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RESEARCH ARTICLE

# Fastness of dye-based ink-jet printing inks in aqueous solution in the presence and absence of oxygen

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**Abstract**

Photodegradation of the ink-jet prints is a complex process in which many external and internal factors are involved. Nevertheless, the role of colorants and various accompanying substances in the ink is often overlooked. Our research work aimed to determine the fastness of water-based ink-jet inks in aqueous solutions. A printing ink often contains a complex mixture of colorants to achieve optimal optical properties of color and a suitable fastness of the print. Therefore, we investigated the composition and stability of cyan, magenta, yellow, and black inks under the influence of UVC light in the presence of oxygen as well as in an inert environment based on TLC chromatography and spectrophotometric analysis. The process of photodegradation was evaluated based on ink amount and half-life. According to the results, the majority of inks consist of at least two colorants that differ in color and polarity. The results have shown that the presence of oxygen negatively affects the stability of inks; therefore, the inert atmosphere prolongs the durability of ink in water solution.

**KEYWORDS**

dyes, fastness, presence of oxygen, printing ink, UVC

## 1 | INTRODUCTION

Due to many advantages, the importance of ink-jet printing technology significantly increased over the last decades. However, the quality and durability of the print still represent a challenge.

The print quality is determined by color range, sharpness of the image and ultimately, the durability of the print. Therefore, the quality of prints depends on the penetration of ink into the paper and the binding of ink to the paper surface. Moreover, the quality of prints is primarily related to the properties of the ink and the paper as well as their interactions.[1–3] In terms of print identification and analysis, prints produced by an ink-jet printer represent an almost infinite number of combinations,[4] as the durability of prints is influenced by several interrelated internal and external factors.[5–7]

In terms of recommendations for preserving and archiving documents, it is necessary to evaluate the impact of specific external factors. In this way, it is easier to ensure appropriate storage and preservation conditions.[2] Despite extensive researches on the light fastness of materials, the process of photodegradation is still not fully understood.[8–11] Photodegradation is induced by absorption of the ultraviolet and visible parts of the spectrum. Moreover, the degradation mechanism is also determined by other factors such as temperature, humidity, chemical structure of the printing material and ink, and many others.[8,12–16] The presence of oxygen is also one of the fundamental factors in the degradation of organic materials. It leads to the formation of peroxides, which, under the influence of heat and light, form free radicals that cause an inevitable chain reaction of accelerating degradation.[13] Several studies have confirmed that anoxic conditions can slow the process of photodegradation.[6,17] Nevertheless, the process of print degradation is not explained in detail as the joint action of the substrate and ink is very complex.

Ink-jet printing inks can be described as dilute solutions containing one or more colorants, roughly classified as pigment-based or dye-based inks.[3,18] The pigments are solid particles dispersed in the carrier liquid, whereas the dyes are dissolved in an appropriate solvent mixture. However, given their lightfastness, pigment-based inks have proven lightfastness over the years compared to dyes. The most common dye structures found in ink-jet inks are azo, cyclic or polycyclic quinones, indigo dyes, cyanines, and phthalocyanines. In addition to azo and phthalocyanine structures, quinacridone-based compounds are also found among the pigments.[11,18]

The primary function of the printing ink is to transfer the colorant to the printing material. Therefore, ink-jet printing inks are composed of several components such as colorant, deionised water and/or organic solvents, dispersants, buffers, anti-foaming agents, biocides and binders, each with its own specific function.[4,19,20]

The aim of our study was a systematic analysis of commercial dye-based cyan (C), magenta (M), yellow (Y), and black (K) ink-jet inks in the aqueous solution. The aqueous solutions of dyes were exposed to UVC radiation in the presence and absence of oxygen. Moreover, we carried out TLC analysis and spectrophotometrical measurements to determine the presence of different dyes in the ink-jet inks. We calculated the ink amount and half-life of the inks in a water solution based on the measurements to follow the process of photodegradation.

## 2 | EXPERIMENTS

Two ink-jet printers (Canon Pixma iP7250 (T1) and Epson L130 (T2)) were included in our experimental part. Both of them use water-based ink-jet inks. The first printer (T1) uses four primary color cartridges with dye-based ink whereas the second one (T2) uses five cartridges with four primary color and the fifth black cartridge with pigment-based ink.

A sample of individual dye-based ink (C, M, Y, K) based were taken directly from the cartridge using the syringe and diluted 1:3000 with water.

For irradiation of water solutions of ink, we have used a high-pressure mercury lamp. The spectral radiant intensity ($I_{es}$) of the lamp was previously measured between 180 and 1100 nm. Assuming that the lamp radiates evenly in all directions, we calculated the total radiant intensity ($I_e = 1.36$ W/sr) and the total radiant flux ($\Phi_e = 20.43$ W). A particular reactor was used, which enables the water cooling of the lamp between operation. The reactor was made of two parts: the first part was a water cooling refrigerator with a reactor, and the second part was a high-pressure mercury lamp (Figure 1). Such approach enabled to maintain the samples' temperature between 16 and 20°C, although they were only 2 cm away from the lamp.

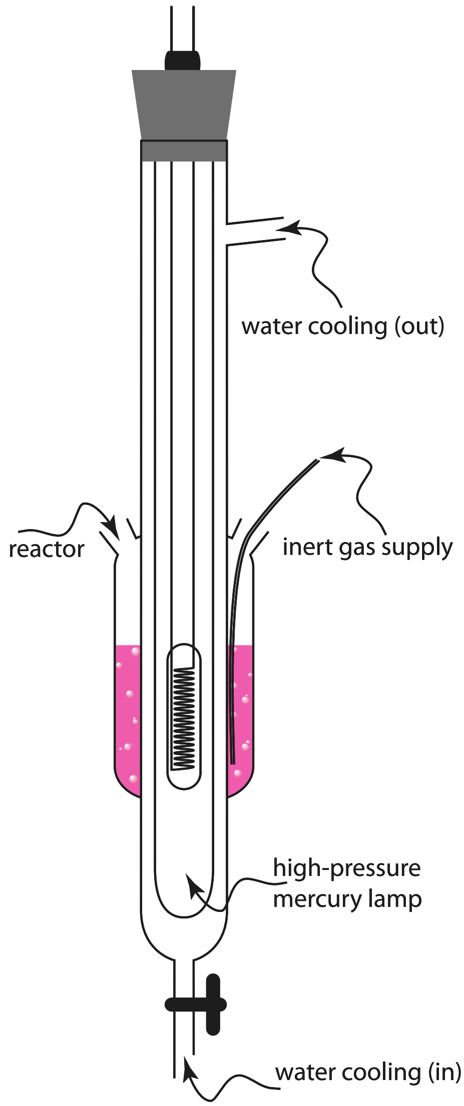


**FIGURE 1** Scheme of reactor during operation of the high-pressure mercury lamp

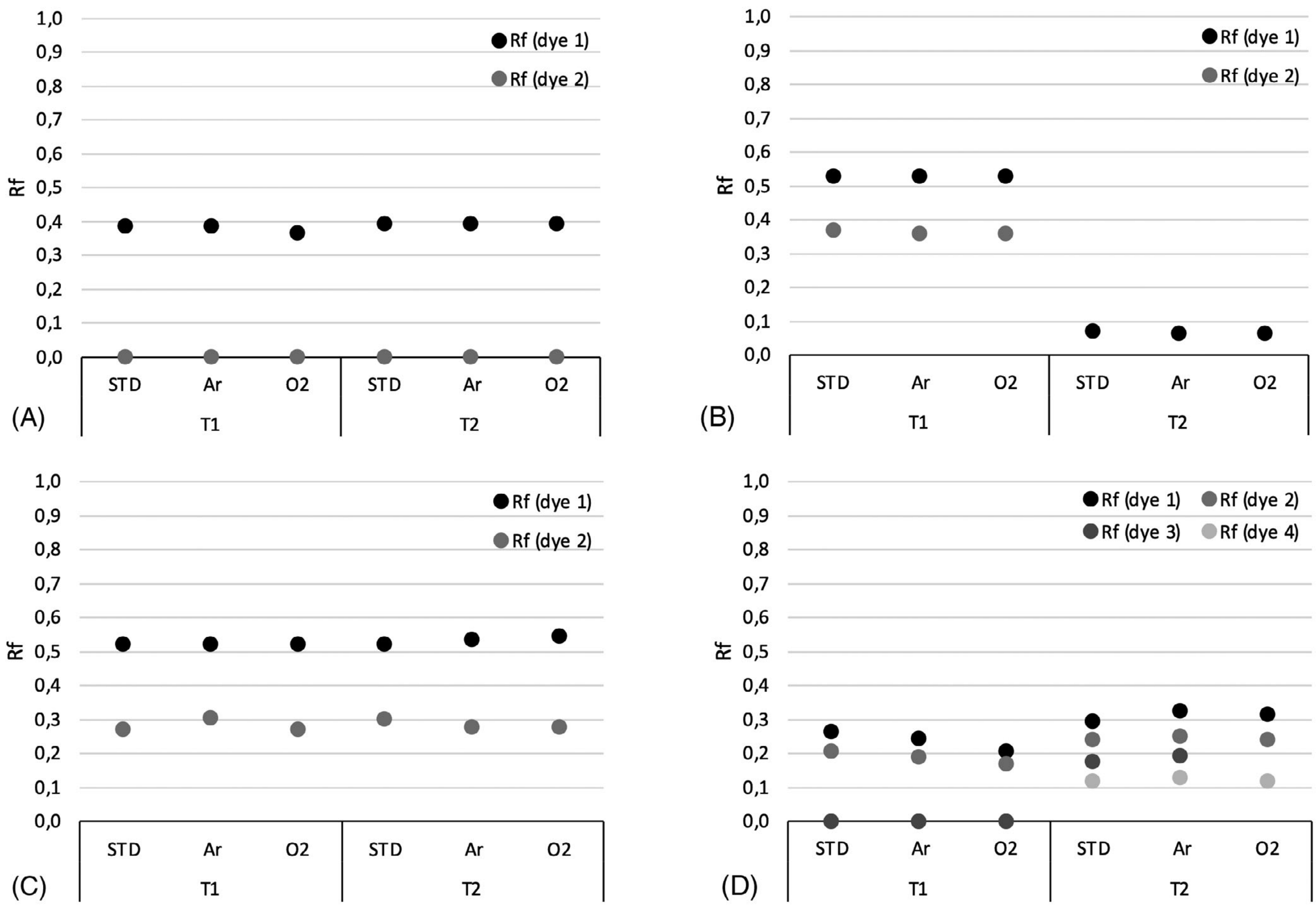


**FIGURE 2** TLC analysis of (A) cyan, (B) magenta, (C) yellow, and (D) black color inks for printer T1 and T2 before (STD) and after 15 min of radiation in an inert (Ar) and oxygen-enriched ($O_2$) environment

About 30 ml of dye solution was poured into the reactor and exposed for 15 min to the radiation of the lamp. Two repetitions in the presence of oxygen or inert gas (Ar) were performed.

After the exposure, the measurements of transmissivity in the range between 220 in 900 nm were performed using UV/VIS spectrophotometer Cary 1E (Varian, USA).TLC chromatography was performed with the silica-coated aluminum plates (Sigma-Aldrich, DE) as a stationary phase. As a mobile phase, the mixture of ethyl acetate, ethanol, and water (70:35:30) was used for magenta, yellow, and black inks, whereas for cyan the mixture of ethyl methyl ketone, acetone, and water (7:5:3) was used. The retention factor (Rf) was calculated. We have also monitored the kinetics of photodegradation following the process after 5, 10, and 15 min of irradiation. Based on the measurements, the ink amount (IA) after 15 min of irradiation was calculated according to Equation (1),

$$\mathrm{IA}\,(\%) = \frac{A_i}{A_0} \times 100\% \qquad (1)$$

where, IA is the calculated ink amount, $A_i$ represents the absorption value after and $A_0$ represents the absorption value before irradiation.

## 3 | RESULTS AND DISSCUSION

Figure 2 shows TLC analysis of cyan, magenta, yellow, and black color inks before (STD) and after 15 min of irradiation in an inert (Ar) and oxygen-enriched ($O_2$) environment. Results show that dye-based printing inks consists of at least two colored components.

Figure 3 shows the absorption spectra of dye-based inkjet printing inks in an aqueous solution. Under the influence of irradiation with a high-pressure mercury lamp, we observe the influence of oxygen ($O_2$) on the samples, which is primarily manifested in the visible part of the spectrum.

Both cyan inks showed only negligible changes in absorption spectra (Figure 3A,B). The cyan ink T1 has a very pronounced absorption maximum in the visible spectrum at 610 and at 683 nm. Cyan ink T2 has two absorption maxima at 614 and 695 nm. According to TLC

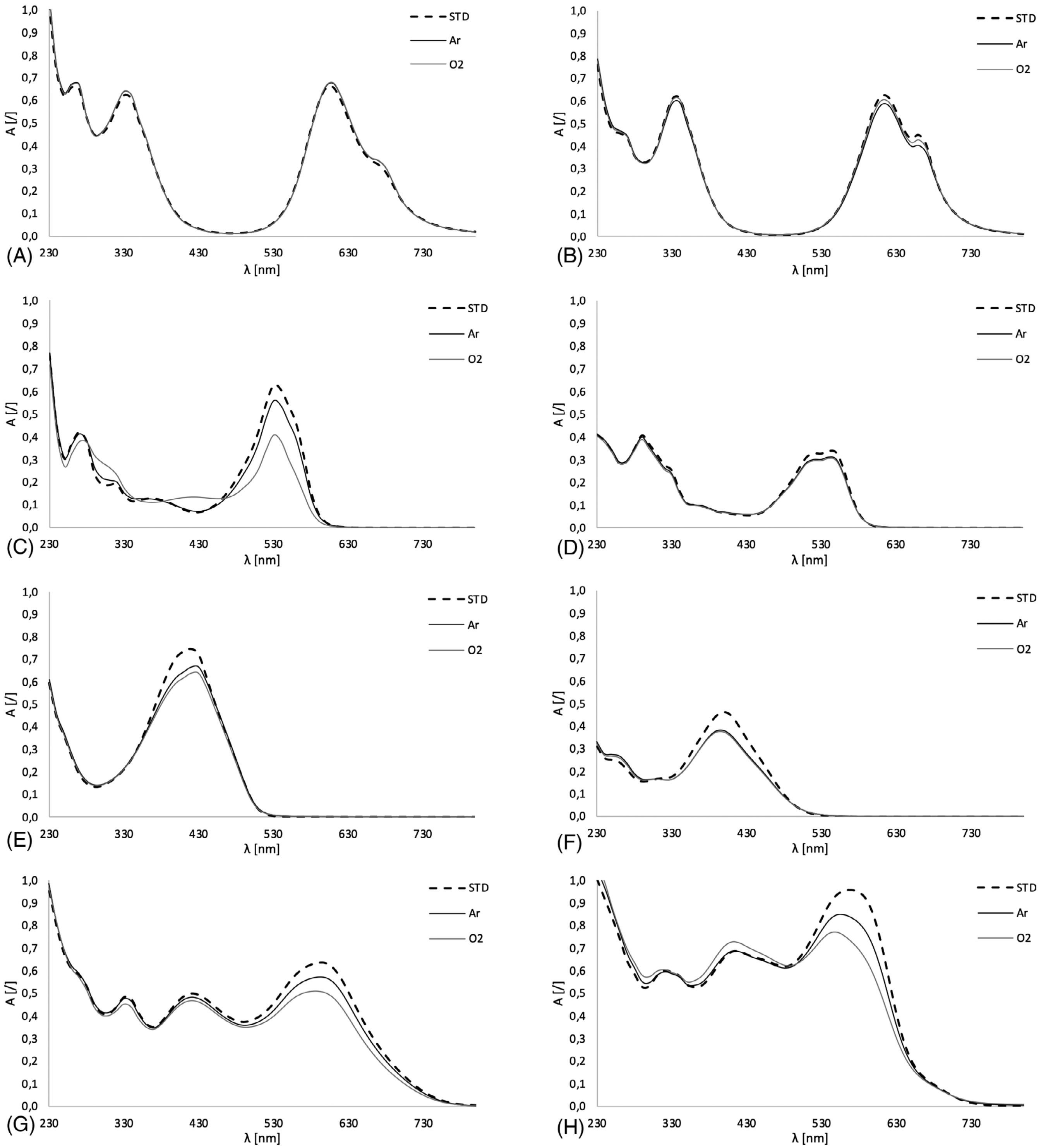


**FIGURE 3** Absorption spectra of (A) cyan T1, (B) cyan T2, (C) magenta T1, (D) magenta T2, (E) yellow T1, (F) yellow T2, (G) black T1, and (H) black T2 color inks before (STD) and after 15 min of radiation in an inert (Ar) and oxygen-enriched ($O_2$) environment

separation (Figure 2A), the structural composition of the cyan inks T1 and T2 is probably very similar. After 15 min of irradiation in an oxygen-enriched environment, we observe a slightly more significant influence of oxygen on one of the components of cyan ink T1. The most commonly used cyan dye for inkjet printing is C.I. DB199 ($\lambda_{max}$ = 610 nm).[18,20,21] However, our samples were very likely a mixture of at least two dyes, so in addition to C.I. DB199, the presence of C.I. DB86 ($\lambda_{max}$ = 695 nm) is also posible.[18]

Magenta ink T1 (Figure 3C) has a clear absorption maximum at 530 nm, and magenta ink T2 (Figure 3D) has two maxima in the visible part of the spectrum at 519 and 544 nm. The negative effect of oxygen is most notable for the magenta T1 sample, as the intensity of the absorption spectrum decreases by 35% in 15 min. According to TLC analysis (Figure 2B), the composition of magenta inks T1 and T2 differs as T1 consists of at least two color components and T2 of probably only one color component. It can be assumed (Figure 3) that magenta ink T2 includes C.I. RR180, which is characterized by absorption maxima at 544 and 520 nm.[22] C.I. RR180 dye is considered the most used dye, either alone or in combination, commonly with C.I. AR52.[23] The magenta ink T1 is very likely to be a mixture of C.I. RR120 ($\lambda_{max}$ = 530 nm) and C.I. BV10 ($\lambda_{max}$ = 543 nm).[24]

**TABLE 1** Ink amount (IA) for aqueous solution of inks T1 and T2 after 15 min of radiation in an inert (Ar) and oxygen-enriched ($O_2$) environment

| | | IA (%) | | | |
|---|---|---|---|---|---|
| | | Cyan | Magenta | Yellow | Black |
| T1 | Ar | 102 | 89 | 89 | 90 |
| | $O_2$ | 103 | 65 | 86 | 80 |
| T2 | Ar | 94 | 92 | 82 | 87 |
| | $O_2$ | 96 | 90 | 81 | 76 |

Both yellow inks T1 (Figure 3E) and T2 (Figure 3F) samples have one pronounced absorption maximum at 422 (T1) or 399 nm (T2), respectively. The negative effect of oxygen is notable at both samples, as the intensity of the absorption spectrum decreases by 15% for yellow T1 and by 20% for yellow T2 in 15 min. According to the TLC analysis (Figure 2C), the composition of yellow inks T1 and T2 is very similar. It can be assumed,[23,25,26] that yellow ink T1 is a mixture of dyes C.I. RY85 ($\lambda_{max}$ = 422 nm) and C.I. AY23 ($\lambda_{max}$ = 425 nm), whereas ink T2 could be a mixture of C.I. AY79 ($\lambda_{max}$ = 400 nm) and C.I. DY86 ($\lambda_{max}$ = 346 nm).

Both black samples (Figure 3G,H) exhibited significant absorption spectra changes. The negative effect of oxygen is most notable at the T2 sample, as the absorption maxima decrease by 24% in 15 min. The absorption maximum of this sample (T2) shows a noticeable shift towards shorter wavelengths (567–546 nm). According to TLC analysis (Figure 2D), both black inks are a mixture of yellow, blue, violet, and black dye. It is very likely[27,28] that those inks are a mixture of C.I. RB31 and C.I. DB168 combined with direct yellow dye C.I. DY86 or C.I. DY132. Consequently, an appropriate hue can be achieved by including different dyes, whereas adding black pigment and cyan dye improves prints' colorfastness.[27]

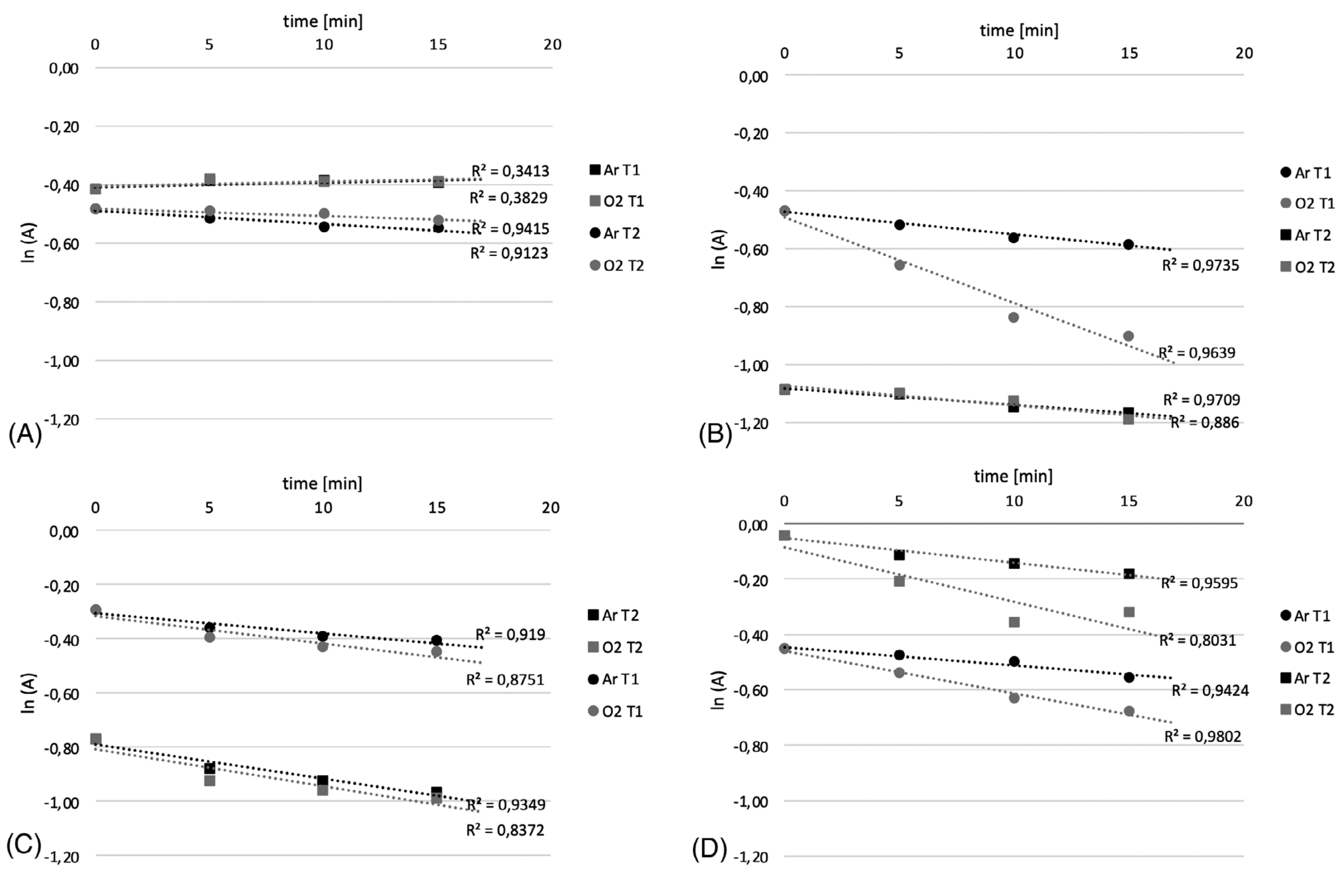


**FIGURE 4** Rate of degradation of (A) cyan, (B) magenta, (C) yellow, and (D) black color inks for printer T1 and T2 under the influence of a high-pressure mercury lamp in an inert (Ar) and oxygen-enriched ($O_2$) environment

**TABLE 2** Coefficient ($k$) and half-life ($t_{1/2}$) for the ink samples T1 and T2 under the influence of a high-pressure mercury lamp in an inert (Ar) and oxygen-enriched ($O_2$) environment

| | | Cyan | | Magenta | | Yellow | | Black | |
|---|---|---|---|---|---|---|---|---|---|
| | | $k$ [$s^{-1}$] | $t_{1/2}$ [min] | $k$ [$s^{-1}$] | $t_{1/2}$ [min] | $k$ [$s^{-1}$] | $t_{1/2}$ [min] | $k$ [$s^{-1}$] | $t_{1/2}$ [min] |
| T1 | Ar | 0.0014 | 495 | −0.0078 | 89 | −0.0074 | 94 | −0.0067 | 103 |
| | $O_2$ | 0.0015 | 462 | −0.0297 | 23 | −0.0101 | 69 | −0.0153 | 45 |
| T2 | Ar | −0.0024 | 289 | −0.0057 | 122 | −0.0126 | 55 | −0.0089 | 78 |
| | $O_2$ | −0.0045 | 154 | −0.0067 | 103 | −0.0137 | 51 | −0.0196 | 35 |

The negative effect of oxygen on the aqueous solutions of ink-jet inks is also reflected in the calculated IA values (Table 1), which are compared to the IA values of samples irradiated with mercury lamp in an inert atmosphere.

The results show that the degradation process was somehow different in the case of cyan inks, which are assumed to be a mixture of phthalocyanine-based dyes (C.I. DB199 and C.I. DB86).[18,20] The so-called redshift or bronzing degradation is particularly noticeable in the case of T1 cyan inks during irradiation in an inert atmosphere and an oxygen-enriched atmosphere; the IA value exceeds 100%. This phenomenon is characteristic of dyes with a higher tendency to aggregate or of dyes with a lower solubility in water.[5,29] In addition, the ozone as a by-product of irradiation with UV lamps, additionally affects the photodegradation of phthalocyanine.[30]

According to the results, the photodegradation reaction very likely follows the pseudo-first-order kinetic model for best fit. Figure 4 shows the parameters which describe the rate of degradation of the ink samples under the influence of a high-pressure mercury lamp in an inert atmosphere and in the presence of oxygen. From the slope ($k$) of the line, the degradation rate and half-life ($t_{1/2}$) were determined (Table 2). The degree of photodegradation was most notable in the case of the magenta ink T1 and both black inks. On the other hand, the degradation of cyan ink was less evident and occurred very similarly both in the presence of oxygen and in an inert atmosphere. Generally, the inert environment slightly slows down the rate of photodegradation, this effect is most pronounced in the case of magenta ink T1 and black ink T1. Thus, we can conclude that the presence of oxygen influences the stability of color solutions and that the inert atmosphere prolongs the durability of ink.

## 4 | CONCLUSION

Ink-jet inks are a complex mixture of several components, which in their specific way influence the process of photodegradation. Therefore, the evaluation or monitoring of the photodegradation process is even more demanding when external factors which initiate this, usually irreversible, process are included.

The photodegradation of cyan, magenta, yellow, and black commercial dye-based ink-jet printing inks in aqueous solution was studied using relatively simple analytical methods, which proved to be very supportive as they enabled both detections of colored components, which were formed during the photodegradation process and calculation of parameters that describe the kinetics of the process.

According to the results, each of the ink studied consists of at least two colorants, with the exception of one magenta ink. As expected, some of the inks were more long-lasting than others. Furthermore, the influence of UVC radiation proved to be particularly destructive. In addition, the presence of oxygen had an additional negative effect on the stability of inks; therefore, the inert atmosphere could prolong the durability of ink in the water solution.

## AUTHOR CONTRIBUTIONS

**Barbara Blaznik** Experimentation, Methodology, Calculation, Writing – original draft. **Franci Kovač** Supervision, Experimentation, Methodology, Writing – Reviewing and Editing. **Grega Bizjak** High-pressure mercury lamp measurements and calculation, Writing – Reviewing and Editing. **Sabina Bračko** Supervision, Methodology, Writing – Reviewing and Editing.

## DATA AVAILABILITY STATEMENT

The data used to support the findings of this study are available from the corresponding author upon request. The data are not publicly available due to privacy restrictions.

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