7** shows an opposite effect to Figure 3, higher values of brightness are attained by increasing the HLB and decreasing the enzyme dose.

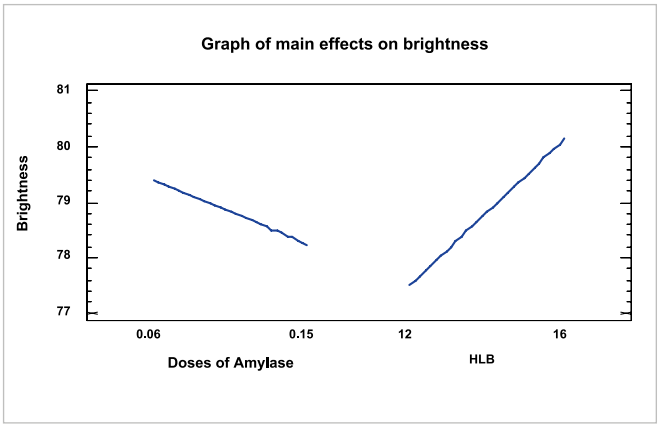

Figure 7. Graph of main effects on brightness ISO using amylase

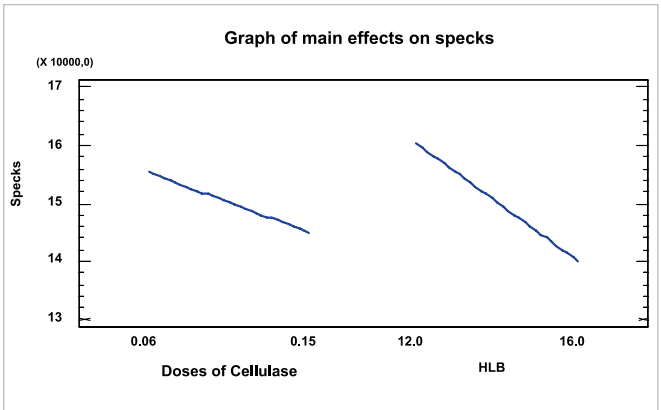

Figure 5. Graph on main effects for specks using cellulase

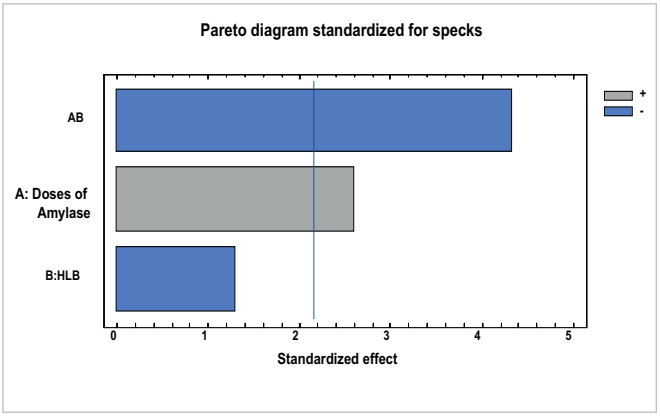

Figure 8. Pareto diagram for specks using amylase

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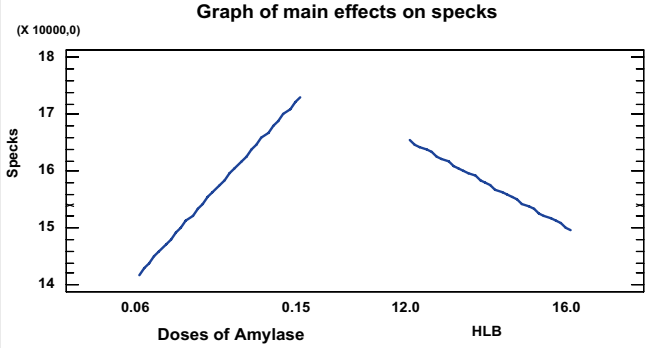

Figure 9. Graph of main effects on specks using amylase

Yield losses in the flotation cell with amylase was from 5% to 10%, which is similar to that reported by Bobu *et al.* [4]; they found that a neutral enzyme deinking process, with cellulase or amylase, presents low loss levels in flotation when compared with a xerographic printing paper in alkaline deinking.

In some cases, Bajpai and Bajpai [3] indicate that treatment with enzymes reduces the size of specks, and reduction in specks size is dependent on time of pulping in presence of cellulase.

CONCLUSIONS

Neutral deinking processes of waste photocopy papers assisted by cellulolytic enzymes or amylase allow the obtainment of pulps with better brightness. In general, pulps deinking with best brightness were achieved with application of amylase. For both enzymes employed, optical properties of pulps from waste photocopy paper are affected by interaction of the HLB value and the enzyme dosage. For pulps treated with cellulase, an ethoxylated fatty acid with HLB value of 12 showed best brightness ISO whereas an ethoxylated fatty acid with HLB 16 value gives best results for brightness when pulps were treated with amylase.

In a future works, we intend to evaluate the influence of the mixture of both enzymes for waste photocopy paper and other waste papers mixtures.

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