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Bio-Based Pigment Water-Based Inks for Piezoelectric Inkjet Printing

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Abstract

The development of bio-based inks represents a promising strategy to reduce the environmental impact of digital printing technologies. This study investigates the formulation and performance of water-based inks incorporating two renewable pigments: a fermentation-derived indigo pigment and a plant-extracted yellow pigment. Special attention was given to dispersion optimization of the poorly water-soluble indigo pigment. Extended mechanical dispersion (115 h in a ball mill) proved critical to achieve colloidal stability, enabling the preparation of inks that met standard rheological and physicochemical criteria for inkjet printing with piezoelectric printheads. Both inks were applied on a variety of substrates, including cotton, polyester, leather, and kraft paper, pre-treated, in the case of the textiles, with either a cationic biopolymer or a synthetic polyurethane-based binder. Colorimetric evaluation confirmed effective deposition and uniformity, with the indigo ink producing deep blue hues and superior overall fastness than the yellow ink, particularly in washing and rubbing tests. The yellow pigment ink showed good stability but once applied to the fabric, the resulting print exhibited poor fastness, particularly against light exposure, indicating limited durability of the coloration on the textile. Shelf-life analysis of the indigo ink revealed a decline in viscosity and surface tension over time, though the colour and particle size remained stable, particularly under room temperature conditions. These findings confirm the potential of fermentation-derived indigo as a robust bio-based alternative to synthetic dyes and its superior performance in relation to other nature extracted pigments, which, although facilitating ink preparation due to their higher water solubility, result in lower-fastness prints.

Keywords: bio-based pigments; indigo; inkjet printing; piezoelectric printhead; digital printing inks; natural pigments

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1. Introduction

Indigo is a historical organic colourant based on a bis-indole chromophore (C.I. 73000) that has been used since antiquity, primarily extracted from *Indigofera* species as a natural blue dye. Among early colouring agents, indigo emerged as one of the most widely used blue pigments, particularly for textile applications [1]. In its typical form, indigo appears as a blue-violet powder composed of small, highly symmetrical molecules that preferentially adopt a stable trans configuration. The molecule is planar in structure,

stabilized by two intramolecular six-membered hydrogen bonds and a high degree of π-electron conjugation. These features contribute not only to its colour properties but also to its remarkable stability [2,3].

One of the key characteristics of indigo is its poor solubility in water and most common organic solvents, a property that, while contributing to its excellent wash fastness, also poses challenges in formulation. Specifically, this limited solubility can adversely affect dispersion stability, which is particularly critical for printing applications where a uniform pigment distribution is essential [4]. The exceptional resistance to fading and degradation is largely attributed to its intrinsic photophysical behaviour. Specifically, the molecule's two intramolecular hydrogen bonds between amino and carbonyl groups play a critical role in maintaining structural rigidity and photostability. Indigo exhibits an extremely low yield of triplet-excited state formation, and the triplet state itself possesses a remarkably low excitation energy. This minimizes the likelihood of photochemical degradation pathways such as hydrogen abstraction or electron transfer. Furthermore, the excited-singlet state undergoes rapid intramolecular proton transfer; a highly competitive and reversible process that effectively quenches alternative deactivation routes. This dynamic may be regarded as a highly efficient photostability mechanism, serving as a "black hole" for excited-state energy dissipation [2].

Originally obtained from plant sources, indigo is now predominantly synthesized through chemical processes developed during the industrial revolution. These synthetic routes rely heavily on toxic chemicals such as aniline, nitrobenzene, and metal salts [5]. This process not only presents health risks to workers but also generates significant environmental pollution through hazardous by-products [2]. To mitigate these issues, current research is shifting toward bio-based production methods. One promising alternative is the biosynthesis of indigo via bacterial fermentation, using genetically engineered strains such as *Escherichia coli* or *Pseudomonas putida* [6]. These microbial processes are cleaner and safer and align with the principles of green chemistry [7]. However, industrial-scale adoption remains limited due to low production yields, high development costs, and the competitive pricing of chemically synthesized indigo [8,9].

Natural pigments derived from plants, microorganisms, and agro-industrial by-products have emerged as sustainable alternatives to synthetic dyes in digital textile printing, driven by the increasing necessity to minimize environmental impact through more sustainable colouration workflows [10,11]. However, their integration into pigment-based digital printing, which has gained prominence to substantially reduce post-washing and steaming steps, remains challenging: poor colloidal stability and large particle sizes hinders printhead compatibility; limited light and wash fastness compromises durability; batch-to-batch variability affects colour consistency; and suboptimal chroma demands complex formulations with dispersants and stabilizers [12–14].

Digital textile printing revolutionizes textile production with superior design flexibility, precision, and sustainability benefits over traditional methods. It uses inkjet technology for direct pattern applications on fabrics, enabling rapid customization, minimal waste, and a reduced environmental impact. Central to its success is ink formulation chemistry, which must meet strict physicochemical requirements like viscosity, surface tension, stability, and fibre/pre-treatment compatibility. Specialized additives, surfactants, dispersants, thickeners, and binders, ensure high print quality, vibrant colours, and durability against washing, abrasion, and UV exposure [15–17]. Piezoelectric printheads are well-suited for textile applications due to their robustness and compatibility with water-based inks. However, integrating bio-based pigments into these systems presents challenges related to particle size, dispersion stability, nozzle jetting behaviour, and substrate interaction [18].

Building upon the findings of [4], the present study represents an optimization effort focused on improving the dispersion behaviour of bio-derived indigo pigments for application in piezoelectric inkjet printheads. Specifically, this work aims to compare two bio-based pigments, a fermentation-derived indigo pigment and a commercially available plant-extracted yellow pigment, in terms of their suitability for water-based inkjet formulations designed for this specific printing technology. Both pigments are formulated into aqueous inks adapted to the rheological and physicochemical requirements of the piezoelectric systems, and their performance is evaluated based on dispersion stability, colorimetric properties, and print quality. To further assess their practical applicability, the developed inks were applied to a range of substrates, including two types of textile fabrics, a cotton-based fabric containing 1% elastane and a 100% polyester fabric, as well as leather and kraft paper. This multi-substrate evaluation provides a broader understanding of the interactions between the bio-based pigments and various material surfaces, enabling the assessment of print quality and colour performance.

By addressing known challenges related to indigo dispersion and demonstrating the applicability of bio-based pigments in water-based inks across multiple substrates, this study contributes to the ongoing development of sustainable pigment alternatives tailored for digital printing technologies. The ability to formulate stable inks compatible with piezoelectric inkjet systems while maintaining performance across diverse materials represents an innovative step towards expanding the use of bio-derived pigments in sustainable printing processes.

2. Materials and Methods

2.1. Materials

The materials used for ink application included two types of textile fabrics, one cotton-based (99% cotton (CO), 1% elastane (EA), 370 g/m^2), and one polyester-based (100% polyester (PES), 295 g/m^2), both supplied by RIOPELE (Vila Nova de Famalicão, Portugal), as well as leather (light cream colour, without chrome-tanning), supplied by Curtumes Boaventura (Alcanena, Portugal), and kraft paper (plane paper, 65 g/m^2), supplied by PROPAGROUP (Turin, Italy).

The polymers used in the pre-treatments were a biopolymer based on a cationic polysaccharide (Biopolymer, viscosity 600–1200 mPa·s, turbidity $\leq$30 NTU), and a polyurethane-based synthetic binder comprising an aliphatic polycarbonate–polyether backbone (Binder A, non-ionic aqueous dispersion, viscosity < 1000 mPa·s, density $\approx$ 1.1 g/cm^3, pH value 6.0–8.0).

The bio-based pigments used were indigo (produced via microbial fermentation using a patented process), supplied by PILI (Toulouse, France), and a commercial yellow pigment (extracted from *Gardenia jasminoides* fruits) supplied by NIG GmbH (Magdeburg, Germany), both in powder form.

2.2. Methods

2.2.1. Pre-Treatment

In accordance with the methodology described in [4], the textile substrates were pre-treated via foulard impregnation (wet pick-up around 80%) using two solutions, a 50% (*v*/*v*) aqueous dilution of Binder A and a 1% (*w*/*v*) Biopolymer solution prepared in 0.5 M acetic acid (pH 4.0–5.0). The treated fabrics were then dried at 100 °C for 3–5 min to ensure fixation and the removal of excess moisture.

2.2.2. Indigo Dispersion

Indigo pigment (20%) was mixed with a dispersing and wetting agent (10%, polyether-modified styrene-maleic anhydride copolymer in an aqueous solution, BYK (Wesel, Ger-

many)), a defoaming agent (0.6%, salted methacrylate block copolymer in an aqueous solution, BYK (Wesel, Germany)), and distilled water (69.4%) and dispersed in a ball mill (PM100 planetary ball mill by Retsch, Haan, Germany) at 350 rpm, using 3 mm-diameter zirconia balls, over 5, 8, 15, and 115 h.

2.2.3. Ink Formulation

According to the formulation strategy reported in [4], the inks were prepared by mixing a combination of 15–20% of a biodegradable binder (polyurethane in aqueous dispersion, Achitex Minerva (Vaiano Cremasco, Italy)), 2.5–5.0% of a crosslinking agent (water based aliphatic blocked polyisocyanate, Covestro (Leverkusen, Germany)), 45.0–65.0% of distilled water, 15.0–25.0% of a hygroscopic agent (alcohol diol, VWR (Rosny-sous-Bois, France)), 3.0–6.0% of a wetting agent (alcohol alkoxylates, BYK (Wesel, Germany)), 0.5–1.5% of an anti-foam agent (polyether-modified polydimethylsiloxane, BYK (Wesel, Germany)), 0–1.0 of a thickening agent (polyacrylate solution, BYK (Wesel, Germany)), and 0.01, 0.1, or 1% (*w*/*w*) of indigo pigment pre-dispersed, at room temperature. For the ink with the yellow pigment, the concentration of the pigment used was 0.5% (*w*/*w*). All the components were mixed at room temperature using an overhead stirrer. Both inks were then filtered using a qualitative paper filter (grade 413, 5–13 µm, VWR International (Leuven, Belgium)). In addition, indigo pigment deposition was evaluated via visual observation for up to 5 days.

2.2.4. Ink Characterization

The physical properties of the inks were analysed as follows, immediately after preparation: viscosity (smart series rotational viscosimeter by Fungilab (Barcelona, Spain)), density (calculated dividing the mass by volume), surface tension (pendant drop method in the optical tensiometer Theta Flex by Biolin Scientific (Gothenburg, Sweden)), and particle size (Zetasizer NanoSeries Nano ZS90 by Malvern Panalytical (Malvern, UK)). Each parameter was measured at least in triplicate, and mean values are reported. The 1% indigo ink was further characterized as to its stability and shelf-life. In short, after one month of storage at room temperature, the ink was exposed to three different storage conditions over a period of two months: (i) room temperature ((24.0 ± 0.4) °C), with a relative humidity of (59.0 ± 0.9)% and (ii) elevated temperature (40 °C), with analyses conducted weekly, (iii) thermal cycling (alternating 24-h periods at 4 °C and 40 °C). The following parameters were monitored for the 3 conditions: viscosity, surface tension, density and particle size (same methods and equipment's as above described), colour coordinates and variation (ΔE) (UV-Vis spectrophotometer equipped with an integrating sphere UV-2600i by Shimadzu (Kyoto, Japan)). Particle size distribution was assessed only at three time points: at the beginning of the study, after one month, and at the end of the two-month period.

2.2.5. Printing

All the materials were printed using a linear printing test bench, developed by KYOCERA NIXKA Inkjet Systems SAS (Aubagne, France), with a KJ4B-Z 1200 dpi printhead with recirculation by Kyocera Corporation (Kyoto, Japan). The design was printed at a resolution of 1200 dpi with 4 pL standard waveform, and the recirculation flow was set at ≈65 mL/min. Once printed, textile and leather samples were thermofixed at 150 °C for 5 min.

2.2.6. Printing Characterization Methods

The printed fabrics were evaluated for colour fastness according to the following most used standards for fashion textiles: domestic washing (ISO 105-C06:2010), water (ISO 105-E01:2013), perspiration (ISO 105-E04:2013), artificial light (ISO 105-B02:2014), and rubbing (ISO 105-X12:2016). For kraft paper substrates, colour fastness was assessed to water spotting (ISO 105-E07:2010) and artificial light (ISO 105-B02:2014). The leather

substrates were evaluated for colour fastness according to the same standards as used in the textiles and water spotting (NP EN ISO 105 E07:2010). Additionally, all the samples were characterized regarding their colour appearance through spectrophotometric analysis using CIELAB coordinates.

3. Results

This study aimed to determine the viability of bio-based pigments as sustainable alternatives to conventional synthetic pigments in digital textile printing, namely when using equipment with a piezoelectric printhead, these being the most common ones for fashion applications [19]. This section presents the experimental results concerning ink development and physical characterization, printing performance on the different materials, an evaluation of colour fastness to different media, and the indigo ink shelf-life.

3.1. Ink Preparation and Stability

3.1.1. Indigo Pigment

The dispersion of the indigo pigment represented a critical step in the ink-development process, due to the low particle size requirements of piezoelectric printheads. The filtration of a previously developed ink without pre-dispersing the indigo pigment [4] showed a high agglomeration of the pigment, which was retained in the filter, and the unviability of its application using this type of printheads. Therefore, in this work, we started by dispersing the indigo pigment. The sedimentation behaviour of inks containing 0.01% and 0.1% pre-dispersed indigo pigment, using processing times of 5, 8, and 15 h in the ball mill, was evaluated.

Table 1 shows the paper filters after ink filtration, while Table 2 demonstrates the ink (0.01 and 0.1% of indigo pigment) deposition evaluation after 5 days since its preparation.

Filtration through a 5–13 µm paper filter revealed considerable pigment retention, particularly in the 5 and 8 h samples, suggesting incomplete de-agglomeration of the indigo dispersion and poor colloidal stability. Additionally, visual analysis over a five-day period indicated the occurrence of sedimentation, most notably in the ink with a higher pigment content; despite the absence of visible sediment after 24 h, after five days, all inks containing 0.1% pigment show some sedimentation.

Table 1. Filters after vacuum filtration of the inks prepared with indigo pre-dispersed for 5, 8, and 15 h in the ball mill.

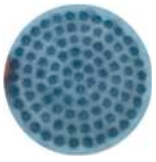
Ink	Time of Indigo Dispersion (in the Ball Mill)		
	5 h	**8 h**	**15 h**
0.01% indigo ink			
0.1% indigo ink			

Table 2. Ink deposition evaluation after 5 days since its preparation.

Time in the Ball Mill	Ink with 0.01% Indigo			Ink with 0.1% Indigo		
	0 h	24 h	5 Days	0 h	24 h	5 Days
5 h						
8 h						
15 h						

To enhance pigment stabilization and overcome the previously observed limitations, the dispersion time was substantially increased to 115 h while maintaining the same milling parameters. Table 3 presents the filters following the filtration of inks containing 0.01% and 0.1% indigo pigment pre-dispersed for 115 h, illustrating the lack of sedimentation after 24 h, which remained after 15 days.

Table 3. Inks prepared with indigo pre-dispersed for 115 h in the ball mill, respective filters after vacuum filtration, and sedimentation analysis.

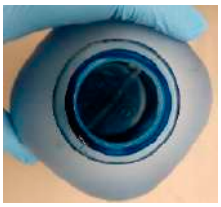
Ink		Filter After Filtration	Sedimentation After 24 h—15 Days
0.01% indigo			
0.1% indigo			

As observed, both inks prepared with indigo pre-dispersed for 115 h successfully passed through the filter without any issues, and the filters appeared noticeably cleaner. Apparently, the sedimentation and agglomeration issues were solved, as demonstrated by the lack of precipitates at the bottom of both ink bottles even after 15 days. These results confirmed that extended mechanical dispersion was essential to achieve a stable and homogenous indigo pigment suspension suitable for inkjet printing.

The preliminary textile application of the ink containing 0.01% and 0.1% pigment resulted in a low-intensity colour, which, in the case of the 0.01% ink, was nearly undetectable to the naked eye. As a result, the need to increase the pigment concentration in subsequent formulations to achieve a more intense and uniform colour deposition, suitable for textile printing applications, was established.

A new ink formulation was prepared with this new pre-dispersion (115 h), increasing the indigo concentration to 1%. The remaining formulation was kept unaltered, just adding some thickener to adjust the viscosity of the ink and, therefore, met the requirements of the inkjet system. Table 4 presents the filter following the filtration of the ink and the sedimentation analysis for 15 days.

Table 4. Ink prepared with 1% indigo pre-dispersed for 115 h in the ball mill, respective filter after vacuum filtration, and sedimentation analysis.

	Ink	**Filter After Filtration**	**Sedimentation After 24 h—15 Days**	
1.0% indigo				

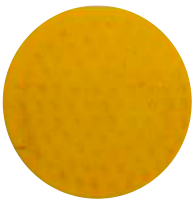
The ink successfully passed through the filter without any issues, although minimal pigment retention was still observed. The intense blue colour of the filter is due to the occurred absorption of ink. Although slight sedimentation at the bottom of the flask was detected upon visual inspection, it did not significantly increase over time, and it was readily redispersed with mild agitation, suggesting good colloidal stability in the ink.

Overall, a dispersion of 115 h in the ball mill was identified as the most effective condition to obtain a stable, homogeneous indigo pigment suspension suitable for inkjet ink formulation.

3.1.2. Yellow Pigment

The commercial plant-based yellow pigment was directly incorporated into the ink formulation without undergoing a pre-dispersion step, due to its inherent water solubility. Unlike insoluble pigments that require mechanical dispersion to break down agglomerates and ensure uniform particle distribution, this pigment readily dissolves in the aqueous medium, enabling immediate and homogeneous integration into the ink system. Table 5 presents the filters following the filtration of the ink and the sedimentation analysis for 15 days.

Table 5. Ink prepared with commercial bio-based yellow pigment, respective filter after vacuum filtration, and sedimentation analysis.

Ink	Filter After Filtration	Sedimentation After 24 h—15 Days
0.5% yellow pigment		

The ink successfully passed through the filter without any issues, during which no visible pigment retention was observed, indicating a fully dissolved or finely dispersed system. The intense yellow colour of the filter is due to the occurred absorption of ink. Furthermore, a visual assessment conducted 24 h post-filtration until 15 days storage revealed no signs of pigment deposition or sedimentation. These observations suggest that the ink exhibits excellent colloidal stability and homogeneity, likely due to the complete solubilization of the pigment in the aqueous medium.

3.2. Ink Properties

Table 6 summarizes the key physical parameters of the most promising inks: two ink formulations containing 1.0% indigo and 0.5% yellow bio-based pigments, each exhibiting different parameter values.

Table 6. Properties of the inks developed with indigo and yellow pigments.

Ink	Viscosity (cP)	Density (g/cm^3)	Surface Tension (mN/m)	Particle Size
Requirements	4.5 to 10 @ 35 °C	0.90 to 1.20	31.5 to 38	<5 µm
1.0% indigo ink	7.71 @ 22 °C	0.94	23.4	<5 µm
1.0% indigo ink	6.33 @ 22 °C	0.96	32.26 ± 0.38	
0.5% yellow ink	4.33 @ 22 °C	1.04	33.64 ± 0.10	
0.5% yellow ink	6.02 @ 22 °C	0.95	32.52 ± 0.52	

The inks analysed were evaluated against standard requirements for piezoelectric inkjet formulations in terms of viscosity, density, surface tension, and particle size. The indigo inks exhibited viscosities of 7.71 cP and 6.33 cP, measured at 22 °C, depending on the amount of thickener. These values fall within the required range of 5 to 10 cP. The densities of both inks (0.94 g/cm^3 and 0.96 g/cm^3) are within the acceptable range of 0.90 to 1.20 g/cm^3. One of the indigo inks had a surface tension of 23.4 mN/m, which is significantly below the minimum acceptable limit. However, the other indigo ink measured 32.26 ± 0.38 mN/m, complying with the specified range of 31.5 to 38 mN/m and exceeding the minimum threshold of 28 mN/m. These results suggest that viscosity influences surface tension; in particular, an increase in thickener content tends to a decrease in surface tension.

The yellow inks exhibited viscosities of 4.33 cP and 6.02 cP, measured at 22 °C; the first value is below the required range of 5 to 10 cP. The densities of both inks (1.04 g/cm^3 and 0.95 g/cm^3) are within the acceptable range. Their surface tensions (33.64 ± 0.10 mN/m and 32.52 ± 0.52 mN/m) also meet the specified requirement range of 31.5 to 38 mN/m. In this case, the variation in viscosity practically did not affect surface tension, indicating

that these properties are independently regulated in the yellow ink formulations under the tested conditions.

Additionally, all the inks meet the particle size requirement of less than 5 µm. All prepared inks conform to the essential physicochemical criteria for inkjet printing applications with piezoelectric printheads, except for one of the indigo inks, which does not meet the surface tension requirement. However, all the inks were tested to assess their performance.

3.3. Printability and Substrate Interaction

Printing trials were carried out on a range of materials to evaluate ink performance and substrate compatibility. These included two types of textile fabrics—one cotton-based and one polyester-based, as well a leather and kraft paper. In all cases, no issues occurred during printing.

Application of the first indigo ink (with a viscosity of 7.71 cP, a density of 0.94 g/cm^3, and a surface tension of 23.4 mN/m) showed poor jetting performance. The low surface tension caused excessive wetting of the nozzle plate, resulting in start-up issues and jet instability. In contrast, the second indigo ink formulation (with a viscosity of 6.33 cP, a density of 0.96 g/cm^3, and a surface tension of 32.26 mN/m) exhibited stable jetting with no problems faced. These results, together with the ones on the 0.1% and 0.01% indigo inks, revealed that the optimal viscosity range lies between 6.0 and 6.5 cP and that the surface tension should be higher than 28 mN/m to prevent ink accumulation at the nozzles and to improve jetting performance. Within this range, a critical performance aspect was achieved: the printhead operated efficiently at a controlled temperature between 28 and 32 °C, preventing excessive heat that could lead to drop drying on the nozzle plate.

In the case of the yellow ink, the first ink produced (with a viscosity of 4.33 cP, a density of 1.04 g/cm^3 and a surface tension of 33.64 ± 0.10 mN/m) was possible to jet, but it was necessary to adjust the printhead temperature to approximately 25–28 °C and modify the recirculation parameters to prevent air from being drawn into the nozzle. These observations revealed that viscosity influences application parameters and therefore must be increased to allow injection at around 30–32 °C and to better control printing performance. For the second yellow ink with all parameters within the required ranges, good jetability was observed, and its physical properties were suitable for the application. However, the yellow ink tends to dry faster than indigo ink. This affects the start-up, causing a few missing jets at the beginning of the pattern, but these recover during printing.

Overall, all the inks (indigo and yellow ink) demonstrated full miscibility with all tested cleaning solutions, indicating no incompatibility and confirming its suitability for the inkjet equipment without the risk of clogging or adverse interactions during maintenance procedures.

3.3.1. Textile Substrates

Figure 1 shows examples of the printed samples on pre-treated cotton fabrics.

Table 7 shows photographs of each textile printed sample, demonstrating that colour intensity and uniformity are significantly influenced by both the type of substrate and the pre-treatment applied. These visual observations are corroborated by the CIELAB colour coordinates reported in Table 8.

The indigo ink produced darker tonalities across all samples, as expected from its inherent colour properties, with L* values ranging from 61 to 65. The a* and b* values were consistently negative, indicating hues shifting toward green (–a*) and blue (–b*). Only minor variations were observed between the two pre-treatments. On cotton, the colour coordinates were very similar for both treatments (e.g., L = 64.00 for Biopolymer vs. 64.74 for Binder A), with small shifts in a* and b*; however, the difference in b* indicates a

noticeable change in the intensity of the blue tone. On polyester, a slightly greater difference was noted, particularly in the a* coordinate (–11.33 vs. –12.67), although the difference remains modest.



Figure 1. Cotton samples (pre-treated with biopolymer for indigo ink and Binder A for yellow ink) printed with inks containing 1.0% indigo pigment (**left**) and 0.5% yellow pigment (**right**).

Table 7. Textile samples printed with inks containing 1.0% indigo and 0.5% yellow pigments with different pre-treatments.

Fabric	Ink with 1.0% Indigo Pigment		Ink with 0.5% Yellow Pigment	
	Biopolymer	Binder A	Biopolymer	Binder A
Cotton				
Polyester				

As expected, the yellow ink produced much higher L* and b* values, corresponding to bright and saturated yellow shades. On cotton, the difference between pre-treatments was again small in L*, but a more notable increase in b* was observed for Binder A (34.44 vs. 42.56), suggesting a possible improvement in chroma. However, without replicate measurements or ΔE analysis, it is not possible to determine whether this difference is

statistically or visually significant. For polyester, b* values ranged from 23.24 to 36.67 depending on the pre-treatment, with Binder A again showing a higher value.

Table 8. Colour coordinates of textile samples inkjet-printed with 1.0% indigo and 0.5% yellow inks.

Ink	Fabric	Pre-Treatment	Colour Coordinates		
			L*	a*	b*
Indigo	Cotton	Biopolymer	64.00	−5.96	−15.55
		Binder A	64.74	−5.58	−13.95
	Polyester	Biopolymer	61.62	−11.33	−23.31
		Binder A	62.06	−12.67	−24.98
Yellow	Cotton	Biopolymer	89.62	−2.06	34.44
		Binder A	89.85	−2.46	42.56
	Polyester	Biopolymer	90.28	−3.93	23.24
		Binder A	90.24	−6.61	36.67

Nevertheless, the overall differences across treatments remained moderate, and the influence of the textile structure and ink–substrate interactions cannot be excluded (e.g., the a* and b* values are always higher in cotton than in polyester, for the same pre-treatment, no matter the ink or the pre-treatment).

In general, the results indicate that both the biopolymer and the synthetic binder pre-treatments enabled similar colour expression on both cotton and polyester fabrics. Although slight variations in chromatic coordinates were observed—more evident in polyester samples—the magnitude of these differences was relatively small, and no definitive conclusions can be drawn regarding the superiority of one treatment over the other only by colour analysis.

3.3.2. Leather

Figure 2 shows leather samples printed with the inks containing bio-based pigments. In this substrate, the colour intensity was significantly lower, for both inks, than the ones obtained in the textile substrates. These visual observations are corroborated by the CIELAB colour coordinates reported in Table 9.

Table 9. Colour coordinates of leather samples inkjet-printed with 1.0% indigo and 0.5% yellow inks.

Sample	Colour Coordinates		
	L*	a*	b*
Without printing	93.98	−0.17	11.00
Indigo Ink	73.20	−6.82	−4.23
Yellow Ink	88.98	2.74	31.64

The unprinted leather showed a high L* value of 93.98, indicating a very light surface, and relatively neutral chromaticity with a* = –0.17 and b* = 11.00. After printing with the indigo ink, a significant decrease in L* was observed (73.20), corresponding to a visibly darker tone. Additionally, the a* and b* values became more negative (–6.82 and –4.23, respectively), reflecting a clear shift towards bluish-green hues, consistent with the deposition of a blue ink over a light cream (with yellow hues) surface. Printing with the yellow ink also resulted in a decrease in lightness (L* = 88.98), although to a lesser extent compared to indigo, due to the much lighter colour intensity of the ink. The a* and b*

values increased more markedly (2.74 and 31.64, respectively), indicating a pronounced shift towards warmer, yellow-red tones. The high b* value confirms successful deposition and chromatic expression of the yellow pigment on the leather surface.



Figure 2. Leather samples printed with inks containing 1.0% indigo pigment (**left**) and 0.5% yellow pigment (**right**).

3.3.3. Kraft Paper

Figure 3 shows leather samples printed with the inks containing bio-based pigments. Similar to what was observed for the leather substrate, lower colour intensity was observed in the printed kraft paper than in the textile printed samples. Furthermore, the printed paper samples also had slightly lower colour intensity than the printed leather, which can be due to some ink absorption by the paper, resulting in fainter colours. These visual observations are corroborated by the CIELAB colour coordinates reported in Table 10.

Table 10. Colour coordinates of kraft paper samples inkjet-printed with 1.0% indigo and 0.5% yellow inks.

Sample	Colour Coordinates		
	L*	**a***	**b***
Without printing	71.28	7.24	21.94
Indigo Ink	56.12	−3.20	5.81
Yellow Ink	69.64	7.95	33.91

The unprinted kraft paper exhibited a relatively high lightness (L* = 71.28) and positive a* (7.24) and b* (21.94) values, indicating a naturally warm tone with reddish and yellowish hues, as typically seen in kraft substrates. After printing with the indigo ink, the L* value decreased significantly to 56.12, indicating a considerable darkening of the paper surface. The a* coordinate shifted from positive to negative (–3.20), and the b* value decreased to 5.81. These changes reflect a clear shift towards bluish-green tones, which aligns with the

expected visual effect of indigo-based pigments. In contrast, printing with the yellow ink resulted in a moderate reduction in lightness (L* = 69.64), maintaining a relatively bright appearance. Both a* and b* values increased (7.95 and 33.91, respectively), suggesting a strong enhancement of warm tones, particularly in the yellow direction. This outcome confirms effective pigment deposition and colour development of the yellow ink on the kraft surface.



Figure 3. Kraft paper printed with the ink containing 1.0% indigo pigment (**left**) and ink with 0.5% yellow pigment (**right**).

3.4. Printing Characterization

Colour fastness tests were conducted following standardized methods to evaluate the performance of the printed materials and to analyse how the pre-treatments (in the case of the textile substrates) influenced the colour fastness.

3.4.1. Textile Printed Samples

The results of the fastness tests carried out on the samples printed with indigo ink are presented in Table 11.

For cotton fabrics, both treatments (Biopolymer and Binder A) showed identical performance in terms of the colour change, scoring grade 4 under all tested conditions (washing, water, alkaline/acid perspiration). However, differences emerge under rubbing and artificial light exposure: b Biopolymer treatment showed slightly better dry rubbing fastness (grade 4–5) compared to Binder A (grade 4), while wet rubbing was notably poorer in both cases, with Binder A scoring 2–3 vs. 3 for Biopolymer. The most significant difference was colour fastness to artificial light, where the Binder A-treated cotton showed a strong degradation (grade 1), indicating poor light fastness, in contrast to grade 3–4 for Biopolymer-treated cotton.

Table 11. Colour fastness properties of textile samples inkjet-printed with 1.0% indigo ink (grey scale evaluation).

Fabric	Pre-Treatment	Colour Fastness to								
				Colour Change	Staining					
					AC	CO	PA	PES	PAN	WO
Cotton	Biopolymer	Domestic washing		4	4–5	4–5	4–5	5	5	5
		Water		4	4–5	4–5	4–5	4–5	4–5	4–5
		Perspiration	Alkaline	4	4–5	4–5	4–5	5	5	5
			Acid	4	4–5	4–5	4–5	5	5	5
		Rubbing		Dry: 4–5; Wet: 3						
		Artificial light		3–4						
	Binder A	Domestic washing		4	4–5	4–5	4–5	5	5	5
		Water		4	4–5	4–5	4–5	5	5	5
		Sweat	Alkaline	4	4–5	4–5	4–5	5	5	5
			Acid	4	4–5	4–5	4–5	5	5	5
		Rubbing		Dry: 4; Wet: 2–3						
		Artificial light		1						
Polyester	Biopolymer	Domestic washing		4–5	4–5	4–5	4–5	5	5	5
		Water		4–5	4–5	4–5	4–5	5	5	5
		Perspiration	Alkaline	4–5	4–5	4–5	4–5	5	5	5
			Acid	4–5	4–5	4–5	4–5	5	5	5
		Rubbing		Dry: 4–5; Wet: 3–4						
		Artificial light		3						
	Binder A	Domestic washing		4–5	4–5	4–5	4–5	5	5	5
		Water		4–5	4–5	4–5	4–5	5	5	5
		Perspiration	Alkaline	4–5	4–5	4–5	4–5	5	5	5
			Acid	4–5	4–5	4–5	4–5	5	5	5
		Rubbing		Dry: 4–5; Wet: 4						
		Artificial light		3–4						

AC—acetate, CO—cotton, PA—polyamide, PES—polyester, PAN—acrylic, WO—wool.

For polyester fabrics, both treatments performed similarly and slightly better overall than on cotton. Colour change ratings were consistently grade 4–5. Rubbing fastness was improved compared to cotton, especially for wet rubbing, where Binder A achieved grade 4 and Biopolymer grade 3–4. Light fastness results for polyester were more stable, with both treatments achieving grade 3–4 (Binder A) and grade 3 (Biopolymer), indicating improved stability over cotton, especially when treated with Binder A.

As to the staining of different fibres during the colour fastness tests to washing, water, and perspiration, all samples gave quite similar results, with grade 4–5 for acetate, cotton, and polyamide and grade 5 for polyester, acrylic, and wool.

Overall, polyester exhibited better and more consistent colour fastness than cotton for both pre-treatments.

The results of the fastness tests carried out on the samples printed with yellow ink are presented in Table 12.

Table 12. Colour fastness properties of textile samples inkjet-printed with 0.5% yellow ink (grey scale evaluation).

Fabric	Pre-Treatment	Colour Fastness to								
				Colour Change	Staining					
					AC	CO	PA	PES	PAN	WO
Cotton	Biopolymer	Domestic washing		3–4	4–5	4–5	4–5	5	5	5
		Water		3–4	4–5	4	4–5	5	5	5
		Perspiration	Alkaline	3–4	4–5	4	4–5	5	5	5
			Acid	3–4	4–5	4	4–5	5	5	5
		Rubbing		Dry: 4–5; Wet: 4						
		Artificial light		1						
	Binder A	Domestic washing		1–2	4–5	4	4–5	5	5	5
		Water		3	4–5	3–4	4–5	5	5	5
		Perspiration	Alkaline	3	4–5	3–4	4–5	5	5	5
			Acid	3	4–5	3–4	4–5	5	5	5
		Rubbing		Dry: 4–5; Wet: 3						
		Artificial light		1–2						
Polyester	Biopolymer	Domestic washing		2–3	4–5	4–5	4–5	5	5	5
		Water		3	4–5	4	4–5	5	5	5
		Perspiration	Alkaline	3	4–5	3–4	4–5	5	5	5
			Acid	3	4–5	3–4	4–5	5	5	5
		Rubbing		Dry & Wet: 4–5						
		Artificial light		1						
	Binder A	Domestic washing		1–2	4–5	4	4–5	5	5	5
		Water		2	4–5	4	4	4–5	4–5	4–5
		Perspiration	Alkaline	2	4–5	3	4	4–5	4–5	4–5
			Acid	2	4–5	3–4	4	4–5	4–5	4–5
		Rubbing		Dry: 4–5; Wet: 4						
		Artificial light		1						

AC—acetate, CO—cotton, PA—polyamide, PES—polyester, PAN—acrylic, WO—wool.

For cotton fabrics, the biopolymer pre-treatment achieved slightly better colour fastness values (grade 3–4) than Binder A (grade 1–2 for washing and grade 3 for water and perspiration) for domestic washing, water, and perspiration (acid and alkaline), yet both treatments demonstrated poor resistance to artificial light (grade 1 or 1–2). Despite the moderate colour fastness values, staining results remained excellent (mostly grade 4–5 to 5) across all adjacent fabrics, indicating low pigment transfer. Rubbing fastness was good for both treatments, with dry rubbing at grade 4–5 and wet rubbing slightly lower (grade 3 for Binder A and grade 4 for Biopolymer).

In the case of polyester fabrics, the trend was similar but with slightly lower fastness results. Biopolymer treatment showed moderate colour fastness (grade 2–3 to 3) to washing and perspiration, while Binder A performed worse (grade 1–2 to 2). Once again, artificial light fastness was poor, consistently rated at grade 1, regardless of the binder. Staining remained with good results (mostly grade 4–5 to 5), though a slight reduction was noted for CO and PA (grade 3–4) in Binder A samples, suggesting some pigment migration in

perspiration conditions. Rubbing fastness was acceptable, with dry and wet values ranging from grade 4 to 4–5.

Overall, the yellow pigment showed weaker colour fastness properties, particularly for washing and light exposure, when compared to the indigo pigment. For yellow ink printed samples, the Biopolymer pre-treatment performed better than Binder A across both substrates. In the case of printed samples with indigo ink, it showed greater affinity with the Biopolymer on cotton fabrics, while on polyester Binder A ensured better performance.

3.4.2. Leather Printed Samples

The printed leather substrates were evaluated for colour fastness according to the same standards as used in the textiles and water spotting. The results are shown in Table 13.

Table 13. Colour fastness properties of leather samples inkjet-printed with indigo and yellow inks (grey scale evaluation).

Ink	Colour Fastness to								
			Colour Change	Staining					
				AC	CO	PA	PES	PAN	WO
1.0% indigo pigment	Domestic washing		4	4–5	4–5	4–5	5	5	5
	Water		4	4–5	4–5	4	4–5	4–5	4–5
	Perspiration	Alkaline	4–5	4	4	4	4–5	4–5	4–5
		Acid	4	4–5	4–5	4	4–5	4–5	4–5
	Rubbing		Dry: 4; Wet: 3						
	Artificial light		2						
	Water spotting		After 2 min: 2 After drying: 3–4						
0.5% yellow pigment	Domestic washing		2–3	4–5	4	4–5	4–5	4–5	4–5
	Water		2–3	4	3	4	4	4	4
	Perspiration	Alkaline	2–3	4	2–3	4	4	4	4–5
		Acid	2–3	4–5	3	4	4	4	4
	Rubbing		Dry:4–5; Wet: 3–4						
	Artificial light		1						
	Water spotting		After 2 min: 2–3 After drying: 4						

AC—acetate, CO—cotton, PA—Polyamide, PES—polyester, PAN—acrylic, WO—wool.

The leather substrates printed with indigo ink demonstrated good resistance to washing, perspiration, and water exposure, with ratings between grade 4 and 5. Dry rubbing fastness was also good (grade 4), while wet rubbing showed a moderate decrease (grade 3), indicating a higher sensitivity to friction under moist conditions. Colour fastness to water spotting was acceptable, with ratings between grade 3 and 4 after drying. However, colour fastness to light was poor (grade 2), reflecting noticeable degradation upon exposure to artificial light.

In contrast, samples printed with yellow ink exhibited generally lower fastness performance, similarly to what was observed for the textile printed samples. Resistance to domestic washing, water, and perspiration was limited (grade 2–3), and light fastness was very low (grade 1). The only acceptable results were observed in rubbing tests, with values

being grade 4–5 for dry rubbing and 3–4 for wet rubbing. Additionally, water spotting showed a rating of 4 after drying.

3.4.3. Kraft Paper Printed Samples

The kraft paper substrates were tested as to their colour fastness to water spotting and artificial light. The results are shown in Table 14.

Table 14. Colour fastness properties of kraft paper samples inkjet-printed with indigo and yellow inks (grey scale evaluation).

Colour Fastness to		**Without Printing**	**1.0% Indigo Ink**	**0.5% Yellow Ink**
Water spotting	Colour change after 2 min	2–3	2	2–3
	Colour change after drying	4–5	4–5	4–5
Artificial light		-	3–4	3–4

The colour fastness results for paper substrates printed with both the bio-based indigo and the yellow inks were similar. After drying, the samples exhibited a rating of grade 4–5 for water spotting, indicating very good resistance to moisture-induced discolouration. In terms of exposure to artificial light, the samples achieved a rating of grade 3–4. These results demonstrate that both the indigo-based ink and the yellow ink perform well on paper substrates.

3.5. Ink Shelf-Life Analysis

The stability of the 1.0% indigo ink formulation was evaluated over an 8-week period under different storage temperatures: 40 °C, 24 °C (room temperature), and cyclic temperature (4–40 °C). The parameters assessed—visual observation, viscosity, surface tension, density, colour, and particle size stability—are critical to ensure proper inkjet printing performance and long-term shelf stability.

3.5.1. Visual Observation

No visible colour changes, phase separation, or agglomeration were detected during this time for any storage condition. Nevertheless, from the second month onwards, slight sedimentation became perceptible in all conditions. This sediment was readily redispersed upon gentle shaking, suggesting that the formulation maintained satisfactory colloidal stability despite minor gravitational settling.

3.5.2. Viscosity, Surface Tension, and Density

Figure 4 summarizes the evolution of three key physicochemical properties—viscosity, surface tension, and density—of the bio-based indigo ink formulation.

- Viscosity

The viscosity profile (Figure 4, top left) shows an initial decline from ink preparation (T0) to the first month of storage, after which the values stabilize under all storage conditions tested (24 °C, 40 °C and 4–40 °C). From week 1 to week 3, viscosity readings stabilize uniformly between 4 and 5 cP, only slightly below the inkjet application requirements (outlined by the orange min-max dashed lines). After week 4, viscosities gradually decrease, remaining outside the mandatory requirement for the inkjet equipment.

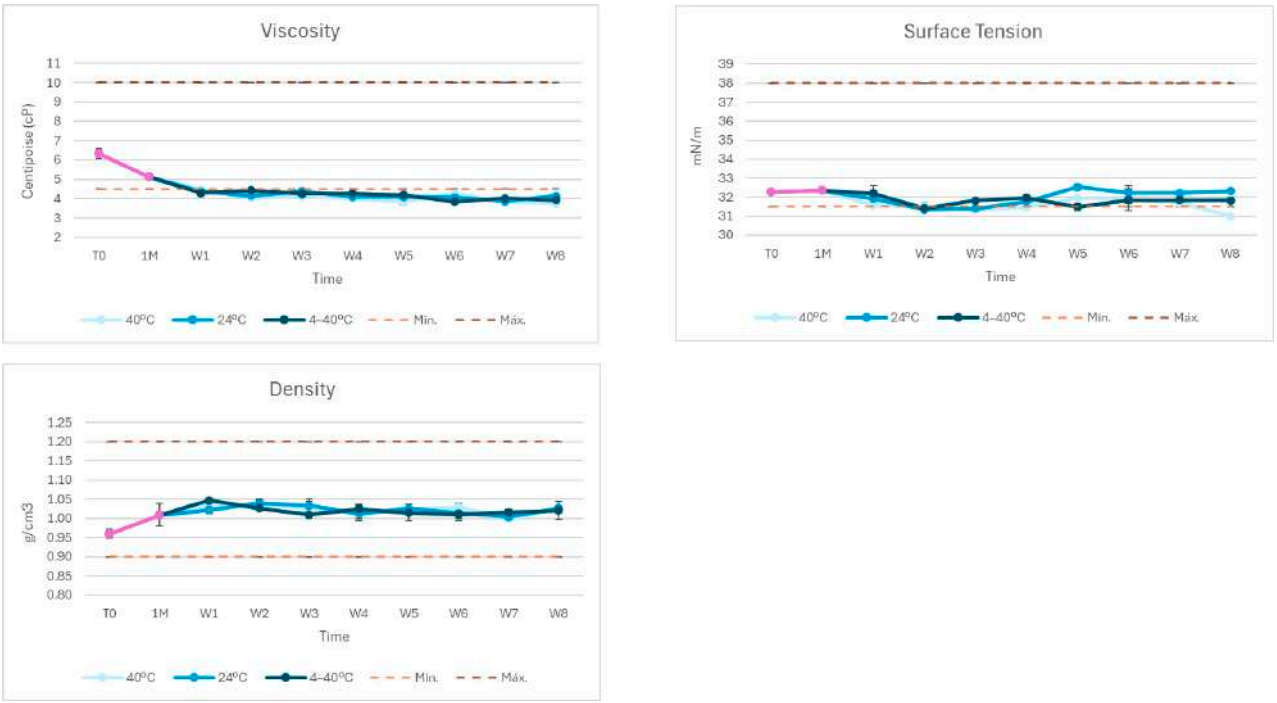


Figure 4. Evolution of viscosity, surface tension, and density of the bio-based 1.0% indigo ink formulation (T0 corresponds to the moment the ink was prepared, 1 M after 1 month at room temperature and W1, W2…W8 the 8 weeks of the shelf-life study. Min and Max represent the reference values for inkjet inks for piezoelectric printheads). Pink line: one-month aged ink under ambient conditions(approx. 24 °C, 59.0% RH).

This indicates that, over time, viscosity tends to decrease regardless of storage conditions, possibly due to a gradual reorganization of the pigment–polymer–dispersant network and partial degradation or redistribution of rheology modifiers within the continuous phase. These structural changes, rather than pigment aggregation or sedimentation, weaken the intermolecular associations that control viscoelastic behaviour. Interactions between the polyurethane binder and hygroscopic agents may further contribute to the loss of network integrity. These findings highlight an intrinsic limitation in the long-term viscosity stability and emphasize the need for more durable stabilizers to sustain consistent jetting performance during extended storage.

- Surface Tension

Overall, the surface tension values (Figure 4, top right) remained relatively constant across all storage conditions, ranging between 31.5 and 33 mN/m and staying within the defined operational range suitable for inkjet printing. Although a slight decrease was observed after the first month, values stabilized for the remainder of the evaluation period. It is noteworthy that the surface tension values were at the lower limit of the required operational range, which could potentially impact optimal ink performance, particularly by causing uncontrolled droplet spreading, poor substrate coverage, or nozzle clogging.

- Density

The inks display an initial lower density (Figure 4, below left), followed by a marked increase after one month (1 M). Beyond this period, the density remains essentially stable across all tested conditions, with only minor fluctuations observed throughout the subsequent eight weeks. All measurements consistently remain within the predefined quality specifications, indicating that this is not a critical parameter over the monitored interval.

3.5.3. Colour Stability

The colour stability of the ink was assessed under the different storage conditions by monitoring both the reflectance spectra and the CIELAB colour coordinates (L*, a*, b*) and calculating the colour difference (ΔE) over time (8 weeks).

Figure 5 shows the reflectance spectra of indigo ink stored under the three different conditions studied.

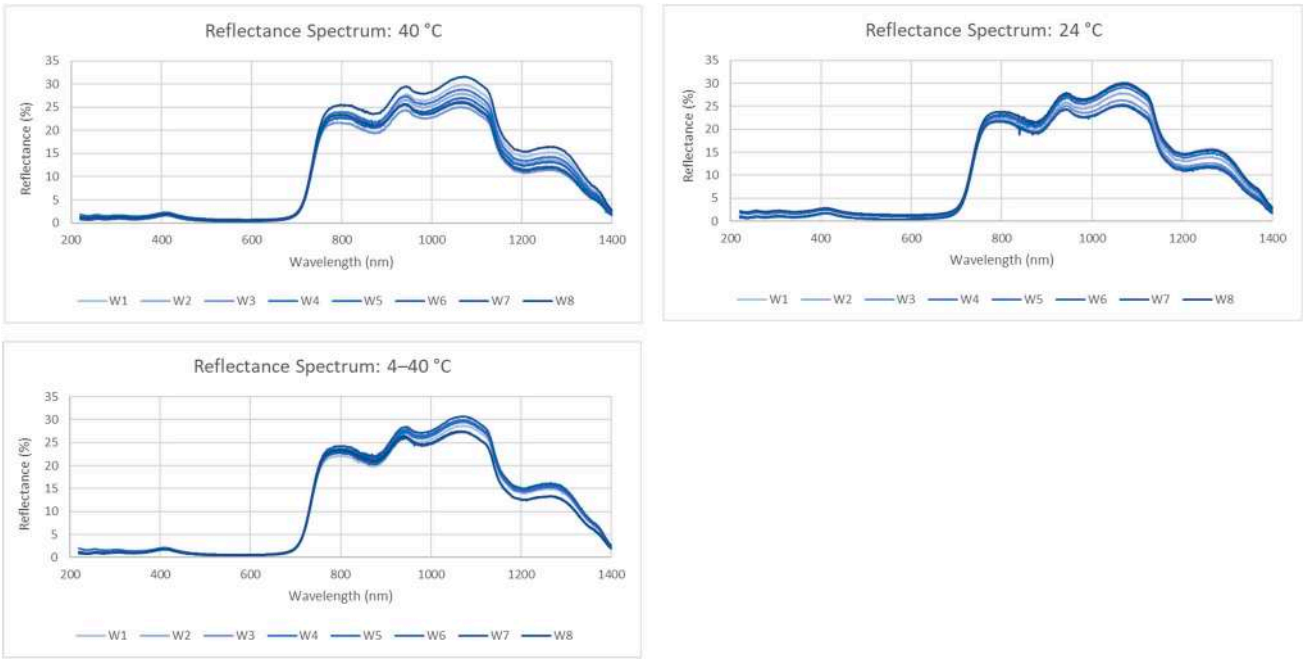


Figure 5. Reflectance spectra of indigo inkjet ink samples at three storage conditions: 40 °C, 24 °C, and 440 °C.

The spectral data reveal two prominent features in the near-infrared (NIR) region: a sharp increase in reflectance beginning near 700 nm, culminating in a main peak just above 1000 nm, followed by a broader secondary peak between 1100 and 1400 nm. Conversely, in the visible spectrum (200–700 nm), reflectance remains low and stable across all conditions. Samples stored at 40 °C exhibit the highest NIR reflectance values. Under the other conditions, 24 °C and cyclic temperatures (4–40 °C), the reflectance intensity gradually declines, particularly in the 1000–1400 nm range. Despite these quantitative changes, the spectral shape remains consistent, signifying uniformity and high reproducibility between samples. These reflectance variations likely arise from changes in the ink's microstructural or electronic properties, such as phonon activity or refractive index changes, influencing scattering and absorption in the near-infrared but not significantly affecting the visible region.

Tables 15 and 16 summarize the results for samples stored under 40 °C and 24 °C and cyclic temperature conditions (4–40 °C). The colour values after one month at room temperature were used as the reference point to evaluate potential changes during subsequent storage periods of two more months.

The evaluation of the colour coordinates (L*, a*, b*) and total colour differences (ΔE) over time revealed that all samples exhibited very minor chromatic variations across the different storage conditions. In most cases, ΔE values remained below 1.0, indicating that changes were visually imperceptible. While some isolated cases presented higher ΔE values, particularly under 40 °C (e.g., W5 with ΔE = 2.1) or after prolonged storage at room temperature (W8 days with ΔE = 5.1 at 24 °C), no consistent or statistically meaningful trends were observed when comparing storage conditions. These results suggest generally good colour stability of the ink formulation under the tested storage scenarios. However,

due to the minimal magnitude of variation and the overlapping range of ΔE values across conditions, no conclusive effect of temperature on colour degradation can be asserted based solely on these measurements. Further studies with replicate measurements and extended ageing periods would be required to validate any potential degradation trends.

Table 15. CIELAB colour coordinates (L*, a*, b*) and ΔE of the 1.0% indigo ink stored under different storage conditions over a period of up to two months. The 1-month sample at room temperature is used as the reference.

	Colour Coordinates											
	L*			**a***			**b***			**ΔE**		
1 month	4.2			3.3			−8			-		
Time/Storage conditions	40 °C	24 °C	4–40 °C	40 °C	24 °C	4–40 °C	40 °C	24 °C	4–40 °C	40 °C	24 °C	4–40 °C
W1	6.6	4.5	4.3	3.8	3.8	3.7	−8.3	−8.2	−7.9	1.6	-	0.5
W2	4.1	4.4	4.2	4.0	3.9	4.2	−8.3	−8.1	−8.1	0.8	0.7	1.1
W3	5.1	4.6	4.9	4.2	4.2	4.0	−8.1	−8.0	−8.1	1.2	1.1	0.9
W4	4.6	4.3	4.5	3.9	3.8	4.1	−8.4	−7.8	−8.0	0.8	0.6	1.0
W5	7.6	9.7	6.0	3.6	2.9	3.6	−8.6	−6.9	−8.9	2.1	3.5	1.3
W6	4.1	4.1	5.0	3.7	3.7	3.6	−8.0	−8.0	−8.3	0.5	0.4	0.6
W7	4.5	4.5	4.3	3.9	3.8	4.1	−8.6	−8.1	−8.2	0.8	0.6	1.0
W8	5.8	12.0	4.6	3.7	2.4	4.0	−8.7	−6.2	−8.3	1.1	5.1	0.8

Table 16. Particle size evolution in the 1.0% indigo ink under different storage conditions over time.

Storage Conditions	**Time**	**Particle Size**		
		PDI	**Z-AVE (nm)**	**Zeta**
40 °C	1 month	0.253	173.6	−48.1
	2 months	0.226	178.0	−45.5
	3 months	0.243	164.7	−36.1
24 °C	2 months	0.229	166.9	−42.8
	3 months	0.244	170.4	−40.8
4–40 °C	2 months	0.247	173.6	−45.4
	3 months	0.248	163.8	−31.2

Overall, the comparison of these colorimetric results with the reflectance data clarifies that, while near-infrared reflectance is sensitive to storage temperature and duration, the visible reflectance—and thus the perceived colour—remains remarkably stable. This reinforces that the ink's chromatic characteristics are well preserved under the tested conditions, supporting its reliability for applications requiring long-term colour fidelity.

3.5.4. Evolution of Particle Size and Zeta Potential

Table 16 presents the particle size distribution data, including the polydispersity index (PDI), Z-average diameter (Z-AVE), and zeta potential (Zeta), for samples stored at 40 °C, 24 °C, and under cyclic temperatures (4–40 °C).

Overall, the PDI values remained stable under all conditions evaluated, with values ranging from 0.226 (after 2 months) to 0.243 (after 3 months) at 40 °C, from 0.229 (2 months) to 0.244 (3 months) at 24 °C, and from 0.247 (2 months) to 0.248 (3 months) under temperature cycling (4–40 °C). These results demonstrate a consistently homogeneous distribution of the nanoparticles with no significant aggregation observed throughout the study.

At 40 °C, the average particle size (Z-AVE) follows a non-linear trend, increasing slightly at 2 months (178.0 nm) before decreasing to 164.7 nm at 3 months. A similar trend is observed for the 24 °C storage condition, with values of 166.9 nm at 2 months and 170.4 nm at 3 months. Under temperature cycles (4–40 °C), the particle size remains stable at 173.6 nm at 2 months and then decreases to 163.8 nm at 3 months. This reduction may indicate some restructuring or compaction of the particle system rather than aggregation.

Regarding zeta potential, the 40 °C condition shows a marked reduction in magnitude over time, shifting from −48.1 mV (1 month) to −36.1 mV (3 months), indicating a progressive decrease in colloidal stability due to diminished surface charge repulsion. At 24 °C, the zeta potential also becomes less negative over time (−42.8 mV to −40.8 mV). Under temperature cycles (4–40 °C), the greatest absolute decrease is observed, with values shifting from −45.4 mV to only −31.2 mV within 3 months, raising concerns about long-term stability due to significant charge loss.

Overall, storage at room temperature confers the highest physicochemical stability, as reflected by the consistently low PDI, stable particle sizes, and the comparatively minimal loss of zeta potential. In contrast, both elevated temperature and temperature cycles induce more substantial decreases in the absolute value of the zeta potential, signalling a higher risk of aggregation or loss of colloidal stability over time.

4. Discussion

This study demonstrates the technical feasibility of using bio-based pigments—namely, fermentation-derived indigo and a plant-extracted yellow pigment—in water-based inkjet formulations for textile, leather, and paper printing.

The dispersion and stabilization of bio-based pigments proved critical to achieve good ink quality and performance. In the case of indigo, extended mechanical milling (115 h) was essential to achieve colloidal stability, as shorter durations (5–15 h) resulted in visible sedimentation, pigment retention during filtration, and unstable ink suspensions. This prolonged milling time reflects the inherent limitations of planetary ball mills' batch-wise operation at laboratory scale, which, despite enabling the precise control of particle size distribution, exhibits lower dispersion efficiency relative to industrial systems. In production environments, pigment dispersion is typically achieved far more efficiently using high-speed pre-mixers (Cowle's dissolvers) followed by circulation bead mills or nano-mills, which deliver finer, narrower particle size distributions at substantially lower specific energy consumption through continuous operation.

Once adequately dispersed, the indigo pigment within the ink formulation demonstrated acceptable particle size (<5 μm), viscosity, and surface tension, meeting inkjet printing requirements. Conversely, the commercial yellow pigment—due to its water solubility—did not require milling, enabling a more straightforward formulation process with superior dispersion homogeneity and storage stability.

Regarding print quality and substrate interaction, both inks exhibited good printability on cotton and polyester fabrics pre-treated with either a cationic biopolymer or a polyurethane-based synthetic binder. CIELAB colour analysis confirmed that the indigo ink yielded deep blue shades with high colour uniformity, while yellow inks resulted in lighter, less saturated tones, particularly on polyester, suggesting limited pigment uptake or weaker interaction with synthetic fibres. Notably, indigo showed a slightly stronger affinity for polyester with Binder A, while yellow ink exhibited higher b* values on cotton treated with Binder A. However, differences were generally moderate, and no clear superiority was established between the pre-treatments. These findings suggest that both treatments are viable, though further optimization could tailor pigment–substrate affinity for improved performance.

Fastness results revealed a clear performance gap between the two pigment types. Indigo-based prints exhibited good to very good resistance to domestic washing, perspiration, and rubbing, with only moderate sensitivity to artificial light (grades between 1 to 4 depending on substrate and treatment). The biopolymer treatment conferred slightly better performance under artificial light on cotton, suggesting improved pigment fixation and photostability. In contrast, the yellow pigment ink showed considerably lower colour fastness, particularly under light exposure (grade 1 in most cases) and washing (grades between 1 to 3 for colour change), despite good staining resistance. These results are consistent with known limitations of nature-extracted pigments, which often suffer from limited photostability and wash durability due to their susceptibility to photodegradation, oxidation, and thermal degradation [20]. These results highlight the superior affinity and fixability of the indigo pigment, particularly when properly dispersed and paired with suitable binders.

Shelf-life analysis showed that the indigo ink remained visually and colloidally stable over three months, with minor sedimentation reversible by soft agitation. However, the viscosity decreased over time under all storage conditions, dropping below the limit after the fourth week. This progressive decrease suggests the degradation of rheological control agents or pigment interactions affecting fluidity and points to the need for viscosity stabilizers or formulation redesigns to ensure long-term stability. Surface tension showed a slight decrease after the first month; values stabilized between 31.5 and 33 mN/m for the remainder of the evaluation period, remaining within the defined operational limits. Colour stability (ΔE) remained within acceptable limits (<1.0 in most cases), indicating minimal pigment degradation. The visible reflectance, and thus the perceived colour, remained consistently stable, supporting the conclusion that the ink's chromatic properties are effectively retained under the tested conditions. Particle size and zeta potential analyses confirmed that room temperature storage offered the best colloidal stability, while thermal cycles and elevated temperatures slightly accelerated the decline in the surface charge (zeta potential), thus increasing the risk of aggregation.

5. Conclusions

This study investigated the feasibility of formulating water-based pigment inkjet inks using two distinct bio-based pigments: a fermentation-derived indigo and a plant-extracted yellow pigment. Both formulations complied with the critical physicochemical parameters required for piezoelectric printhead compatibility, namely, viscosity, density, surface tension, and particle size, and were successfully applied across diverse substrates including cotton, polyester, leather, and kraft paper, showing their versatility.

Due to the superior colour fastness results obtained, the indigo ink emerged as a robust and technically viable alternative to conventional synthetic colourants, combining a renewable origin with good printability, stability, and durability. To further enable the adoption of bio-based inks in industrial inkjet printing, future research should prioritize optimizing stabilizers and rheology modifiers to enhance long-term viscosity stability, the extension of ink shelf-life (6 months or more) in order to meet industrial requirements, the enhancement of natural pigments fastness, particularly for lighter hues, and the development of bio-based pigments across a wider chromatic spectrum. These efforts should be supported using scalable, energy-efficient dispersion technologies and the replacement of synthetic components with bio-based alternatives within the ink formulations, wherever possible. Finally, integrating Life Cycle Analysis (LCA) will be fundamental to validate the environmental and economic sustainability of these bio-based solutions and accelerate their translation into industrial practice.

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