

## **DEINKING PAPER IN A NEUTRAL MEDIUM, THROUGH A TREATMENT WITH AMINO ACIDS, IN FLOTATION COLUMNS.**

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### **ABSTRACT**

Mixed waste from office paper (MOW) is an excellent source of low-cost, high-quality fiber for the papermaking industry. The limitations in the application of conventional deinking to such paper are related to the negative environmental impacts that chemical substances can cause, which is why deinking in a neutral medium is receiving increasing attention. This study focuses on investigating the effect of the application of the amino acids Aspartate Glutamate and Asparagine, in the deinking of office paper, using a flotation column on a laboratory scale.

The methodology involves the sample preparation, a pretreatment, flotation, the manufacture of paper, microscopy analysis, and finally the evaluation of optical properties. Different doses for each of the amino acids and of the mixture of the three were tested, at different conditions of temperature and pH in the pretreatment.

The best optical characteristics were obtained when using the mixture of the three amino acids at 0.6% on a dry weight basis of the paper to be deinked, proposed in this study, with 90.8% whiteness. From scanning electron microscopy analysis, no superficial damage to fiber morphology is observed in any of the fiber samples after deinking.

## 1. INTRODUCTION

Paper, as one of the largest solid waste materials, is relatively easy and inexpensive to recycle. Recycling of waste papers reduces environmental pollution by reducing the flow of waste papers to landfills. Recycled and reused waste papers are important low-cost fiber resources (raw materials) for the Pulp and Paper Industry.

Mixed office waste paper is a fast-growing source of materials for recycling and the most difficult raw material to deink [1]. The rank of difficulty in removing the ink depends mainly on the types of ink, fiber, and the printing process. Currently, paper mills use a chemical method of deinking waste paper, which is generally more efficient and economically feasible, with regard to ink removal. However, this method requires the use of a large number of chemicals agents, which are harmful to the environment. Additionally, deinking under high pH conditions causes stained Pulp or low brightness, requiring the addition of chemicals to bleach the fiber, resulting in a significant increase in the level and concentration of harmful emissions to the environment and waste that are costly to contain within environmental regulations [2].

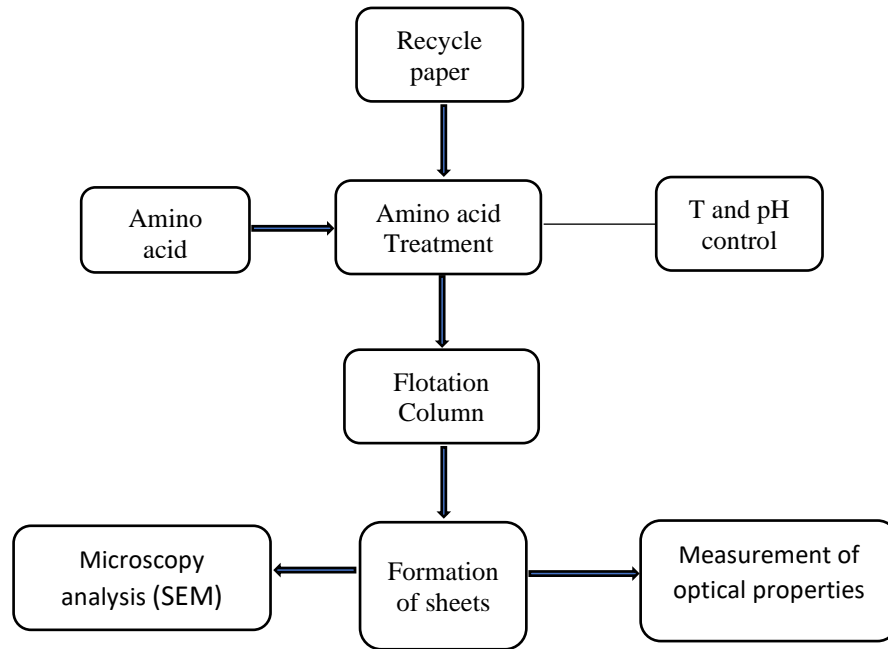
Due to the large number of disadvantages of conventional methods, the development of an alternative method for deinking is required. The use of enzymes has been reported as a potentially efficient solution to overcome the problems encountered with traditional deinking techniques. However, enzymes require an acidic environment in high temperatures for their activation and effectiveness. One of the benefits of the use of enzymes in deinking is the minimal treatment of the effluent produced due to a lower DQO content compared to the conventional deinking process [3]. In addition, it has been described that the use of cellulases is capable of deinking high quality waste paper, such as mixed office waste papers (MOW), which is the most difficult raw material to deink by a conventional deinking process. In this way, a better brighter and cleaner pulp can be obtained [1,4]. In addition to ink removal, enzymatic deinking can improve the strength properties of paper by removing fines content and improving the interfibrillar bond of the paper [4,6]. Additional benefits include the improved performance of additives used in papermaking, due to better drainage. Better drainage can result in faster machine speed, leading to significant savings in energy and therefore overall cost [7]. Computational chemistry studies have reported that the cellulase enzyme molecule contains

mainly 3 amino acids: Aspartate, Glutamate and Asparagine, with a significant rank of absorption in the cellulose molecule [8], which are responsible for the hydrolysis and depolymerization of this. By partially hydrolyzing and depolymerizing cellulose molecules of the fiber surface, the bonds between the fibers are weakened and therefore easier separation is achieved [9,10,11,12,13]. Optimal fiber separation leads to facilitation of ink detachment. This can lead to the removal of fibrils contained in the fiber Surface, a process known as “peeling”, which also contributes to ink detachment [12,13,14]. Furthermore, the separation of the fibrils from the ink particles causes an increase in the hydrophobic behavior of the particles and, therefore, improves the flotation efficiency [10,11,13,14].

## **2. METHODOLOGY**

The objective of the methodology applied in this work was to investigate the effect on the optical characteristics of MOW type of paper, deinked by means of the application of the enzyme Cellulase Thricodema Sp. And the amino acids, Aspartate, Glutamate and Asparagine, using a flotation column on a laboratory scale. To this end, the methodology began with the preparation of the office waste paper samples that were used for the execution of the subsequent processes, that is, the implementation of the pulping process, the application of the treatment with amino acids, the implementation of flotation, the manufacturing procedure of the sheets of paper, and finally the evaluation of the optical properties of the paper and its surface morphology, by means of scanning electron microscopy.

The applied methodology is illustrated in Scheme 1 and describe below.



Scheme 1. Work scheme of the enzymatic deinking procedure.

### 2.1 Preparation of the sample.

The methodology began with the preparation of the sample, that is the office waste paper. To avoid variability in results as a result of print type and paper, “standard” text was printed on a letter-size sheet using an all-in-one (Xerox Work Centre 3346, monochrome). Approximately 20% softwood (Pine) and 80% hardwood (Eucalyptus and Oak).

### 2.2 Pulping.

The paper samples are cut into small pieces (approximately 2 cm by 2 cm) by hand and 46 gr. are added in a 2 L Heidolph Laboratory pulper, with 1 L of tap water, to obtain a consistency of the mixture of the 4%.

The pulping time is maintained for all tests at 3 minutes.

### 2.3 Treatment with the enzyme and amino acids.

The Pulp obtained in the previous process is passed to a treatment unit, which consists of a 2 L glass beaker, equipped with a rod stirrer, a heating plate, a digital pH meter, and a thermometer. The Pulp was kept under constant agitation to achieve homogeneity of the mixture.

9 experimental series were carried out, modifying the amino acid dose from 0.1% to 0.2% on a dry paper basis. In the first test with Aspartate, the temperature of the mixture was raised to 50°C and the PH was adjusted to 5, with sulfuric acid. Upon reaching these conditions, 0.1% Aspartate is added on a dry paper basis. The treatment time was 30 minutes.

In the following tests, the treatment is carried out ambient temperature conditions (25°C) and pH of the mixture, neutral (pH=7). Maintaining the same reaction time with each amino acid under constant stirring for 30 minutes.

Table 1 shows the dose, type and mixture of amino acids that had an effect in each for the tests carried out.

Table 1. Amino acid treatment control parameters.

FACTORS	units	Test 1	Test 2	test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9
Type of amino acid		ASP	ASP	ASP	GLU	GLU	ASN	ASN	ASP:GLU:ASN	ASP:GLU:ASN
Dose of amino acid	%	0.1	0.1	0.2	0.1	0.2	0.1	0.2	0.1: 0.1: 0.1	0.2: 0.2: 0.2
Consistency	%	4	4	4	4	4	4	4	4	4
Time of rxn.	min	30	30	30	30	30	30	30	30	30
pH	-	5	7	7	7	7	7	7	7	7
Temperature	°C	50	25	25	25	25	25	25	25	25
Surfactant	ppm	100	100	100	100	100	100	100	100	100

Note: Percentages are based on the mass of the dry paper.

## **2.4 Flotation.**

After treatment with amino acids, the ink is separated in a laboratory flotation column (10 cm in diameter and 4.5 m in height. Figure 1). In this process, the following were fixed as constants: flotation consistency (0.1% on dry paper basis), flotation time (20 min), surfactant concentration (100 ppm), feed streams (10 LPM) and tails (6 LPM), as well as the air flow fed to the column (6 LPM). The water used in the flotation column was from the commercial drinking network.

Pine essence (Pine oil) was used as surfactant, provided by the company ALKEMIN, S. DE RL DE CV (Annex A).

During the flotation runs, samples of the pulp were collected on the tailings stream, for the formation of the sheets and determination of the properties of the deinking cellulose.

## **2.5 Formation of the sheets.**

The fiber taken from the tails stream (deinked fiber) is taken to a sheet former, Lorenzent & Wettre (Sweden), and to a laboratory press, to make the paper sheets according to the TAPPI T-205-OM-81 (Annex B).

## **2.6 Evaluation of the properties of deinked paper.**

The quality evaluation of the paper was carried out after the measurement execution of the optical properties of the paper (brightness, tonality, opacity and content of impurities), and the analysis of the scanning electron microscope (SEM).

The optical properties of the deinked paper sheets were measured in the following equipment: the ISO whiteness in the Brightimeter-Micro S-5, the opacity in a Monitor Smoothness model No. 5802, the tonality (variables  $a^*$  and  $b^*$ ) in the Exact X-rite Pantone.

By using the scanning electron microscope (SEM; JEOL, model JSM-7600F FEG-SEM), images of the fiber morphology were obtained before and after the treatment with the amino acids in question. The samples were prepared with a copper bath (metallized), used as a treatment to optimize the observation. The images were taken at 100X, 250X, 500X and 1000X, in two different areas of the sample.

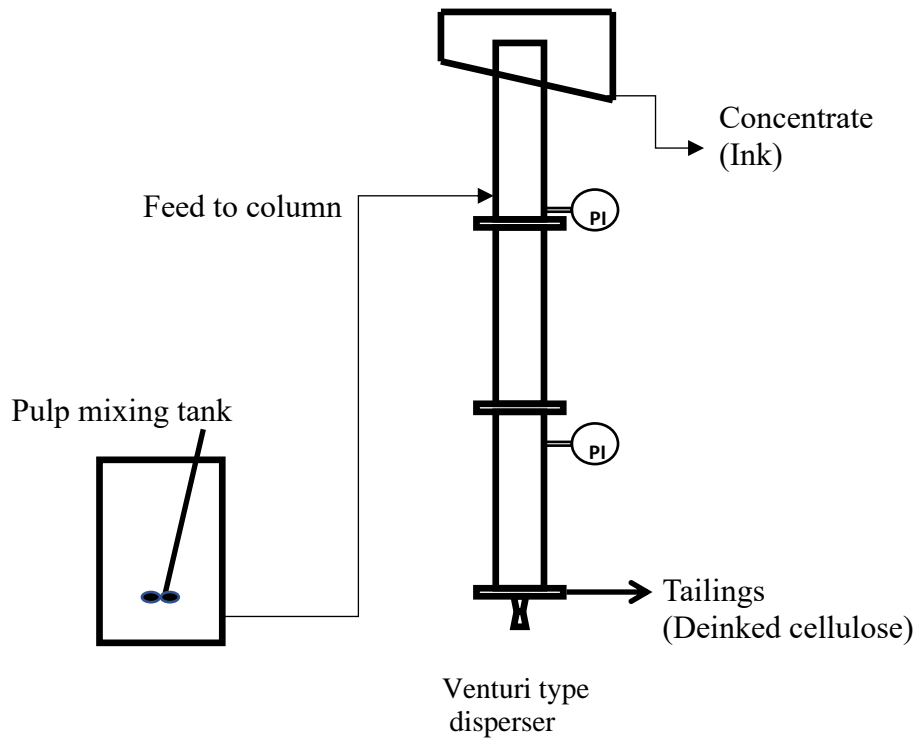


Figure 1. Experimental design for deinking paper using a laboratory flotation column. PT are the pressure transducers.

## RESULTS

The experimental results are presented in table 2. In test 1, treatment with Aspartate (ASP), the medium was modified at pH=5 and T=50°C. However, the quality results of the deinked fiber in this medium were not good. The ISO whiteness obtained was 75%, and therefore the variable L\* (tonality reference with respect to white) was also low, 89.75. The tonality variables a\* (redshift) and b\* (blueshift), 1.1 and -1.2, respectively, result with values close to one, remembering that zero value for these variables would mean the absence of color in these shades. The above is a product of sulfuric acid, used to modify the pH in the treatment, by inducing the yellow color in the fibers. The impurities or black spots were high 720.6ppm, that is, a lower separation of the immersed ink between the fibers. The opacity and reflectance are not greatly diminished, and result in values close to the established quality standards.

Continuing with Aspartate, when carrying out the experiment with a dose equal to the previous one, 0.1% (test 2) on a dry paper basis, and 0.2% (test 3), but without adding sulfuric acid, or raising the temperature of the system, an increase of 10 percentage points in ISO whiteness.

85% and 86%, was achieved with respect to test 1. The black spots 445.2 and 512.5 ppm, respectively. For L\* tonality, values of 93.05 were obtained in test 2, and 94.25, in test 3. The tonality a\* and b\*, manifested with practically equal values, 1.6 and -3.3 for both cases. The same occurs in reflectance and opacity, with very close values, 41.5 and 42.7% reflectance, and 88.3 and 89.5% opacity.

For Glutamate, when increasing the dose from 0.1% to 0.2%, an increase in whiteness of 2% is obtained, that is, from 84.9% it rises to 86.9%. The black spots are a direct reflection of the quality of the deinking and the effectiveness of flotation, and this number also decreases with increasing GLU dose, from 455.3 to 377.1 ppm. The tonality variables L\*, a\* and b\*, as well as the opacity, undergo only slight changes, without major implications. The reflectance, on the other hand, is modified to a good extent, from 39.57% to 47.15% when increasing the dose of the amino acid in question.

When treating the MOW paper with Asparagine, greater changes are noted between both tests. When 0.1% of the amino acid is dosed, the ISO whiteness obtained is 81.5%, the black spots 550.8ppm and the L\* of 91.6, all of which are number far below those reached in the other tests. In this case the variables a\*, b\*, reflectance and opacity do not show major changes between both tests.

By mixing the three amino acids (test 8), adding 0.1% of each one based on the weight of dry paper to be inked, a whiteness result is obtained well above what was achieved in the previous tests. In test 8, the resulting whiteness was 89.1% and the black spots 333.0 ppm. The variable b\* changes to a lesser extent to -4.3. The parameters L\*, a\*, and opacity remain above the average of those obtained in the previous test. But the reflectance does decrease considerably, 35.9, this being inversely proportional to the whiteness.

In test 9, the MOW paper was treated with 0.2% of each amino acid. This produces the best quality results in deinking. ISO whiteness of 90.8% and black points 303.4 ppm, data much higher than expected, taking into consideration that the MOW paper is not being treated with any chemical bleaching agent and is only working with basically 3 process stages: pulping, treatment chemical and flotation. The original whiteness of deinked paper, "Copy Paper 75 gr/m<sup>2</sup>", has an acceptance range between 91 and 97%. Which implies that obtaining 90.8% whiteness is practically reaching its original quality. The tonality parameters achieved L\*=95.3,

$a^*=1.7$  and  $b^*=-4.52$ , oscillate within the values obtained in previous test and fall within the expected. It should be noted that these variables for the type of paper in question are standard:  $L^*$ , from 92.5 to 95.5,  $a^*$  from 1.3 to 2.3,  $b^*$  from -9 to -8, reflectance from 32 to 40% and minimum accepted opacity of 87%.

The variable  $b^*$  is controlled with a pigment from aniline, and the negative of its value indicates the color shift towards blue. The addition of such pigment in the manufacture of paper is directly proportional to the negativity of this parameter, that is, the higher the aniline, the more negative the  $b^*$ . In deinking these pigments responsible for the color are detached from the vicinity of the fiber and removed by flotation. Therefore, a decrease in this parameter after deinking is to be expected.

Opacity is necessary on all printing papers. It should be enough to prevent printing on the reverse side of the paper from negatively affecting the appearance of a print, so the higher the opacity, the higher the print quality. And the result in this test was the best opacity 89.9%.

The scanning electron microscopy analysis seeks to know the surface morphology of the fiber after deinking. In order to appreciate the level of fibrillation and that it is not greater, such that it can affect the mechanical properties of the fiber. In test 1 where lower quality was obtained in terms of optical characteristics, a slight abrasion can be observed (fig, 3) in certain areas of the fiber surface, a probable result of the action and effect of the sulfuric acid used in said experiment. Some impurities, agglomerated calcium carbonate and starch specks can also be seen in these micrographs; but no, a greater fibrillation, representative of an excessive attack of amino acid in question. The low quality of the whiteness, cleanliness and brightness is a consequence of the yellowing caused by the sulfuric acid added to the test. This can be justified as follows: the calcium carbonate contained in the areas as filler increases the floss and therefore reducing its amount in the paper produced and consequently, to the reduction of the brightness and whiteness of the paper.

In the micrographs of the pulp deinked with Aspartate, Glutamate, Asparagine (Fig. 4 to 8) and the mixture of the above, all at 0.2% on a dry paper basis, something similar to that described in the previous paragraph can be observed. The depolymerization induced by the amino acids does not represent an excessive fibrillation that affects the internal morphology of the cellulose fiber and therefore the mechanical properties of the fiber would not be affected. No particles of

toner or printing ink are seen except for only small agglomerations, likely from starch, precipitated calcium carbonate, and/or residues of other additives, typical of paper manufacture. Fig. 8, shows the micrograph of test 9, which yielded the best results of the optical characteristics, from this it can be seen that the morphological structure of the fiber retains its robustness, some fibers appear flatter than others, as a result of the formation of the sheet, however, there is no presence of fibrillation or excessive formation of fines. The fragmentation of inks is another Phenomenon that occurs in deinking processes, which is desirable up to a certain point, so that the particles formed from these acquire the appropriate size to be floated more efficiently, without considerable repercussions on the mechanical properties of the deinked fiber.

Table 2. Results of the measurements of the optical characteristics of the sheets of deinked paper with amino acids.

	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9
	ASP 0.1%, 50°C, pH=5	ASP 0.1%	ASP 0.2%	GLU 0.1%	GLU 0.2%	ASN 0.1%	ASN 0.2%	ASP:GLU:ASN 0.1%	ASP:GLU:ASN 0.2%
ISO WHITENESS (%)	75	85	86	84.9	86.9	81.5	85.8	89.1	90.8
Black spots (ppm)	720.6	445.2	412.5	455.3	377.1	550.8	423.3	333.0	303.4
L*	89.75	93.05	94.25	93.8	94.44	91.6	94.6	94.7	95.3
a*	1.1	1.6	1.6	1.67	1.27	1.5	1.3	1.65	1.7
b*	-1.2	-3.3	-3.36	-2.55	-2.1	-2.8	-2.5	-4.3	-4.52
Reflectance (%)	37.5	41.5	42.7	39.57	47.15	40.2	39.32	35.9	34.7
Opacity (%)	87.1	88.3	89.5	88.9	89.9	88	89.5	89.6	89.9

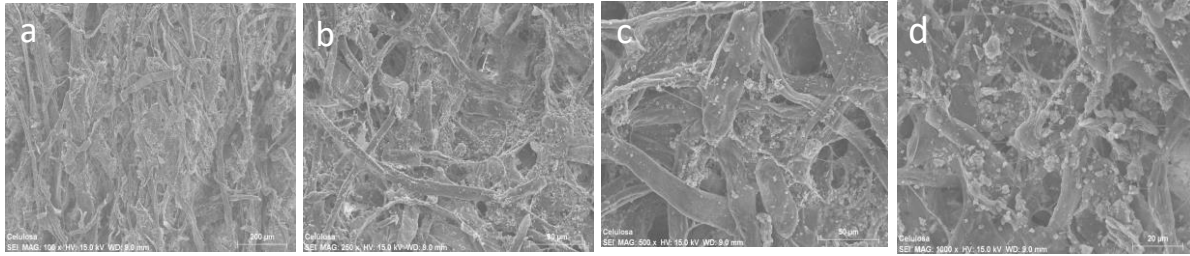


Fig. 2. Micrographs of the paper pulp before deinking. a) Micrograph at 100X, b) micrograph at 250X, c) Micrograph at 500X, d) Micrograph at 1000X.

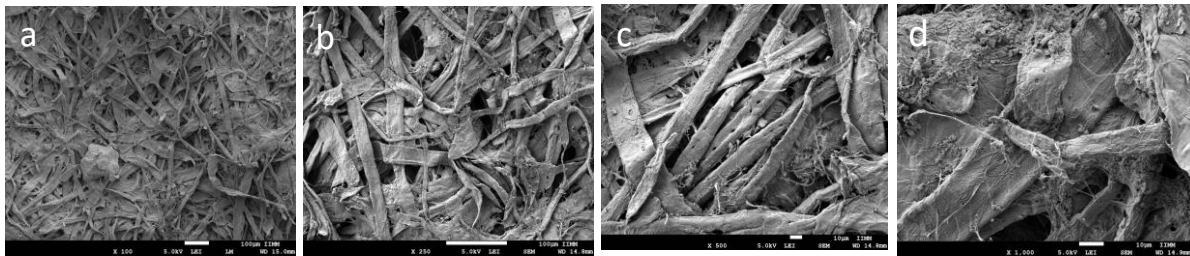


Fig. 3. Micrographs of the paper pulp after deinking, test 1. a) Micrograph at 100X, b) micrograph at 250X, c) Micrograph at 500X, d) Micrograph at 1000X.

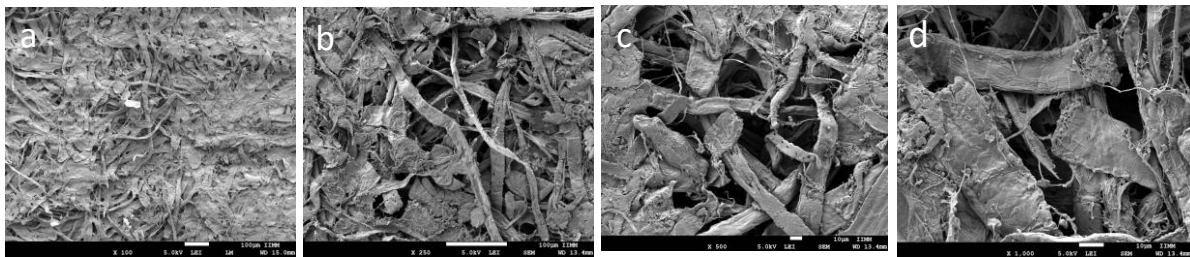


Fig. 4. Micrographs of the paper pulp after deinking, test 3. a) Micrograph at 100X, b) micrograph at 250X, c) Micrograph at 500X, d) Micrograph at 1000X.

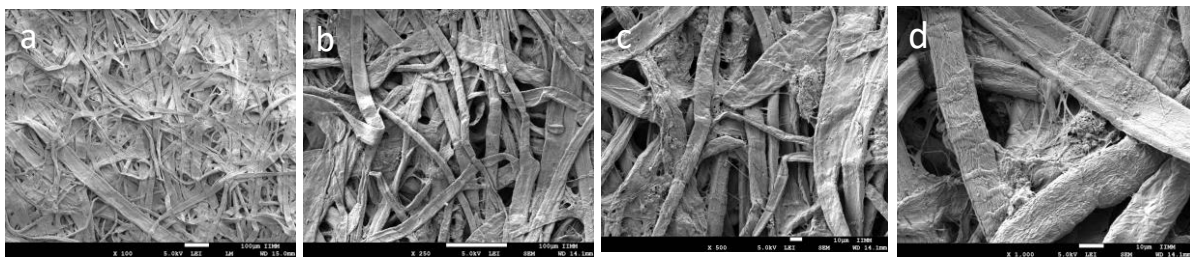


Fig. 5. Micrographs of the paper pulp after deinking, test 5. a) Micrograph at 100X, b) micrograph at 250X, c) Micrograph at 500X, d) Micrograph at 1000X.

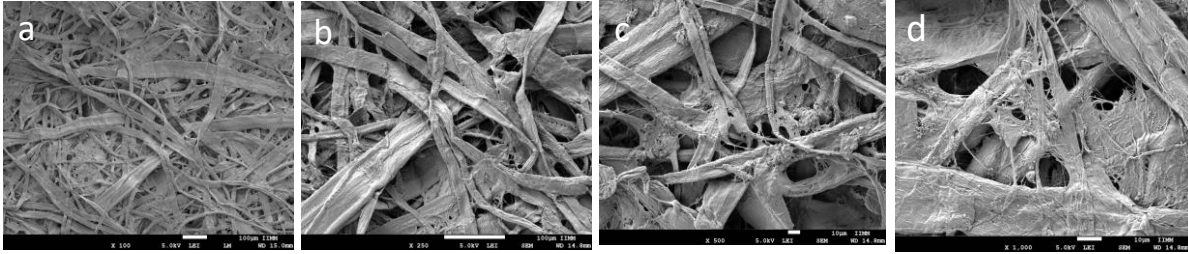


Fig. 6. Micrographs of the paper pulp after deinking, test 7. a) Micrograph at 100X, b) micrograph at 250X, c) Micrograph at 500X, d) Micrograph at 1000X.

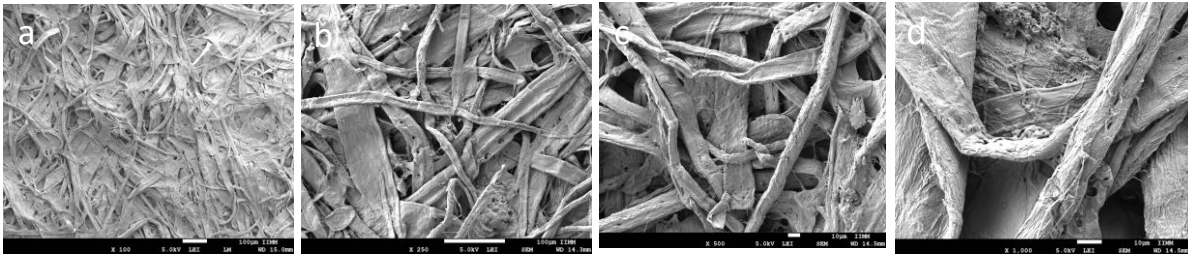


Fig. 7. Micrographs of the paper pulp after deinking, test 8. a) Micrograph at 100X, b) micrograph at 250X, c) Micrograph at 500X, d) Micrograph at 1000X.

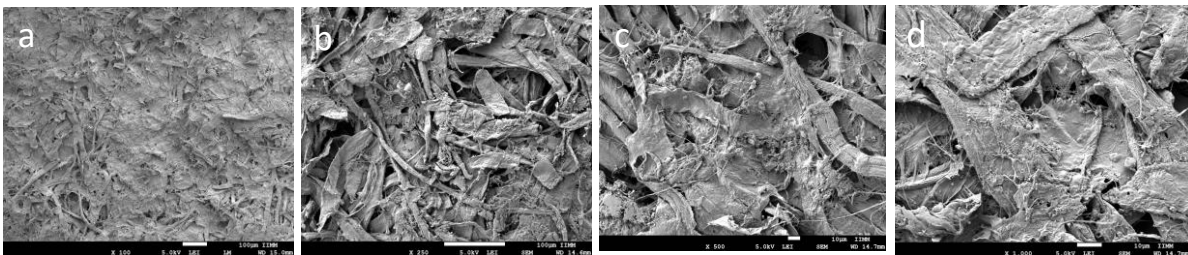


Fig. 8. Micrographs of the paper pulp after deinking, test 9. a) Micrograph at 100X, b) micrograph at 250X, c) Micrograph at 500X, d) Micrograph at 1000X.

## CONCLUSIONS

The product of the mixture of the three amino acids, Aspartate, Glutamate and Asparagine, is useful and affective in the deinking of MOW paper, and it is also respectful with the environment, since only with its reactivity in this process, it achieves results of whiteness, cleanliness, color and shine far superior to those obtained by conventional methods. It should be noted with the importance it deserves, the help of the flotation column so that the process is completed with the efficiency that the results show, since without it and its correct operation, even if the ink particles and impurities that the process requires.

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