The challenges of printed electronics on cellulose - Towards a sustainable approach

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Abstract— More and more electronic waste (e-waste) are emitted worldwide. Most electronic equipment is embedded on a Printed Circuit Board (PCB). The recycling of these electronic cards is complex due to the use of resin and fiberglass which compose their support. Whereas their recycling represents an economic, and environmental benefit. In order to improve the recyclability of these cards, an alternative substrate is proposed: paper. Paper recycling technologies are mature and paper recycling rates are high. Using these recycling technologies in this work it is shown that it is viable to recover 70% of the metal used in simple paper-based electronics designs.

Keywords—recycling, printed electronics, metals, paper

I. INTRODUCTION

From 2010 and 2022, the amount of e-waste worldwide has doubled from 34 Mt to 62 Mt [1]. Over the same period, the rate of e-waste formally identified as collected and recycled has increased from 8 Mt to 13.8 Mt, i.e. from 23.5% and 22.3% of the total e-waste volume [1]. The amount of waste emitted is growing linearly, with a prediction of 82 Mt by 2030, while recycling is not yet able to grow as quickly [1].

Among these wastes are PCBs, which account for 2 to 3% of the total mass of WEEE [2]. On average, PCBs are constituted of a metallic fraction representing 30-35% of the total PCBs mass, 24-30% of resin and 35-42% of refractories [3]. The metals employed are of varying degrees of nobility. The metals present on PCBs are mainly copper (22.3 ± 9.5 %), iron (6.4 ± 10.4 %), aluminum (3.7 ± 3.3 %) and others. In these devices, noble metals such as silver (1171 ppm ± 1570) and gold (991.5 ppm ± 1210.2) could be used [4]. Some studies point that 41 smartphones are necessary to obtain 1 g of gold, giving in this context higher metal concentrations in PCBs than in the ores themselves [2].

The recycling of PCBs is difficult due to the complex nature of the substrates made with resins. In order to improve the recyclability, the main approach is to use recyclable substrate. Paper is a suitable candidate, as it is already employed for printing flexible electronics. Paper is cheap, easily processable, biodegradable and highly recyclable. Paper-based PCBs are developed in the CircEl-Paper European project (https://circelpaper.eu/). The idea is to reach, as far as possible, the characteristics of a conventional PCB while remaining recyclable. As the technologies developed in this project are still on progress, this article focuses on the recycling of a silver antenna printed on an industrial paper roll.

The purpose is to use conventional graphic paper recycling processes and adapt them to the recycling of paper-based electronics. The first stage of recycling involves disintegration in an aqueous medium, followed by separation processes such as screening (separation of elements by size) and centrifugal cleaning (separation of elements by density). Silver and cellulose fibers are tracked at the input and output of each process to ensure reliable mass balances.

II. Materials and methods

II.1. Materials

A. *Printed electronics on paper*

Powercoat XD80® is provided by Fedrioni for printed electronics applications; it is an 80 g/m² paper on which a silver ink is printed by flexography. The silver ink is not printed directly onto the cellulose fiber but on a layer of inorganic fillers. If the ink penetrates the paper, this inevitably reduces the conductive properties of the printed tracks.

B. *Unit operation of conventional paper recycling*

In order to recycle electronics printed on paper, the already known and well-established processes for recycling graphic papers are adapted to the recycling of electronics on paper. The key unit operations are optimized individually with powercoat XD80® unprinted paper. Three major unit operations are optimized (see below). The recycling is carried out at laboratory scale in batch mode.

Disintegration: the first operation consists of separating the various elements constituting the printed electronics in an aqueous medium using a pulper. In this study, the *LAMORT* pulper consists of a helical blade rotating at 45 Hz in a 20-liter capacity tank (Figure 1 A). To promote defibrillation, i.e. the separation of fibers, papermakers often use NaOH at a maximum concentration of 2.5% of the total dry mass. NaOH allows the cellulose fibers to swell, which disrupts the hydrogen interactions between the fibers and decreases the time required to separate them. This operation can be carried out at various fiber concentrations (high concentrations of 8 to 18% and low concentrations below 8%), also known as pulp consistency:

$$Cp = \frac{m_{dry}}{m_{dry} + m_{water}} \times 100$$

Cp: pulp consistency (%)
M_{dry}: dry mass of printed electronic (g)
M_{water}: mass of water during pulping (g)

Mechanical action combined with an aqueous alkaline medium, separates the fibers from each other and favors silver ink detachment from the fibers.

Screening: it is used to separate elements according to their size. Screens with holes or slots of different sizes ranging from 100 µm to 5 mm are used for this purpose (Figure 1 B). All elements larger than the screen dimensions remain on it and are considered as rejects and are therefore removed from the recycling circuit. In our study, the rejects consist essentially of fibrous aggregates that have not been properly pulped during the disintegration. Everything that passes through the screens is considered to be the accepted fraction. Properly individualized fibers and silver inks pass through the aforementioned screens.

The heavy centrifugal cleaner: it separates elements according to their density. In this context, the cleaner separates metal particles from the cellulosic fibers. The pulp suspension is sent tangentially to the wall of the cleaner, creating a vortex (Figure 1 C). The centrifugal force pushes down the particles with a density greater than 1. The cellulosic fibers rise in a vortex that reverses and exits the cleaner. The heavy particles trapped in the apex of the cleaner form the rejects, while the elements (in this case the fibers) leaving the cleaner form the accepts.

II. 2. Methods

A. *Disintegration kinetics of fibrous aggregates*

In order to optimize the first recycling stage (pulping), it is essential to quantify the disintegration kinetics of the paper. To achieve it, the paper is sampled during the pulping process. In order to quantify the rate of fiber defibrillation, the pulp is passed through a 150 µm screen. The fibrous aggregates remain on the screen while individualize fibers pass through it. The fibrous aggregates are then dehydrated and weighed. According to several studies [5], the rate of fibrous flocs in a pulper follows a 1^{st} order kinetics over time:

$$\frac{dF}{dt} = -K_d . F$$

F: Floc index, fraction of fibrous aggregates (%)
t: pulping time (min)
K_d: kinetic constant of disintegration (min^{-1})

By applying a natural logarithm to the rate of fibrous aggregates and a linear regression on the resulting values, it is possible to access the disintegration constant K_d. The higher this constant is, the faster the floc rate is disintegrated in the pulper. This method enables to investigate the effect of variables such as Cp or chemical concentration, on the pulping efficiency.

B. *Tracking and quantification of silver particles*

In each unit operation, the pulp is sampled at input and output in order to track the silver. The sampled pulp is dehydrated and calcined in a furnace at 900°C to concentrate the metallic fraction. The ash obtained is leached using 65% nitric acid. The leached solutions are then analyzed using an atomic absorption spectrometer, which provides ppm-level detection of the Ag^+ ions obtained in the leachates [6].

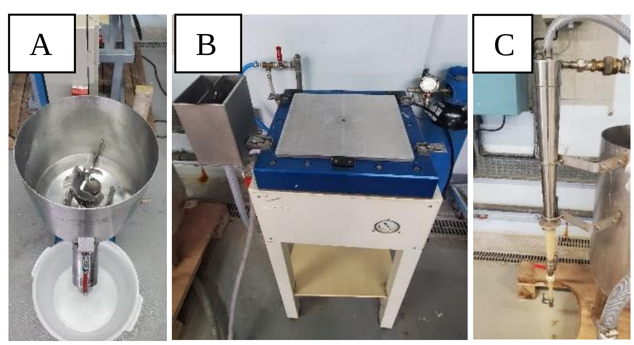

Figure 1: (A) LAMORT laboratory pulper used for high pulp concentration (HC pulper) pulping. (B) Lab screening and (C) Lab centrifugal cleaner.

III. Results

Figure 1 illustrates the pulping kinetics, through the analysis of the floc content, varying the pulp consistency from 8 to 15%. Other parameters such as the NaOH dose (1% w/w), pulping time (10 min) and process water temperature (65°C) are fixed for all trials.

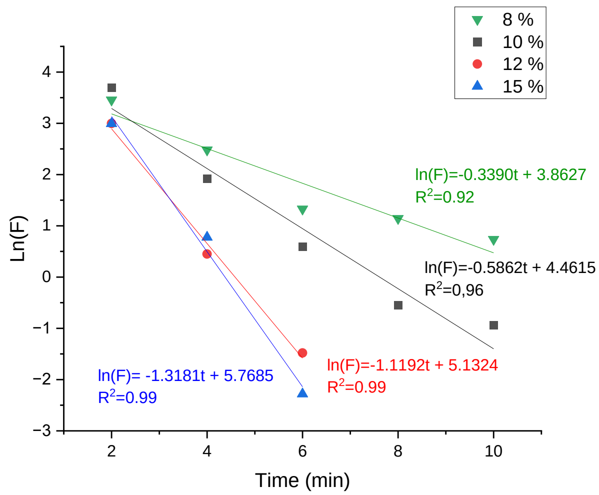

Figure 2: Effect of pulp concentration on the floc content (F) over pulping time

The kinetics constant of disintegration K_d is given by the slope of the linear regression. It can be seen that increasing the pulp concentration from 8 to 10% w/w multiplies the kinetics constant by 1.73. With concentrations of 12 and 15% w/w, the disintegration coefficient is multiplied by 3.30 and 3.9 respectively, but the gain is much limited. 12% w/w pulp concentration seems to be optimal. At laboratory scale, concentration of 12% w/w is more processable than 15% w/w. Indeed, at 15% w/w the pulp is extremely thick, making sampling and handling more difficult.

After 10 minutes pulping in alkaline condition (1% NaOH) and in water at 65°C, no fibrous floc remains in the pulp. This is why there is no need for screening process to remove the fibrous aggregates. The resulting pulp containing the silver inks is then directly processed by the cleaner.

The process conditions of the cleaner have been optimized for the recycling of paper printed electronics, enabling most of the metallic ink particles to be recovered in 10 minutes. To separate the silver particles from the fibers, an equivalent of 50 g of dry pulp is sampled and diluted with water to obtain a total volume of 10 L at a concentration of 0.5% w/w. After operating for 10 minutes in the cleaner, the rejects fraction is recovered, dried and calcined to obtain ashes. Following leaching of the ash, about 70 % of the silver from the process inlet is recovered in the rejects. In a similar experiment, cellulose fibers were monitored. Over 90% of the fibers were recovered in the accept fraction and could therefore be further recycled. Centrifugal cleaning is therefore efficient for separating metal particles on one side and cellulose fibers on the other.

IV. Conclusion

For a simple case study, i.e. the study of the recyclability of RFID tags printed on paper, it was established that it is possible to recover about 70% of the silver ink and over 90% of the cellulose fibers using conventional paper recycling processes. The project current and future work focuses on more complex samples, i.e. impregnated with resins, flame retardants or multi- layered paper. The main challenge is to ensure that this type of device exhibits high-performance and that it can be recycled.

Acknowledgments

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