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Exploring changes in browning kinetics, color, and antioxidants due to dealcoholization of wine

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Abstract. The growing global demand for partially or non-alcoholic wine is driven by health concerns, religious beliefs, and personal preferences. However, the removal of alcohol significantly modifies the wine's chemical and sensory properties, posing challenges for consumer acceptance. This research investigates the kinetics of browning (A420 nm) and its correlation with ethanol reduction, alongside the effects on color stability, antioxidant capacity, phenolic profile, SO_2, and oxygen consumption during aging of three types of wines: white, red, and rosé wines. Results demonstrated that browning at 420 nm and color intensity follow zero-order kinetics. Dealcoholized (<0.5% v/v) white ($18*10^{-4}$) and rosé ($31*10^{-4}$) wines showing the highest browning rates, indicating a significant impact of alcohol removal. Similar trend was observed for color intensity. Red wine exhibited no significant changes in color parameters due to a short 28-day storage period. Phenolics content decreased linearly with storage time, fitting a zero-order model ($R^2 = 0.865$ to 0.986), and positively correlated with antioxidant capacity ($r = 0.709$-0.959, $R^2 = 0.722$-0.999) in the three types of wine. Anthocyanin content decreased significantly in rosé and red wines, while white wines showed minimal changes due to initial very low anthocyanin content. Oxygen consumption followed first-order kinetics. Original red and rosé wines had lower oxygen consumption rates (OCRs) during aging compared to both partially and dealcoholized wines. For white wine, dealcoholized products exhibited the lowest OCRs (0.054 mg O_2/L/day), while original white wines had the highest (0.064 mg O_2/L/day). OCRs were positively correlated with free SO_2 ($r > 0.94$), total SO_2 ($r > 0.85$), total phenols ($r > 0.91$), antioxidant activity ($r > 0.80$), and pH ($r > 0.92$). Free and total SO_2 significantly decreased during storage, with reductions positively correlated with total phenols, antioxidant activity, oxygen, and pH.

1. Introduction

The International Organization of Vine and Wine (OIV) has introduced two key resolutions: OIV-ECO 432-2012, "Beverage obtained from the Dealcoholization of Wine," and OIV-ECO 433-2012, "Beverage obtained from the Partial Dealcoholization of Wine" [1]. Partial vacuum evaporation, membrane techniques, and distillation are among the dealcoholization methods approved in resolution OIV-OENO 394A-2012. A beverage resulting from the dealcoholization of wine may have an alcohol content by volume lower than 0.5% v/v, whereas a beverage resulting from the partial dealcoholization of wine may have an alcohol strength by volume equal to or greater than 0.5% v/v but lower than the minimum applicable alcoholic strength by volume for wine or special wine.

The European union (EU) recently created categories for products to be marketed under the legal names "dealcoholized wine" and "partially dealcoholized wine," defined as having actual alcoholic strengths of "no more than 0.5% v/v ethanol" and "above 0.5% v/v ethanol and below the minimum actual alcoholic strength of the wine category," respectively [2]. The label must include the actual alcoholic strength of partially or totally dealcoholized wines, as well as the minimum durability date or a 'use by' date. As regulatory standards for these wine products tighten, it is crucial to bridge these regulations with scientific research on storage effects, particularly oxidation phenomena, to ensure product quality.

The control of wine oxidation is crucial during both production and storage, as it significantly impacts the wine's quality and sensory attributes. Wine oxidation involves the interaction between oxygen and wine components, primarily polyphenols, which undergo oxidative reactions that can alter the wine's color, aroma, and taste. In red wines, oxidation generally stabilizes color, reduces astringency, and enhances the aroma profile. Conversely, in white wines, oxidation often leads to browning, a loss of fruity aromas, and the development of off-flavor [3,4]. The primary factors influencing oxidation include the wine's chemical composition, the presence of metal ions such as iron and copper, and the levels of antioxidants like sulfur dioxide (SO_2) and polyphenols. The mechanism of wine oxidation primarily involves the interaction of oxygen (O_2) with wine polyphenols, mediated by metal catalysts like iron (Fe) and copper (Cu). Oxygen does not directly react with polyphenols due to its electronic configuration; instead, Fe cycles between its ferrous (Fe (II)) and ferric (Fe (III)) states, with O_2 oxidizing Fe (II) to Fe (III), which then oxidizes polyphenols. Copper further accelerates this oxidation [5,6]. Sulfur dioxide (SO_2) plays a dual role by reducing quinones back to polyphenols and reacting with hydrogen peroxide (H_2O_2), preventing further oxidative damage. The interaction between polyphenols and oxygen generates H_2O_2 and quinones, with SO_2 reacting in a 2:1 molar ratio with H_2O_2 and quinones under ideal conditions [7,8]. The Fenton reaction, involving catalytic iron, converts H_2O_2 into hydroxyl radicals, leading to strong and less selective oxidants that react with the first reducible substrate it encounters, which in wine is ethanol due to its abundance, producing acetaldehyde.

The dealcoholization process significantly alters both the volatile and non-volatile profiles of wine, with far-reaching implications for wine quality, stability, and sensory characteristics [9]. As ethanol is removed, the concentrations of fixed compounds such as acids, salts, and polyphenols change due to concentration effects. It is indicated that 1% vol. alcohol removal corresponds approximately to 1.1% concentration. So reducing a wine with 13% to 0.5 corresponds to minimum 13.75% concentration [10]. These compositional changes can significantly impact the wine's oxidation phenomena, potentially accelerating browning reactions and altering color stability. This study aimed to investigate the kinetic aspects of browning development (A420 nm) and its correlation with the reduction in ethanol concentration. In addition, to understand the influence of ethanol on color stability, antioxidant capacity, and phenolic profile during aging. These experimental findings expand the knowledge of browning phenomena, oxidation processes, and color stability in wines post-ethanol removal, providing critical insights for determining minimum durability or 'use by' dates.

2. Materials and methods

2.1. The wines

Three wines were used in the study: a Merlot red wine (vinified in 220 L oak barrel for 7 months, 13.15% v/v), a Pinot Noir rosé wine (vinified in stainless steel, 12.92% v/v), and a Riesling white wine (vinified in stainless steel, 13.13% v/v), all from the 2022 vintage produced at Hochschule Geisenheim University winery.

2.2. Dealcoholization with Vacuum Distillation

The dealcoholization of all three wines was conducted using Hei-VAP Industrial Rotary Evaporators (Heidolph Instruments GmbH & Co. KG, Germany). This system was equipped with a heating bath accommodating water for temperature settings up to 180 °C, a vacuum pump (Hei-Vac Valve Industrial) to evacuate, evaporate, and pump out gases and vapors, and a chilling system (Hei-CHILL 3000) for condensation. The dealcoholization process was performed at 50 mbar vacuum pressure, with a water bath temperature of 50 °C, and a feed flask rotation speed of 70 rpm. Each wine was dealcoholized to ethanol levels of 6% v/v and below 0.5% v/v. The volume loss during the process is mentioned in Table 1.

Table 1. Volume loss (%) during wine dealcoholization.

Type of wine	EtOH content	Sample name	Volume loss (%)
White	13% v/v	OW-White	-
	6% v/v	PDW-White	16.1
	<0.5% v/v	DW-White	30
Rosé	13% v/v	OW-Rosé	-
	6% v/v	PDW- Rosé	19.7
	<0.5% v/v	DW- Rosé	37
Red	13% v/v	OW- Red	-
	6% v/v	PDW- Red	19.5
	<0.5% v/v	DW- Red	35

2.3. Bottling and storage

Sulfur dioxide (SO_2) was added to the original wine and dealcoholized wines to achieve a free SO_2 concentration of 30 mg/L. The wines were bottled using a heat exchanger at 62°C for 10-15 seconds in 200 mL glass bottles (without headspace) under screw cap closures. Subsequently, the samples were stored for 28 days under controlled heating at a constant temperature of 35 ± 1°C in the Climatic Hood, all under conditions of darkness.

2.4. O_2 measurement

An OXI-330 dissolved oxygen meter, equipped with a Dissolved Oxygen Probe (CellOx 325 from Xylem Analytics Germany), was utilized for measurements following the procedure outlined by Danilewicz [11].

2.5. Spectrophotometric measurement

The color parameters, including absorbance at 420, 520 and 620 nm, as well as color intensity (420+520+620 nm) were measured using a photoLab® 7600 UV-VIS spectrophotometer (Xylem Analytics Germany). Total polyphenol content (as mg/L (+)-catechin equivalents, CE) in wine samples was determined using the Folin–Ciocalteu (FC) reagent as described by Paixao et al. [12]. Antioxidant capacity (AC) was determined as mmol/L of Trolox equivalents (TE) according to the ABTS$^{\cdot+}$ method [12,13]. Total polymeric pigments (large polymeric pigments (LPP) + small polymeric pigments (SPP)) and total anthocyanins (expressed as mg/L malvidin-3-glucoside) were measured as previously detailed by Casassa et al. [14] and Harbertson et al. [15].

2.6. Free and total SO_2 measurement

Free and total SO_2 in wine samples were determined using the method suggested by Mulani et al. [16], with minor modifications. Briefly,

Free sulfur dioxide: A 25 mL wine sample was pipetted into a conical flask. To this, 5 mL of 25% sulfuric acid and 2 mL of starch indicator were added. The solution was then titrated with a 1/128 N iodine solution until a blue color appeared.

Total sulfur dioxide: A 25 mL wine sample was pipetted into a conical flask, and 5 mL of 15% caustic soda was added. The flask was shaken well and left for 15 minutes. After this, 10 mL of 25% sulfuric acid and 2 mL of starch indicator were added. The solution was then titrated with a 1/128 N iodine solution until a blue color appeared.

Free & total SO_2 (mg/L) = (Volume of iodine solution (mL) x Normality of iodine solution x 32000) / Volume of wine same (mL) (1).

2.7. Statistics

All measurements were conducted in triplicate, and mean values along with standard deviations (± SD) were calculated. Figures were generated using Excel software. Error bars representing ± SD are included in all relevant figures.

3. Results and discussion

The study examines the influence of ethanol concentration on the kinetic behavior of color parameters (including absorbance at 420, 520, and 620 nm, and color intensity), total phenols (TP), antioxidant capacity, and oxygen consumption in white, rosé, and red wines over 28 days under controlled conditions. To ascertain the reaction order, the integrated kinetic equations for zero, first, and second orders were tested to find the best fit for the experimental data (data not shown). The results indicated that oxygen consumption follows first-order kinetics, while the other parameters exhibit zero-order kinetics, showing a linear increase over time for absorbance at 420 and 520 nm, and color intensity. The total phenols and antioxidant capacity exhibited a linear decrease over time.

3.1. Evolution of color parameters, total phenolics, antioxidant activity, total anthocyanins, and polymeric pigments during accelerated aging in bottle

The results indicated that during storage under dark conditions at 35 °C, white wines showed an increase in yellow pigments (Abs 420 nm), while red pigments (Abs 520 nm) remained unchanged, leading to an increase in color intensity (CI) (figure 1 (A, B and D)). This increase in yellow pigments is probably due to the oxidation and polymerization of phenolic compounds, forming yellow-brown pigments [17]. In contrast, rosé wines exhibited increases in both yellow (Abs 420 nm) and red pigments (Abs 520 nm), resulting in a higher CI over time (figure 2 (A, B and D)). The higher anthocyanin content in rosé wines leads to reactions such as copigmentation, formation of pyranoanthocyanins, and polymerization with other phenolic compounds, enhancing color intensity and stability. Oxidation reactions also contribute to the formation of yellow-brown pigments in rosé wines, similar to white wines.

The linear increasing trend observed in the data (for abs 420 nm and CI) aligns well with a zero-order reaction model, with R^2 values ranging from 0.849 to 0.996. Rate constants (k) were graphically determined from the slopes of the regression lines. Higher ethanol concentrations (13% v/v) in both white and rosé wines resulted in lower kinetic rates (Table 2) for A420 nm and CI compared to wines with lower ethanol concentrations (6% and 0.5% v/v), suggesting that ethanol may slow down the degradation or transformation processes affecting color intensity and absorbance. Additionally, an increase in color parameters was observed due to the removal of alcohol and the concentration effect of the wine.

The change in browning can be explained by rate of $HO^\bullet$ reaction, react with the first possible substrate it comes into contact with near its production site at diffusion controlled rates [18]. Generally, in white wine ethanol is the first potential substrate and it is followed by acids (specifically tartaric acid) according to their molarity. In dealcoholized wine, the primary substrate available is likely to be tartaric acid, radicals may react with tartaric acid and form yellow xanthylium cations in the presence of catechin [19]. Briefly, glyoxylic acid that is formed from the oxidation of tartaric acid, can react with two (+)-catechin to produce colorless dimer that eventually form yellow xanthylium cations [20–24].

Table 2. Changes in pH, total SO_2, anthocyanin content, and polymeric pigments during bottle storage of different wines.

Type of Wine	Sample name	Day	pH	Total SO_2 (mg/L)	Anthocyanin content (mg/l MAE)	Polymeric pigments (AU@520nm)
White	OW-White	1	3.05 ± 0.02^{a}	109.9 ± 0.26^{a}	1.9 ± 0.00^{a}	0.01 ± 0.00
		16	2.67 ± 0.04^{b}	101.7 ± 1.52^{b}	1.6 ± 0.57^{ab}	-
		28	2.62 ± 0.02^{b}	92.0 ± 0.40^{c}	1.3 ± 0.57^{ab}	-
	PDW-White	1	3.01 ± 0.02^{a}	104.7 ± 0.36^{a}	1.6 ± 0.57^{a}	0.01 ± 0.00
		16	2.54 ± 0.01^{b}	102.2 ± 0.53^{ab}	1.6 ± 0.57^{a}	-
		28	2.50 ± 0.03^{b}	97.0 ± 1.00^{b}	1.6 ± 0.57^{a}	-
	DW-White	1	2.90 ± 0.0^{a}	128.6 ± 0.71^{a}	1.6 ± 0.57^{ab}	0.01 ±0.00
		16	2.48 ± 0.02^{b}	119.8 ± 0.25^{b}	1.9 ± 0.00^{a}	0.01 ± 0.00
		28	2.43 ± 0.01^{c}	109.7 ± 1.42^{c}	1.3 ± 0.57^{ab}	0.01 ± 0.00
Rosé	OW-Rosé	1	3.51 ± 0.01^{a}	82.8 ± 0.56^{a}	9.5 ± 0.57^{a}	0.02 ± 0.00
		16	3.38 ± 0.02^{b}	81.5 ± 0.50^{a}	8.8 ± 0.00^{a}	0.02 ± 0.00
		28	3.34 ± 0.03^{b}	72.2 ± 0.97^{b}	7.5 ± 0.57^{b}	0.02 ± 0.00
	PDW- Rosé	1	3.39 ± 0.01^{a}	78.5 ± 0.50^{a}	10.5 ± 1.50^{a}	0.04 ± 0.00
		16	3.29 ± 0.02^{ab}	70.2 ± 0.31^{b}	9.5 ± 0.57^{a}	0.04 ± 0.00
		28	3.25 ± 0.03^{ab}	65.1 ± 1.01^{c}	8.8 ± 0.00^{ab}	0.04 ± 0.00
	DW- Rosé	1	3.33 ± 0.01^{a}	73.7 ± 0.42^{a}	13.1 ± 0.57^{a}	0.05 ± 0.01
		16	3.25 ± 0.02^{b}	68.4 ± 1.02^{b}	12.7 ± 0.98^{ab}	0.05 ± 0.00
		28	3.17 ± 0.01^{c}	60.1 ± 0.95^{c}	11.1 ± 0.57^{b}	0.05 ± 0.00
Red	OW- Red	1	3.34 ± 0.01^{a}	51.0 ± 0.50^{a}	278.4 ± 7.84^{a}	1.48 ± 0.00
		16	3.28 ± 0.01^{b}	45.4 ± 1.10^{b}	269.6 ± 11.89^{ab}	1.47 ± 0.02
		28	3.22 ± 0.01^{c}	44.4 ± 1.40^{b}	248.4 ± 7.36^{b}	1.58 ± 0.0
	PDW- Red	1	3.22 ± 0.01^{a}	56.0 ± 0.80^{a}	332.3 ± 2.59^{a}	1.74 ± 0.02
		16	3.16 ± 0.01^{b}	48.1 ± 1.03^{b}	315.4 ± 5.91^{b}	1.70 ± 0.01
		28	3.09 ± 0.01^{c}	45.0 ± 0.93^{c}	298.7 ± 4.08^{c}	1.76 ± 0.03
	DW- Red	1	3.14 ± 0.01^{a}	57.3 ± 0.87^{a}	413.4 ± 4.93^{a}	1.96 ± 0.03
		16	3.05 ± 0.01^{b}	51.0 ± 0.33^{b}	409.8 ± 4.28^{ab}	2.02 ± 0.07
		28	3.01 ± 0.02^{c}	48.0 ± 1.00^{c}	377.8 ± 10.80^{b}	± 0.04

Table 3. Kinetic rates of browning (A_{420} nm), color intensity, total phenol, and oxygen consumption, and $SO_2:O_2$ molar reaction ratio during wine oxidation.

		A420 nm ($A_{420} = A^0{}_{420} + kt$)		Color intensity ($CI = CI^0 + kt$)		Total phenol (mg /L Catechin) ($TP = TP^0 + kt$)		$[O_2]_t = [O_2]_0\ e^{-kt}$		
Wine sample	Ethanol content	K (day^{-1}) $*10^{-4}$	R^2	K (day^{-1}) $*10^{-4}$	R^2	K (day^{-1})	R^2	K (mg O_2/L/day)	R^2	$SO_2:O_2$ molar reaction ratio
OW-White	13% v/v	13	0.944	16	0.849	-2.60	0.958	0.064	0.99	1.9:1
PDW-White	6% v/v	16	0.937	20	0.952	-2.91	0.980	0.061	0.99	1.2:1
DW-White	0.5% v/v	18	0.928	21	0.920	-1.46	0.933	0.054	0.99	2.0:1
OW-Rosé	13% v/v	22	0.990	32	0.989	-3.04	0.979	0.053	0.99	2.0:1
PDW- Rosé	6% v/v	26	0.996	37	0.992	-2.96	0.965	0.068	0.99	1.6:1
DW- Rosé	0.5% v/v	31	0.956	52	0.919	-2.16	0.953	0.063	0.99	1.9:1
OW-Red	13% v/v					-19.04	0.971	0.041	0.99	1.1:1
PDW-Red	6% v/v					-14.50	0.865	0.054	0.98	1.3:1
DW-Red	0.5% v/v					-17.51	0.986	0.054	0.98	0.9:1

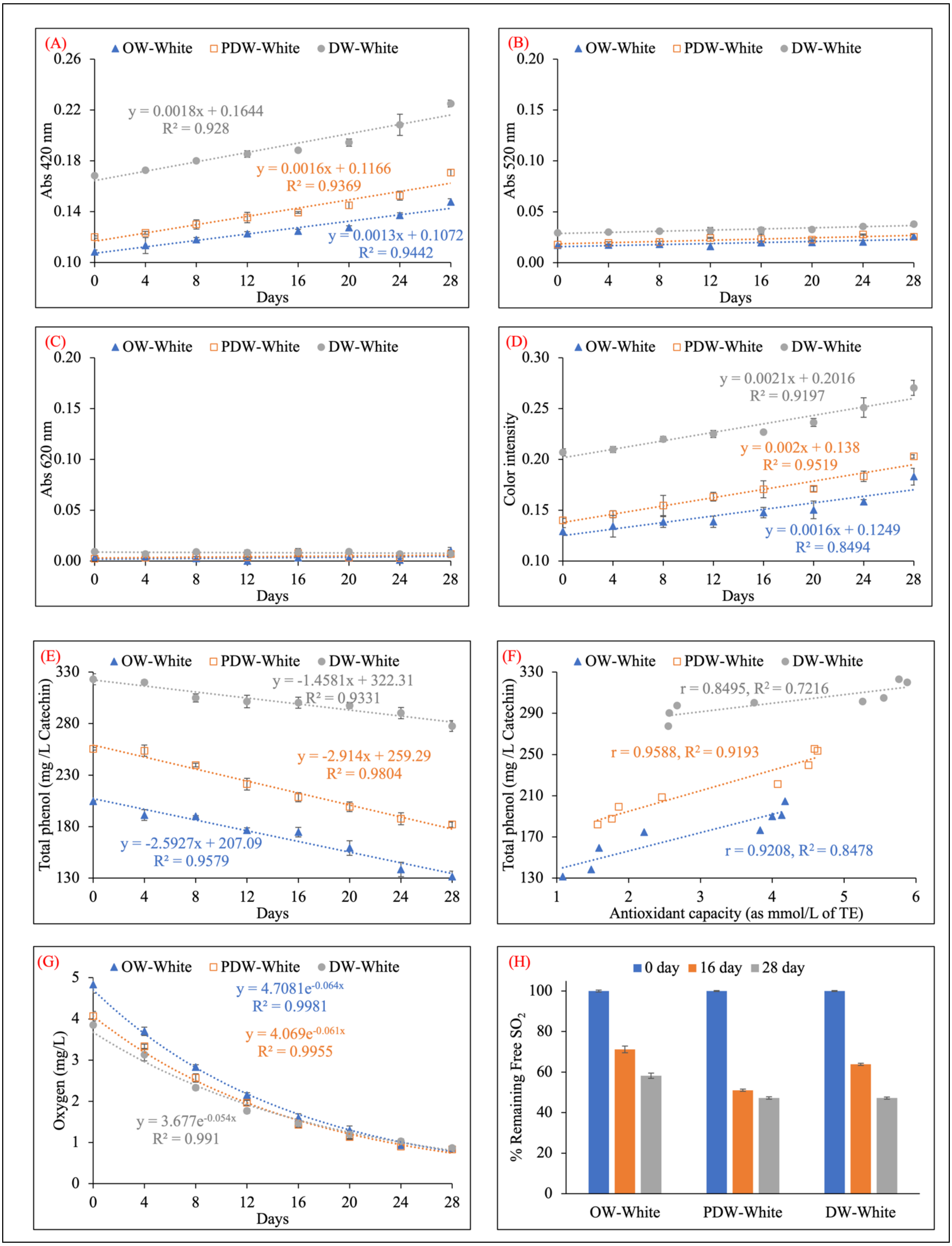

Figure 1. The changes in studied parameters of original, partially dealcoholized and dealcoholized white wines during storage at 35°C. (A) 420 nm, (B) 520 nm, (C) 620 nm, (D) color intensity, (E) total phenol, (F) total phenol vs. antioxidant capacity, (G) oxygen consumption, and (H) free SO_2.

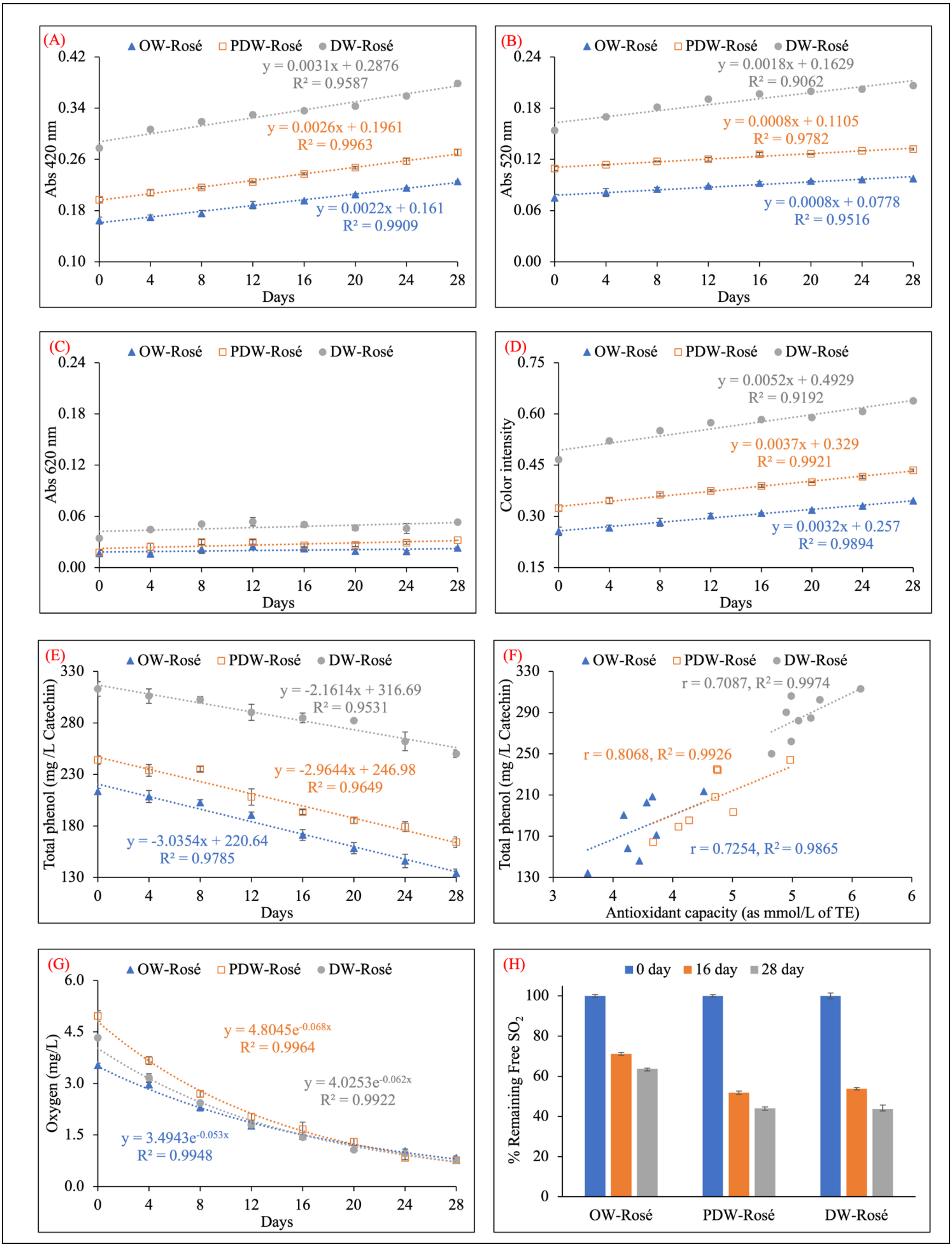

Figure 2. The changes in studied parameters of original, partially dealcoholized and dealcoholized rosé wines during storage at 35°C. (A) 420 nm, (B) 520 nm, (C) 620 nm, (D) color intensity, (E) total phenol, (F) total phenol vs. antioxidant capacity, (G) oxygen consumption, and (H) free SO_2.

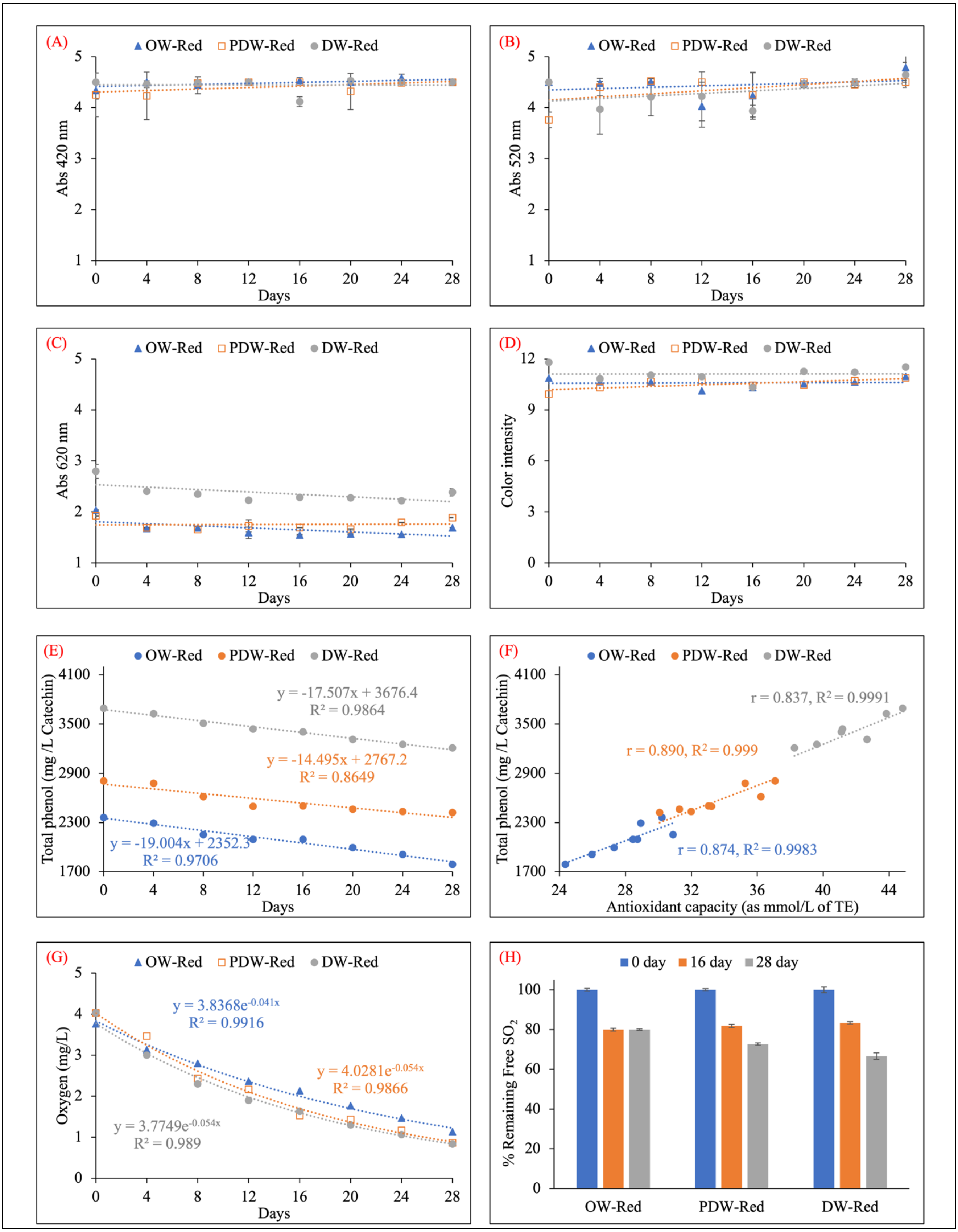

Figure 3. The changes in studied parameters of original, partially dealcoholized and dealcoholized red wines during storage at 35°C. (A) 420 nm, (B) 520 nm, (C) 620 nm, (D) color intensity, (E) total phenol, (F) total phenol vs. antioxidant capacity, (G) oxygen consumption, and (H) free SO_2.

Red wine showed no significant change in color parameters over a short 28-day storage period at 35°C (figure 3 (A, B, C and D)). This lack of change in red wine could be attributed to several factors, such as the brief timeframe, which may be insufficient for notable color alterations that usually occur over months or years. Additionally, although the storage temperature is higher than ideal, it isn't extreme enough to cause exponential degradation. The high phenolic content of red wines, particularly anthocyanins and tannins, contributes to color stability and provides antioxidant protection.

The dealcoholization process significantly increased the total phenol concentrations (mg/L (+)-catechin) in all three types of dealcoholized wines—white, rosé, and red—by 58.3%, 46.9%, and 56.3%, respectively, compared to the original wines. This increase is primarily due to the removal of ethanol and water, which leads to a concentration effect for the remaining non-volatile compounds, including phenolics [9]. A linear decreasing trend was observed in the phenolics content with storage time, and the data align well with a zero-order reaction model, with R^2 values ranging from 0.865 to 0.986. Rate constants (k) were graphically determined from the slopes of the regression lines (figure 1E, 2E and 3E). The slower decline in phenol content in the lower alcohol wines suggests that the dealcoholization process may have concentrated these compounds and that lower alcohol levels could help preserve phenolic stability during storage. Furthermore, it can be observed that the phenolics content correlates with their antioxidant capacity. A high correlation was observed between phenolics content and antioxidant activity for partially dealcoholized white wine ($r = 0.9588$, $R^2 = 0.9193$) (figure 1F), confirming that phenolic compounds are likely to contribute to the antioxidant activity of these wines. The variations might be due to changes in the chemical interactions and solubility of phenolic compounds as the ethanol level varies.

The total anthocyanin content was measured in original and dealcoholized wines. The total anthocyanin content in white, rosé, and red wines was found to be 1.9, 9.5, and 278.4 mg/L MAE, respectively (Table 2). Following dealcoholization, the total anthocyanin content increased by 37.8% in rosé wines and 48.5% in red wines with an alcohol content of 0.5%. This increase is attributed to the concentration effect resulting from the removal of alcohol and water during the dealcoholization process. In contrast, white wine exhibited negligible changes due to its initially low anthocyanin concentration. Temperature and aging time significantly impacted the total anthocyanin content in rosé and red wines. Over 28 days, the total anthocyanin content in original (OW-Rosé), partially dealcoholized (PDW-Rosé), and dealcoholized (DW-Rosé) rosé wine decreased by 20.7%, 15.7%, and 15%, respectively. Similarly, in red wines, the total anthocyanin content decreased by 10.8%, 10.1%, and 8.6% in original (OW-Red), partially dealcoholized (PDW-Red), and dealcoholized (DW-Red) wines, respectively, over the same period. Similarly, Vanzela et al. [25] observed an 88% loss in the anthocyanin content of commercial red (Violeta grape) wines after 120 days of aging at 35 °C. The decrease in anthocyanins during aging can be explained by different mechanisms: the formation of stable polymers through co-pigmentation with flavan-3-ols and flavonols, acetaldehyde-mediated condensations, and/or the formation of co-polymers with the quinone of caftaric acid and anthocyanins [26]. Furthermore, Monagas and Bartolomé [27], mentioned that during long aging, the formation of polymeric pigments occurs, which become insoluble in wine and precipitate, thus contributing to losses in total anthocyanin content.

The total polymeric pigment content was measured as absorbance units (AU) at 520 nm for all the studied wines (Table 1). Red wines exhibited significantly higher levels of polymeric pigments compared to rosé and white wines. Additionally, the short aging time did not significantly affect the polymeric pigment content, likely due to the fact that polymeric pigments in wines primarily develop during longer aging periods through the oxidative polymerization of anthocyanins and tannins.

3.2. Evolution of Dissolved Oxygen Content and Sulfur Dioxide

The O_2 measurements were carried out for each wine sample just after bottling, and the initial oxygen concentration varied from 3.8 to 4.8 mg/L. To determine the reaction order, the integrated kinetic equations for zero, first, and second orders were tested to find the best fit for the experimental data. The results indicated that oxygen consumption follows first-order kinetics ($[O_2]t = [O_2]_0 e^{-kt}$), with $R > 0.98$ for each wine sample (figure 1G, 2G and 3G). The results show that higher ethanol content in wine generally leads to lower oxygen consumption rates (OCRs) during aging, especially in red and rosé wines (Table 3). In rosé wine, original wine (13% v/v) results in a lower k value (0.053 mg O_2/L/day) compared to partially dealcoholized (6% v/v: 0.068 mg O_2/L/day) and dealcoholized (0.5% v/v: 0.063 mg O_2/L/day) wine. Red wine shows the most significant reduction in oxygen consumption with higher ethanol (13% v/v: 0.041 mg O_2/L/day) compared to both medium and low concentrations (6% and 0.5% v/v: 0.054 mg O_2/L/day each). On the other hand, for white wine, the oxygen consumption rate (K) values indicate that wines with 13% and 6% v/v ethanol have similar kinetic rates, at 0.064 mg O_2/L/day and 0.061 mg O_2/L/day, respectively, while dealcoholized wine with 0.5% v/v ethanol shows a significantly lower kinetic rate of 0.054 mg O_2/L/day (Table 3). Higher ethanol content in wine is associated with lower oxygen consumption rates during aging, particularly in red and rosé wines. This effect is less pronounced in white wines, possibly due to their lower phenolic content compared to red wines. Furthermore, variations in kinetic rates for different wine samples may be due to differing initial dissolved oxygen concentrations, pH levels, and inherent wine compositions. Correlation analysis revealed that only a limited set of chemicals was related to the different OCRs. The OCRs were positively correlated with free SO_2 (r > 0.94), total SO_2 (r > 0.85), total phenol (r > 0.91), antioxidant activity (r > 0.80), and pH (r > 0.92).

The consumption of free SO_2, and total SO_2 of the wines during oxidation was summarized in Figure 1H, 2H and 3H and Table 3, respectively. Wines with higher ethanol concentrations consistently show lower reductions in free SO_2, indicating better preservation. For white wines, the reduction in free SO_2 by 41.8, 52.8 and 52.8 % in the wine with 13%, 6% and 0.5% ethanol. In rosé wines, a similar trend is observed, with the highest ethanol concentration (13% v/v, OW-Rosé) showing a 36% reduction in free SO_2, while the wines with 6% (PDW-Rosé) and 0.5% (DW-Rosé) ethanol exhibit much higher reductions of 55.9% and 56.3%, respectively. For red wines, the reduction in free SO_2 is 20% in the wine with 13% ethanol (OW-Red), increasing to 27.3% in the wine with 6% ethanol (PDW-Red), and further to 33.3% in the wine with 0.5% ethanol (DW-Red). The reduction in free SO_2 were positively correlated with total phenol (r > 0.88), antioxidant activity (r > 0.71), oxygen (r > 0.94) and pH (r > 0.87).

To understand the mechanism of SO_2 as an antioxidant, the ratio of total SO_2 to O_2 was calculated at the end of the storage period. The proposed mechanism involves the reaction of SO_2 with H_2O_2 and quinones, rather than directly with oxygen [5]. Danilewicz et al. [7] found that the ratio of SO_2 to O_2 reaction is close to 2:1 in model wine solution. The same ratio was observed for OW-Rosé and DW-White, while for wine samples DW-Rosé and OW-White, the SO_2/O_2 ratio was 1.9:1. For red wines, this ratio ranges from approximately 0.9:1 to 1.3:1 (Table 3). The lower ratio in red wines is possibly due to nucleophilic compounds (i.e. polyphenol, anthocyanin and tannin) being better able to compete with bisulfite for quinones as SO_2 concentration decreases [28,29]. The reaction ratio between SO_2 and O_2 is less than 2:1, likely because the monitoring period was insufficient for all reactions to reach equilibrium.

4. Conclusion

Dealcoholized (<0.5% v/v) and partially dealcoholized (6% v/v) white, rosé and red wines were produced using vacuum evaporation. The removal of alcohol plays a crucial role in various chemical reactions and interactions that contribute to the development of wine's characteristics.

In conclusion, the browning (420 nm) and color intensity of white and rosé wines followed zero-order kinetics. The rate of browning and color intensity was highest in dealcoholized wines, followed by partially dealcoholized wines, and was lowest in original wines. In contrast, red wines showed no significant changes in color parameters, likely due to a short storage period. The reduction in total phenols followed a zero-order kinetic equation ($R^2 = 0.865$ to 0.986) and was positively correlated with antioxidant activity (r = 0.709–0.959, $R^2 = 0.722$–0.999). Anthocyanin content decreased significantly in rosé and red wines, while white wines exhibited minimal changes due to their initially low anthocyanin levels. Furthermore, O_2 levels significantly decreased with aging time, following first-order kinetics. The molar ratio of consumed O_2 to total SO_2 was highly variable and depended on several factors, correlating with free SO_2 content, total phenols, antioxidant activity, oxygen levels, and pH.

From a practical standpoint, the kinetic results of this study can aid in predicting the shelf life and quality of wine, allowing better optimization of storage conditions to minimize quality loss over time.

Considering that ethanol removal during dealcoholization is expected to reduce acetaldehyde levels, future research should focus on elucidating how this reduction influences copigmentation dynamics in dealcoholized wines (especially young red wine), particularly regarding its effects on the stability and expression of anthocyanin-derived pigments.

5. References

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