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Influence of Printing Technique and Printing Conditions on Prints Recycling Efficiency and Effluents Quality

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Abstract: The aim of this work was to determine the influence of the conventional offset printing technique and digital electrophotography printing with liquid toner (LEP) on some optical properties of recycled fibres. A series of LEP prints was made with the variation of the negative voltage of the developing drum (−200 V, −280 V, −350 V, and −430 V) after calibration of the machine and achieving standard densitometry values. Besides deinkability aspects, the quality of wastewater effluents after process of prints recycling was observed in order to make a conclusion regarding how different printing techniques, conditions in printing process, and different types of inks can affect the wastewater effluents. Results of image analysis showed that by increasing the negative voltage of developing drum in LEP printing technique, the formation of large ink particles on handsheet from recycled pulp increases. Depending on the size of the negative voltage of the developing drum, under the same experimental conditions, handsheets made from LEP recycled fibres have lower whiteness gain, brightness gain, and ΔERIC of handsheets compared to those made from the offset prints. In addition, a certain correlation was found between IE_{ERIC} (ink elimination), chemical oxygen demand (COD), and total organic carbon (TOC) of wastewater effluents after recycling of LEP prints and offset prints as well. Organic water pollution parameters (COD and TOC) showed higher values in wastewater after recycling of offset prints compared to recycling of LEP prints.

Keywords: paper recycling; LEP technology; developing drum; offset printing; optical properties; wastewater

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1. Introduction

Sustainability approach includes energy and material flows, closed loop systems, cleaner technologies and waste reduction, and economic and social factors. One of the key factors is movement towards development of sustainable products, which are defined by their lifecycles and which will, in the end, have a competitive advantages in the market [1]. European laws have proposed different strategies for the reduction of all kinds of produced waste streams, but generally waste prevention has the highest priority [2]. However, for the produced waste streams, current waste management strategies are shifting from waste disposal to recycling, reusing, and recovering.

The printing industry consumes various amounts of raw materials resulting in generation of different types of wastes. Thus, the printing industry can be classified as a diffuse and permanent polluter, while the produced wastes are classified as solid, liquid, and gaseous wastes [3]. Waste streams from the offset printing, as the most common printing process, mainly originate from the used raw materials (printing substrates, inks, fountain solutions, metal printing plates, solvents, biocides, varnishes, and energy) [3–5].

The digital printing process contributes to sustainable development since, in comparison to conventional offset printing technique, it has lower environmental impact due to its ability to be ready faster along with the absence of printing plates making, cleanliness, competitiveness, and its related chemicals, materials, emissions, and wastes [3]. Kadam, Evans, and Rothenberg (2005) in their research showed that digital printing process generates less waste compared to offset [6]. Digital process generates 5–20% per impression of paper waste and 0.2–1.1 g per impression of chemical waste, while sheet-fed offset process produces 35–75% paper waste and 3.2–7.3% chemical waste per impression [6]. When designing a new sustainable graphic product, innovative sustainable solutions should be sought in the field of printing substrates, inks, printing process, and post-press finishing process as well as in the waste recycling and recovering options [4].

Most of the waste graphic products, like paper and board, still tend to be disposed by means of classic paper recycling process for the production of recycled paper and board [7]. Different authors have shown that different factors in printing process (printing inks, different printing processes and conditions in printing, paper substrates) can have a great impact on the paper recycling process [4,8–11]. Thus, it is crucial to optimize those factors in order to produce an adequate printed product with its acceptable end-of-life solution [4,12]. Profitable conversion of recovered paper into quality recycled products requires an effective process for removal of ink particles, which can be strongly influenced by used deinking methods and chemicals [7,13–15]. The chemical flotation deinking process is common practice for removal of ink from recovered paper. The method uses chemicals and air to form bubbles, which can collect and carry away ink particles in the reject stream. A successful flotation consists of few steps: the detachment of ink particles from the hydrophilic cellulose fibres in alkaline solution, adhesion of hydrophobic ink particles onto air bubble surfaces, and the removal of flotation froth containing ink particles from the flotation cell [16]. Usage of chemicals (surfactants and soaps) can improve ink detachment and the agglomeration of unfloatable ink particles [17]. In addition, recent studies have shown that recycling repetition may have a positive effect on deinkability efficiency [11,13,18]. Bajpai states that the tonne of recycled paper that displaces a tonne of virgin fibre compared to a tonne of recycled paper results in reduction of wood for 100%, wastewater for 33%, energy consumption for 27%, air particulate emissions for 28%, and solid waste for 54% [19]. Sometimes, recycling of recovered paper has some negative environmental impacts; for example, the quality of recycled paper is far poorer than the quality of paper made from virgin pulps due to short length and reduced tensile strength of fibres [10,20]. Additionally, the recycled paper sometimes may contain residues (toxic substances) mainly originating from printing inks, which are undesirable for health and safety reasons [21–26]. This problem occurs when the printing inks are not entirely removed during paper recycling [22]. For example, printing inks may contain heavy metals (copper, lead, zinc, chromium, and cadmium) and solvents [23]. Furthermore, paper recycling process produces a sludge that contains short fibres, fillers, inks from the deinking process, and extractive substances and deinking additives [27].

Besides sludge, the wastewater effluents are generated as well. The characteristics of the wastewater generated from various processes of recycled paper industry depends upon the processes types, management practices, raw materials, applied process technology, deinking chemicals, recirculation of the effluents for recovery, and amount of water used in a particular process [28,29]. Moussavi and Aghanejad (2017) showed that real wastewater effluent obtained from a paper recycling plant has high biochemical oxygen demand (BOD_5) (535 mg/L) and chemical oxygen demand (COD) (4300 mg/L) values and very low biodegradability potential (BOD_5/COD = 0.12), indicating that the wastewater was composed mainly of recalcitrant organic compounds [30]. In a research by Birjandi et al. (2014), high BOD (870–974 mg/L) and COD (3348–3765 mg/L) values for paper-recycling wastewater were detected as well [31]. Lee and co-authors showed that enzymatic and chemical deinking not only influence the optical and mechanical properties of deinked paper but also influence the wastewater effluent quality [32]. COD analysis indicated that effluent produced from enzymatic deinking were about 33.9% and 33.8% lower compared to chemical deinking of old newspaper and mixed office wastepaper, respectively [32].

The aim of this work was to determine the influence of the conventional offset printing technique and digital electrophotography printing with liquid toner on the optical properties of recycled fibres. Besides the deinkability aspects, the characterization of wastewater effluents after process of prints recycling was observed in order to make a conclusion regarding how different printing techniques and conditions in the printing process can affect the quality of effluent.

2. Materials and Methods

2.1. Materials

The printing substrate used in this study was coated art paper (marked as P) (Fedrigoni Paper mill). The characteristics of the used paper are presented in the Table 1.

Table 1. Properties of the used printing substrate.

Paper	Basis Weight, g/m^2 (ISO 536)	Thickness, mm (ISO 534)	Brightness, % (ISO 2470)	Roughness, mL/min (ISO 8791-2)
P	115	0.99	99	77

The used paper is an environmentally friendly ECF paper with a high content of recycled material. Paper substrate was printed with two printing techniques: digital and offset. Offset prints were made on the KBA (Koenig & Bauer) Rapida sheetfed, four colour offset printing press (series O). Some of the features of an offset press are automated plate change, automatic inline colour control, control based on grey balance, very low emissions, and reduced waste. The printing form contained different printing elements: a standard CMYK step wedge in the 10–100% tone value range, a standard ISO illustration for visual control, textual positive and negative microelements, wedges for determining greyness, and the standard wedge with 378 patches for the production of ICC profiles and a 3D gamut. In offset printing, the printing plate that carries the printing elements and free surfaces is placed on the base cylinder. Hydrophilic free surface of the printing plate accepts the wetting liquid, while the printing elements of the printing plate are oleophilic, so they accept the ink due to characteristics of the binder, which is chemically composed of oils and resins. For the printing, metal printing plates, one for each colour, were used in the printing process. Production speed was 10,000 sheets/h.

Digital prints were made on HP (Hewlett Packard) Indigo TurboStream machine based on indirect electrography with liquid toner ElectroInk (series LEP), with a resolution of 800 dpi. The printing speed was 2000 A4 sheets/h. The printing process includes following stages: Photo Imaging Plate (PIP) charging, laser imaging-PIP charging, laser imaging-PIP exposure, Binary Ink Developer (BID) units, image transfer from PIP units to blanket, ink transfer from blanket to the media, and PIP cleaning. This machine was chosen because it enabled the calibration of the machine for standard conditions and then the printing of the printing form with correction of the developing drum. The printing form contained different printing elements: a standard CMYK step wedge in the 10–100% tone value range, a standard ISO illustration for visual control, textual positive and negative microelements, wedges for determining greyness and the standard wedge with 378 patches for the production of ICC profiles, and a 3D gamut. After the calibration of the HP Indigo machine, the process of printing followed, with the correction of the voltage of the developing drum as follows: −200 V, −280 V, −350 V, and −430 V (prints marked as: LEP_{-200V}, LEP_{-280V}, LEP_{-350V}, LEP_{-430V}). During the experiment, only one parameter in the printing process was varied, while all other parameters remained constant as defined by the initial calibration of the printing machine.

Two series of offset prints were prepared with two different ink composition, i.e., from vegetable-based inks free of mineral oils (marked as I_VO) and from mineral oil-based inks (marked as I_MO). Inks that were used are available as a four-process colour offset ink set, produced by Sun Chemical® Europe.

2.2. Methods

2.2.1. Flotation Deinking

For the recycling of prints, alkaline chemical deinking flotation was used according to Figure 1. All chemicals (sodium hydroxide 1%, hydrogen peroxide 1%, sodium silicate 2%, DTPA 0.2%, and surface-active substance 0.4%) were added in the disintegration stage of the process. Pulp was disintegrated using Enrico Toniolo disintegrator. As the pulp was disintegrated and converted into pulp suspension, in order to achieve satisfied consistency, it was diluted. After homogenisation, a part of pulp suspension was taken out from the process in order to make undeinked pulp handsheets (marked UP). Remained pulp suspension was transferred to laboratory flotation cell. During flotation process, flotation froth (foam), which contained different ink particles and other impurities, was collected and removed from pulp suspension. Residual pulp was used for the production of deinked pulp handsheets (marked as DP). Laboratory paper handsheets (UP and DP) were made with the use of standard sheet former Rapid–Köthen (PTS), according to standard method ISO 5269-2:2004 [33].

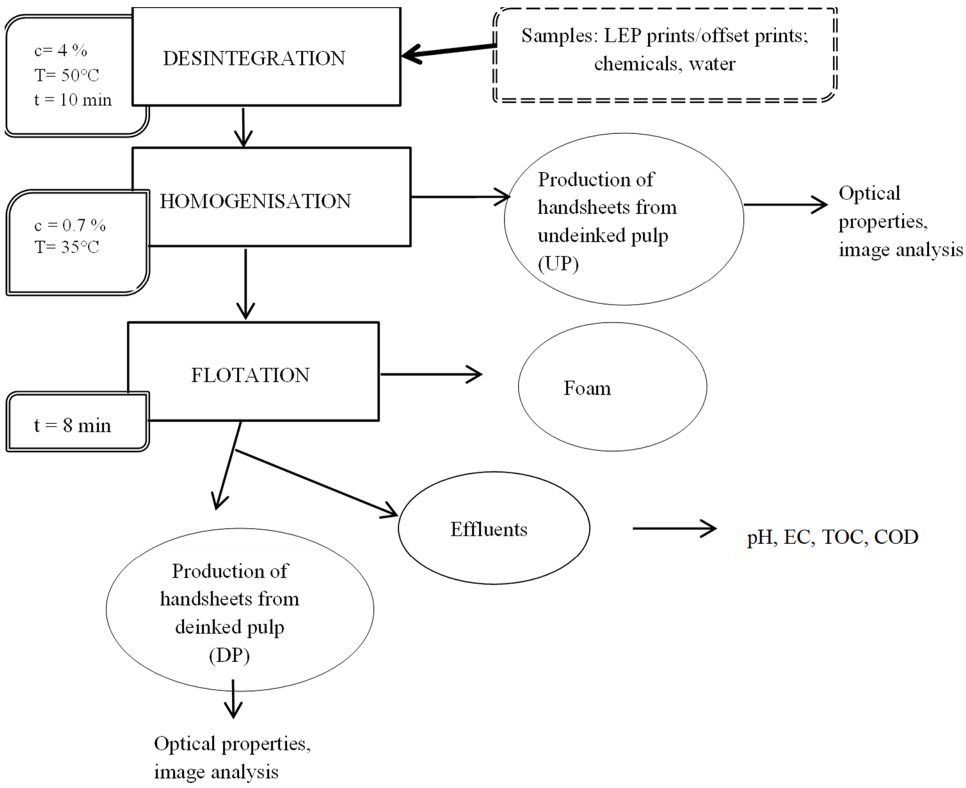

Figure 1. Schematic view of samples recycling process.

2.2.2. Determination of Optical Properties

Obtained laboratory paper handsheets (UP and DP) were examined for their optical properties. They were analysed using spectrophotometer Technidyne Color Touch 2 in the terms of CIE whiteness, ISO brightness, ISO opacity, and ERIC according to standard methods [34–37].

From the obtained ERIC values, ink elimination (IE_{ERIC}) was determined according to the Equation (1).

$$IE_{ERIC}\ ,\ \% = \frac{ERIC_{UP} - ERIC_{DP}}{ERIC_{UP}} \times 100 \quad (1)$$

where:

$ERIC_{UP}$-obtained ERIC value was observed on undeinked laboratory paper (UP) handsheets (ppm);

$ERIC_{DP}$-obtained ERIC value was observed on deinked laboratory paper (DP) handsheets (ppm).

2.2.3. Image Analysis

To determine the total number of ink particles and their area, image analysis was performed using Apogee SpecScan® software. The software uses a statistical method to quantify differences by analysing the frequency distribution of the grayscale value of each pixel in the image in accordance with standard method [38]. Handsheets were scanned under a resolution of 600 dots/inch. Measurements were performed on 3-inch square area of laboratory handsheets surface to detect particle size distribution in range from 0.001 to 5.00 mm^2. The samples were measured 5 times, and the results were shown as mean value. For the purpose of visual evaluation, 3-inch square area of laboratory handsheets were scanned under a resolution of 600 dots/inch, and scanned images were presented.

2.2.4. Analysis of Effluents

Effluents generated in laboratory paper recycling process were collected after flotation process in order to determine their physical-chemical characteristics. The effluent samples were collected from pulp suspension, filtrated through Büchner funnel in order to remove residual pulp, and analysed in terms of the pH, electrical conductivity (EC), total organic carbon (TOC), and chemical oxygen demand (COD) values. pH and EC values were determinate by WTW Multi 9310 (InoLab_IDS), while HACH DRB 200 Reactor Block and HACH DR/890 Colorimeter were used for TOC and COD concentration measurements.

3. Results and Discussion

The process of deinkability evaluation includes the ink detachment from the fibres and removal of the ink from the system. The influence of the printing conditions (negative voltage of developing drum) in indirect electrophotography with liquid toner (LEP) in prints recycling on the total number of ink particles and their area on laboratory paper handsheets from deinked pulp is presented in Figure 2.

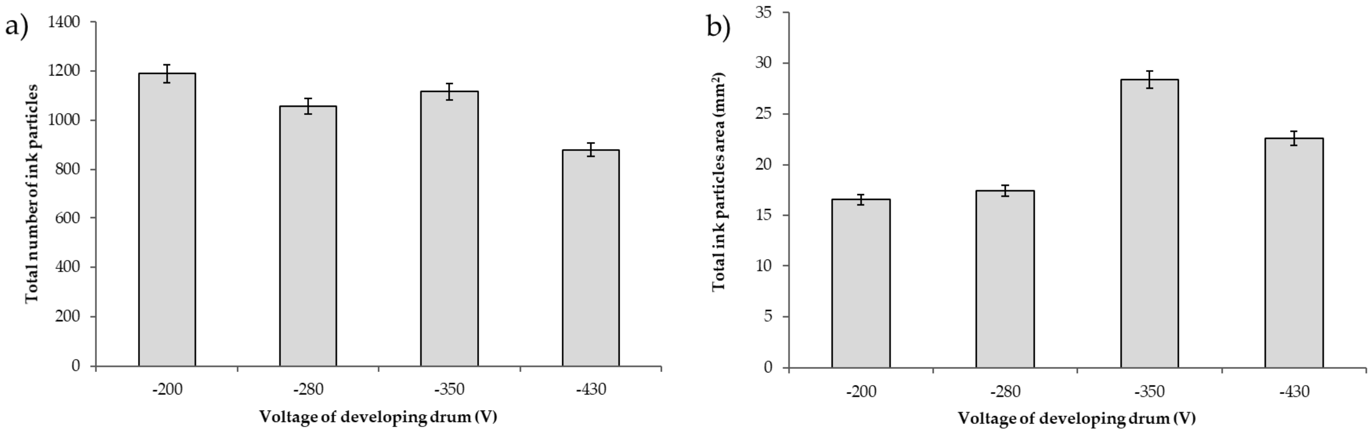

Figure 2. Total number of ink particles (**a**) and their area (**b**) on handsheets from deinked pulp versus voltage of developing drum in the process of LEP prints recycling.

From the obtained results, it can be seen that by increasing the negative voltage of the developing drum, a decrease of the total number of ink particles occurs as follows: $N_{-200V}/N_{-280V} = -11.26\%$, $N_{-200V}/N_{-350V} = -6.14\%$, and $N_{-200V}/N_{-430V} = -26.06\%$. On the other hand, the dependence of the ink particles area upon the change in voltage shows an inverse trend (Figure 2). Thus, by increasing the negative voltage of the developing drum, the increase in the total surface area of the ink particles is determined as follows: $A_{-200V}/A_{-280V} = 5.47\%$, $A_{-200V}/A_{-350V} = 44.89\%$, and $A_{-200V}/A_{-430V} = 18.41\%$.

Given that a decrease in the total number of ink particles by the increase of negative voltage of developing drum is accompanied by an increase in the surface area of ink particles, it can be assumed that during deinking flotation, the removal of larger ink particles in not efficient; thus, they remain in the pulp suspension. The high temperature in the printing process results in polymerization of ink during printing, which causes the formation of large particles during pulp disintegration. This behaviour, i.e., the formation of larger ink particles and their retention in deinked pulp suspension, can also be visible from the results of the total surface area of ink particles smaller than 0.04 mm^2 (<0.04 mm^2) and ink particles larger than 0.04 mm^2 (>0.04 mm^2) with respect to the voltage of the developing drum, which is presented in Figure 3.

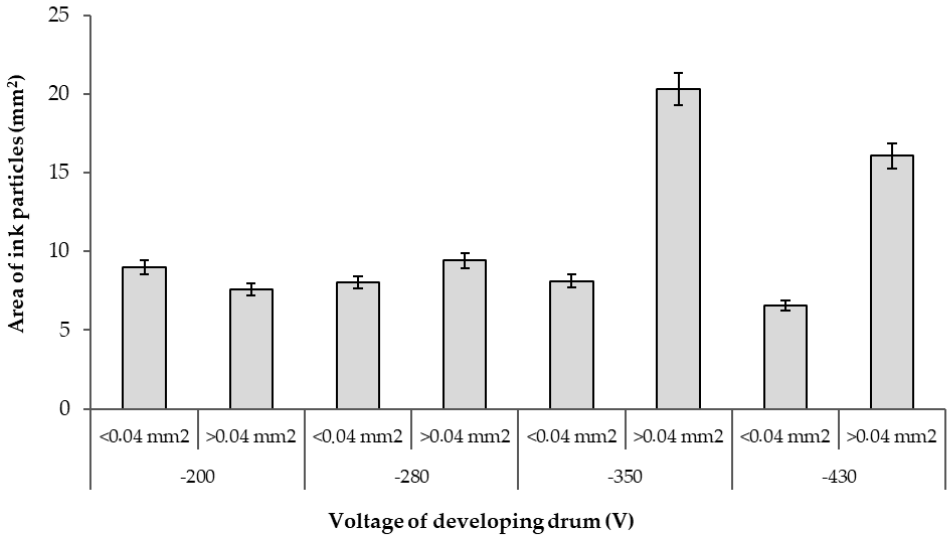

Figure 3. Area of ink particles <0.04 mm^2 and >0.04 mm^2 on laboratory handsheets made from deinked pulp versus voltage of developing drum in the LEP prints recycling process.

The results of the study show that an increase in the negative voltage of the developing drum does not significantly affect the area of ink particles <0.04 mm^2 on the laboratory handsheets obtained from deinked pulp. Only a slight decrease of surface area was observed for the samples printed at −280 V and at −350 V in relation to the sample printed at −200 V ($A_{-200V, <0{\cdot}04\ mm}{}^2/A_{-280V, <0{\cdot}04\ mm}{}^2$ = −10.76%, $A_{-200V, <0{\cdot}04\ mm}{}^2/A_{-350V, <0{\cdot}04\ mm}{}^2$ = 9.77%), while the highest difference was observed for sample printed at −430 V ($A_{-200V, <0{\cdot}04\ mm}{}^2/A_{-430V, <0{\cdot}04\ mm}{}^2$ = −27.26%). Additionally, the area of ink particles >0.04 mm^2 on the DP laboratory handsheets by an increase of the negative voltage of developing drum increases for the samples printed at −280 V, −280 V, and at −430 V in relation to the sample printed at −200 V, as follows: ($A_{-200V, >0{\cdot}04\ mm}{}^2/A_{-280V, >0{\cdot}04\ mm}{}^2$ = 4.71%, $A_{-200V, >0{\cdot}04\ mm}{}^2/A_{-350V, >0{\cdot}04\ mm}{}^2$ = 125.74%, $A_{-200V, >0{\cdot}04\ mm}{}^2/A_{-430V, >0{\cdot}04\ mm}{}^2$ = −78.62%) (Figure 3).

The formation of larger particles by an increase of the voltage of developing drum can also be seen from the ratio of area of ink particles >0.04 mm^2/<0.04 mm^2 on the DP handsheets. Results show that the ratio of area of ink particles >0.04 mm^2/<0.04 mm^2 is the highest for the prints obtained at −350 V and −430 V ($A_{-200V, >0{\cdot}04\ mm}{}^2/A_{-200V, <0{\cdot}04\ mm}{}^2$ = −18.65%, $A_{-280V, >0{\cdot}04\ mm}{}^2/A_{-280V, <0{\cdot}04\ mm}{}^2$ = 14.76%, $A_{-350V, >0{\cdot}04\ mm}{}^2/A_{-350V, <0{\cdot}04\ mm}{}^2$ = 60.03%, and $A_{-430V, >0{\cdot}04\ mm}{}^2/A_{-430V, <0{\cdot}04\ mm}{}^2$ = 59.28%).

The most common issues related to deinkability are generally related to extensive ink fragmentation, poor hydrophobic character of the ink, and bad ink detachment, which is dependent upon the type of the ink. Another factor affecting deinkability is the printing technique and the printing conditions as well as the used paper and its surface. In this study, a fixed parameter was the printing substrate, while variable parameters were inks, printing techniques, and printing conditions, as shown in Table 2.

Table 2. Total ink particles number and their area on laboratory handsheets from deinked pulp versus type of inks, printing techniques, and conditions.

Samples		Total Ink Particles Number	Total Ink Particles Area (mm^2)
electrophotography	LEP_{-200V}	1190	16.580
	LEP_{-280V}	1056	17.451
	LEP_{-350V}	1117	28.428
	LEP_{-430V}	880	22.614
offset	I_VO	847	4.674
	I_MO	803	3.536

From the results presented in Table 2, it can be seen that by recycling of LEP prints the higher number of ink particles and their area at handsheets from DP pulp are observed compared to those made by offset printing. Moreover, differences between ink formulation, in the case of offset prints, and their influence on prints recycling can be noticed as well. By the recycling of offset prints made from the mineral based ink, the smallest number of ink particles was obtained on the handsheets made from deinked pulp.

The results obtained by deinking flotation of LEP prints can be explained by the position of the developing drum with the photoconductor in the printing press and its function. Due to the opposite rotation, the developing drum does not touch the surface of the photoconductor, and there is a gap between in which the ElectroInk is injected. During printing, a negative voltage is formed on the developing drum, which establishes an electrostatic field with the photoconductor. In order to accept the dye, the virtual printing elements need to be more electrically positive than the developer drum. As the voltage of the developing drum increases, the power of the electrostatic field will increase, resulting in an increase of ElectroInk deposition on the printing element. Thus, the thickness of ElectroInk's deposition on the print depends on the variation of the developing drum voltage, which as an ink formulation in general, can affect its detachment and deinkability. However, it should be emphasized here that the surface of the paper used in printing is one of the significant factors that additionally may affect the ink detachment ability.

The ink particles generated during recycling of ElectroInk prints are large, flexible, and thin, and their surface area increases with the increase of negative charge of the developing drum (Figure 4). The reason for this has already been stated, but it should be noted that LEP ink in formulation contain polymers, which are consequently the potential source of primary stickies.

Figure 4. Visual evaluation of laboratory handsheets made from deinked pulp versus voltage of developing drum in the LEP prints recycling process.

Offset prints with the same recycling and experimental conditions have been found to have better deinkability than LEP prints in dependence of the voltage of the developing drum. In the process of deinking flotation, the differences between sizes, shape, and surface properties of ElectroInk and offset inks particles were determined, which is evident through the presented results (Figures 4 and 5).

I_MO **I_VO**

Figure 5. Visual evaluation of laboratory handsheets made from deinked pulp in the offset recycling process.

During ink drying and ageing, the ink is subjected to oxido-polymerisation reactions and formations of crosslinks that improve the cohesiveness of the ink particles as well as the bond strength between the ink particles and the printing substrate [39]. Sheet-fed offset inks contain in their formulation oxidizing components, which leads to ink detachment problems. Oxidation of mineral oil ink could take up to 4–6 months, while oxidation of vegetable oils is much faster due to its organic structure. By oxidation, the vegetable-oil-based inks results in formation of carbonyl groups (C=O) and hydroxyl groups (–OH), which leads to cross-linking and cleavage of fatty acids [39]. Besides unsaturated vegetable oils, resins can induce strong oxidation as well. The correct selection of the ink components can slow down the oxidation mechanism. Ink detachment from fibres becomes easier when paper is coated. In lightweight coated paper, the ink is fixed onto coating particles (mineral filler) and is not easily removed, resulting in poor detachment. Mineral fillers would be more or less grey and would result in lower brightness [40,41].

Besides image analysis, deinkability aspects of prints can be evaluated by examination of optical properties and effectiveness of ink removal as well (Tables 3 and 4).

Table 3. Optical properties of undeinked and deinked laboratory handsheets made from LEP technology prints recycling process as the function of voltage changes of the developing drum.

Property		**Voltage of Developing Drum (V)**			
		−200	**−280**	**−350**	**−430**
CIE Whiteness, %	UP	96.88	101.49	95.71	99.79
	DP	100.20	101.71	98.35	102.97
ISO Brightness, %	UP	77.82	79.48	78.07	80.14
	DP	78.67	79.82	78.45	81.01
ERIC, ppm	UP	73.55	66.45	72.62	71.02
	DP	67.93	65.13	69.59	68.69
IE_{ERIC}, %		7.64	1.99	4.17	3.28
Opacity, %	UP	84.50	81.53	78.07	82.38
	DP	80.09	81.64	80.86	81.76

Table 4. Optical properties of undeinked and deinked laboratory handsheets made from offset technology prints.

Property		I_VO	I_MO
CIE Whiteness, %	UP	86.30	84.84
	DP	92.89	90.57
ISO Brightness, %	UP	69.12	68.53
	DP	78.71	77.52
ERIC, ppm	UP	103.95	91.89
	DP	57.92	52.35
IE_{ERIC}, %		44.28	43.03
Opacity, %	UP	82.93	81.21
	DP	78.45	77.93

The efficiency of the deinking process is further evaluated through whiteness and brightness gain (whiteness gain ΔW = differences of whiteness DP and whiteness UP; brightness gain ΔB = differences of brightness DP and brightness UP).

The CIE measure of whiteness is a measurement of the light reflected by the paper across the visible spectrum. From the results presented in Table 3, it can be concluded that whiteness gain is 3.32 points in the case of LEP_{-200V}, 0.78 points in the case of LEP_{-280V}, 2.64 points for LEP_{-350V}, and 3.18 points for the LEP_{-430V}. Residual constituents influence the whiteness gain of the laboratory handsheets; however, it does not show a pronounced trend depending on the increase of the negative voltage of the developing drum. The general property of the UP and DP laboratory handsheets obtained from recycling of offset prints is a slightly lower absolute CIE whiteness value compared to LEP prints as well as higher whiteness gain (W I_VO $_{DP}$ 92.89–W I_VO $_{UP}$ 86.30 = 6.59, I_MO– $_{DP}$ 90.57–W I_MO $_{UP}$ = 5.73).

ISO brightness is defined as paper reflectivity on light wavelength at 457 nm in blue region with d/0 geometry. It is known that the difference in reflectance on handsheets from recycled fibres and handsheets made from virgin fibres as measured in the brightness region is very small in comparison with reflectance changes at higher wavelengths [42]. A similar trend of brightness was found on handsheets made from deinked pulp versus voltage of developing drum compared to particle size on handsheets (Table 3). The expected ratio was achieved since by the decrease of the particles with the surface area < 0.04 mm^2, an increase of handsheets brightness occurs. Brightness gain of handsheets obtained by recycling of the offset prints is higher than those obtained by processing of the LEP prints (ΔB $_{LEP\ -200V}$ = 0.85; ΔB $_{LEP\ -280V}$ = 0.34; ΔB $_{LEP\ -350V}$ = 0.38; ΔB $_{LEP\ -430V}$ = 0.87; ΔB I_VO = 9.59; ΔB I_MO = 9.00) (Table 3). Brightness gain of the handsheets obtained by recycling of the offset prints is much higher than those obtained by processing of the LEP prints, while the impact of different offset inks composition on brightness gain has no significant effect. Brightness differences after pulping provide information about the ink fragmentation. This value closely relates to visually observed CIE whiteness.

Efficient way of quantifying residual ink is by the measurement of light absorption in the near infrared spectrum as an effective residual ink concentration (ERIC), which is a measure of deinking efficiency. The measurements in this spectral area are relatively free of the influences of lignin, chromophores, and bleaching [43]. UP laboratory handsheets obtained from the recycling of the LEP prints have lower ERIC values versus UP handsheets obtained from recycling of the offset prints (Table 4) ($ERIC_{LEP-200V}$ = 73.55 ppm; $ERIC_{LEP-280V}$ = 66.45 ppm; $ERIC_{LEP-350V}$ = 72.62 ppm; $ERIC_{LEP-430V}$ = 71.02 ppm; $ERIC_{LEP-200V}$ = 73.55; $ERIC_{LEP-200V}$ = 73.55 ppm; ERICI$_V$O = 103.95 ppm; ERICI$_M$O = 91.89 ppm). The obtained results can be explained by the fact that if the residual ink particles are large, accumulated in the form of agglomerates, the handsheets reflection is small, and the ERIC values are lower. Such handsheets then appear brighter or lighter compared to those where the remaining particles are smaller and uniformly dispersed. Uniform dispersion of ink particles without greater optical inhomogeneity makes the handsheet darker, and consequently, ERIC has higher values. These results are confirmed by some literature data [44].

Laboratory handsheets obtained from the recycling of the offset prints have higher ΔERIC values than those obtained by processing of LEP prints ($\Delta ERICI_VO$ = 46.03; $\Delta ERICI_MO$ = 39.54 $\Delta ERIC_{LEP-200V}$ = 5.62; $\Delta ERIC_{LEP-280V}$ = 1.32; $\Delta ERIC_{LEP-350V}$ = 3.03; $\Delta ERIC_{LEP-430V}$ = 2.33), which is in accordance with number, area, and shape of the ink particle on handsheet. Laboratory handsheets obtained from the recycling of the LEP prints have lower the ink elimination IE_{ERIC}% values versus handsheets obtained from offset prints, as follows: $IE_{ERIC\ LEP\ -200V}$ = 7.64%; $IE_{ERIC\ LEP\ -280V}$ = 1.99%; $IE_{ERIC\ LEP\ -350V}$ = 4.17%; $IE_{ERIC\ LEP\ -430V}$ = 3.28%; IE_{ERIC} I_VO = 44.28%; IE_{ERIC} I_MO = 43.03%.

The best process efficiency was obtained by recycling under the described experimental conditions of samples LEP_{200V} (ΔW = 3.32; ΔB = 0.85; IE_{ERIC} = 7.64), while the smallest differences were obtained for the sample LEP_{280} (ΔW = 0.22; ΔB = 0.34; IE_{ERIC} = 1.99).

Slightly better optical properties of handsheets were obtained from recycled offset prints based on innovative inks from renewable raw materials of natural origin (ΔW I_VO = 6.59; ΔB I_VO = 9.59; IE_{ERIC} I_VO = 44.28) compared to those obtained by recycled offset prints based on raw materials of petrochemical origin (ΔWI_MO = 5.73; ΔB I_MO = 8.99; IE_{ERIC} I_MO = 43.03).

The ERIC measurement in recycled paper depends on the paper's opacity. The type of fibres, the degree of whiteness, the presence of dyes, fillers, and coatings influence the opacity of the paper. Opacity is the most important property of all printing papers. Handsheets made from UP pulp of LEP−200V have the highest opacity value (84.50%), while the lowest opacity value was obtained for the laboratory handsheet of LEP−350 V (78.07%) sample (Table 3). UP laboratory handsheets obtained from the recycling of the offset prints have higher opacity values (opacity $_{IvO}$ = 82.93%; opacity $_{IMO}$ = 81.21%) than those obtained from DP handsheets (opacity $_{IvO}$ = 82.93%; opacity $_{IMO}$ = 81.21%).

During deinking flotation, besides ink removal, the loss of fibres and fillers occur. Due to loss of fillers, the obtained DP laboratory handsheets show lower values of opacity after deinking process. It was found that undeinked laboratory handsheets do not have a uniform trend in opacity values; however, all values are smaller than 97%. For an opacity value less than 97%, the ERIC measurement is based on the Kubelka–Munk theory to diffuse reflection from paper.

The influence of negative voltage of the developing drum in indirect electrophotography with liquid toner on wastewater quality after paper recycling process is presented in Figure 6. The effluent characteristics studied in this research can be related to recycling efficiency. As the presented results show (Figure 6), COD and TOC values follow the ERIC removal (IE_{ERIC}) pattern.

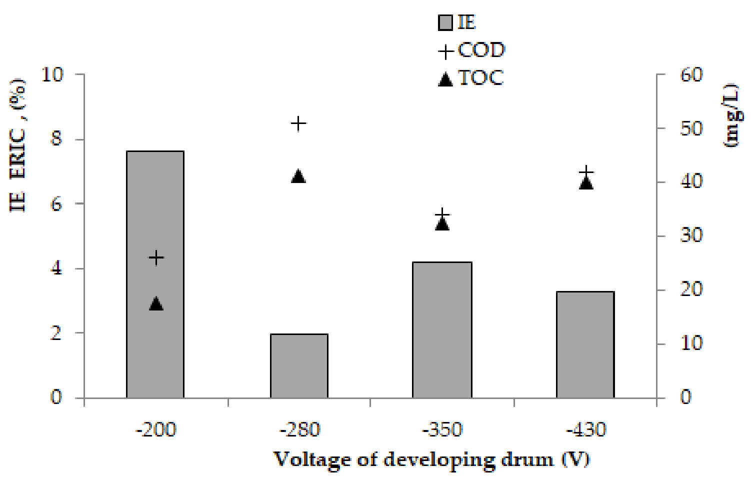

Figure 6. COD and TOC values of wastewater generated by LEP technology prints recycling as the function of voltage changes of the developing drum and ink elimination.

As the ERIC removal (IE_{ERIC}) is higher, the concentrations of chemical oxygen demand (COD) and total organic carbon (TOC) are lower. COD concentrations show higher values than TOC (Figure 6). This correlation result leads to a conclusion that an organic pollution of wastewater effluent generated during recycling process is mostly influenced by very small ink particles, which cannot be removed by froth flotation. Low values of COD and TOC show high biodegradability potential of wastewater generated during LEP technology prints obtained by different negative voltage changes of developing drum.

For the effluents generated during offset prints recycling, COD and TOC values were higher than those observed for the effluents from LEP prints recycling (Table 5, Figure 6). Moreover, the values can be explained by the difference in printing ink formulation between ElectroInk and conventional offset inks, by the ElectroInk technology, and the ink drying process as well. The process of ink drying affects the binding of organic matter in the ink and consequently the release of organic matter into the aqueous solution during paper recycling process. The offset printing ink based on the vegetable oil dries by the oxido-polymerization process, while mineral oil-based offset ink dries by penetration into the paper structure without polymerization. If the polymerization is present, the release of organic matter is lower. Consequently, the values of COD and TOC of wastewater from LEP technology prints are lower than those obtained from recycling of offset prints.

Table 5. COD and TOC values of wastewater generated by offset technology prints recycling.

Sample	COD (mg/L)	TOC (mg/L)
I_MO	141.5	148.0
I_VO	134.8	142.5

After recycling the offset prints with a vegetable oil-based printing ink, wastewater has COD values 6.5 points lower compared to those obtained after recycling of prints made by mineral oil-based ink (Table 5). A similar result is noticed for the TOC values of effluents obtained after recycling, as a result of the offset ink composition (for 7.7 smaller TOC values for the effluents generated after recycling of vegetable oil-based inks compared to those obtained after recycling of prints made by mineral based inks). Moreover, in this case as well, the previously mentioned behavior is noticed that, at higher ERIC removal (IE_{ERIC}), the concentrations of COD and TOC are lower. The ratio of TOC and COD is a function of the oxidation state of the carbon in the compound.

Obtained pH values show neutral wastewater stream for the effluents generated during LEP prints recycling process (Table 6). Results of the pH for the effluents generated during vegetable-based offset prints recycling show slightly lower pH, while for the mineral oil based offset prints, the pH of the effluents is slightly alkaline. The analysis and control of wastewater pH is an important factor when it is necessary to apply wastewater purification treatment. The resulting pH value would be useful when using biological or chemical wastewater treatment, but that is not an objective of this study.

Table 6. pH and conductivity values of wastewater generated by offset technology and LEP prints recycling as the function of voltage changes of the developing drum.

Sample	pH	Conductivity (µS/cm)
LEP_{-200V}	7.144	801
LEP_{-280V}	7.296	797
LEP_{-350V}	7.520	816
$LEVP_{-430V}$	7.100	836
I_VO	6.681	675
I_MO	8.400	770

Conductivity has more or less the same value for the effluents generated during recycling of samples printed by LEP technology. The effluents generated during recycling of the offset prints have slightly lower conductivity than those obtained by LEP technology and the developing drum variation (Table 6). Higher values of conductivity of wastewater from the recycling of LEP prints indicate that during recycling, a part of the conductivity agent present in the ElectroInk formulation is released into the aqueous solution. From the obtained results, it can be concluded that wastewater should not have a great impact on the environment. The results obtained contribute contribute to the progress of new knowledge in the field of development of environmentally friendly graphic products, and they are useful for development of new insights in the field of environmental sustainability in this domain.

4. Conclusions

The aim of this study was to evaluate the influence of different printing technique, conditions in printing process, and different types of inks on the efficiency of prints recycling and wastewater quality. Results of image analysis showed that by increasing the negative voltage of developing drum in LEP printing process (−200 V, −280 V, −350 V, −430 V), the formation of large ink particles in recycled pulp increases. Based on the printing technique principle, the thickness of the ElectroInk prints depends on the variation of the voltage of the developing drum, which affects detached ink particles and their deinkability. In the deinking flotation process, a difference was observed between the size, shape, and surface properties of ElectroInk compared to offset inks, which is evident through the small increase in brightness and whiteness of the laboratory handsheets made from the deinked pulp and IE_{ERIC}, respectively. In all analysed samples, there is a trend of opacity decrease on recycled paper handsheets due to loss of fillers during flotation process. In addition, some correlation was found between IE_{ERIC} and organic pollution parameters (COD and TOC) in wastewater after recycling of LEP and offset prints. Moreover, mentioned indicators of wastewater pollution are higher after recycling offset prints and dependent, among other things, upon the chemical composition of the offset inks and their drying mechanisms.

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