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Research Article

The Effect of Ethanol, SO₂, and Transition Metals on Browning Kinetics in Low- and No-Alcohol Model Wine

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Received 9 June 2024; Accepted 23 October 2024

Academic Editor: Marcos Dos Santos Lima

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The study delved into the rate of browning (A_{420} nm) within a model wine solution, aiming to elucidate mechanisms impacting real product scenarios, including low- and no-alcohol wines. The model wine solutions were prepared by adding tartaric acid, caffeic acid, and catechin into an aqueous ethanol solution containing transition metals (iron [Fe] and copper [Cu]) along with sulfur dioxide (SO₂). The results indicated that the model wines without ethanol exhibited the highest browning rates both in the presence ($k = 0.0022 \text{ day}^{-1}$) and absence ($k = 0.0035 \text{ day}^{-1}$) of SO₂. Notably, ethanol concentration showed a negative correlation with kinetic rates in both scenarios: with SO₂ ($r = -0.9317$) and without SO₂ ($r = -0.9667$). The addition of Fe and Cu separately led to a slight elevation in browning, particularly evident with Fe, while adding only Cu exhibited nonsignificant impact. However, their combined addition revealed a marked synergistic effect, rendering the rate notably sensitive to Cu concentration.

Keywords: chemical oxidation; copper; iron; low alcohol wines; no-alcohol wines

1. Introduction

Most recently, the EU introduced the category of “dealcoholized wine,” including wines where “for actual alcoholic strength no more than 0.5% v/v ethanol” and “partially dealcoholized” “for actual alcoholic strength above 0.5% v/v ethanol is below the minimum actual alcoholic strength of the wine category” [1]. Furthermore, according to International Organization of Vine and Wine (OIV), partially dealcoholized wine contains more than 0.5% ABV (alcohol by volume) and can include wine, sparkling wine, and aerated semisparkling wine, with ethanol content reduced through processes such as partial vacuum evaporation, membrane techniques, or distillation. On the other hand, dealcoholized wine has 0.5% ABV or less, achieved through similar processes, and is restricted to products without a designation of origin or geographical indication [2]. In addition, OIV member countries are currently working on a framework defining specific enological practices that

would be applicable to these new products. As regulatory bodies impose stringent standards on the production of low-alcohol wines, there arises a crucial need to bridge the gap between these regulations and the scientific exploration, particularly in terms of the browning and oxidation phenomena of these alternative products.

Browning is the major concern associated with white wines. Browning is an oxidative process and a complex phenomenon that involves a number of redox-active constituents, such as tartaric acid, transition metal (copper [Cu] and iron [Fe]) ions, phenolic compounds, sulfur dioxide (SO₂), ascorbic acid (if added), and ethanol [3–5]. Furthermore, phenolic compounds are considered the major substrate to cause browning, among others, and the oxidation of phenols is quite intricate, relying heavily on phenolic compositions and levels, with o-diphenols being the most oxidizable [4, 6, 7]. In addition, Fe functions as a vital catalyst in the oxidative processes of wine when combined with Cu [8]. The average concentration of Fe and

Cu in wine from different regions worldwide has been reported to range from 2.8 to 16 mg/L and 0.11 to 3.6 mg/L, respectively [9, 10]. Legal limits for “quality wine,” according to the OIV are 10 mg/L, 1 mg/L, and 150–200 mg/L for Fe, Cu, and total SO₂, respectively [11, 12].

The cascade of oxidative (browning) reactions commences with the oxidation of catechol (o-diphenol) derivatives, such as catechin and caffeic acid [13, 14]. The oxidation of caffeic acid mediated by Fe leads to the formation of dihydroxy benzaldehyde, followed by its subsequent reaction with catechin. This chemical interaction yields both colorless and yellow/red pigmented compounds, as elucidated in Scheme 1 [14–18].

Furthermore, Danilewicz [19] mentioned that HO• radical is a powerful oxidant which reacts with the first possible substrate it comes into contact with near its production site at diffusion controlled rates. Generally, in white wine, ethanol is the first potential substrate and it is followed by tartaric acid according to their molarity. In dealcoholized or nonalcoholic wine, the primary substrate available is likely to be tartaric acid; radicals may react with tartaric acid and form yellow xanthylum cations (λ_{\max} 440 nm) in the presence of catechin [20]. In brief, glyoxylic acid that is formed from the oxidation of tartaric acid can react with two (+)-catechin to produce a colorless dimer with yellow xanthylum cations [14, 21–24]. The formation mechanism of yellow xanthylum cations are shown in Scheme 2. Metal ions have been found to increase the production of xanthylum cations in model wine. A study by Clark and Scollary [25] demonstrated that Cu(II) enhances the production of xanthylum cation pigments when present in concentrations of 0.3 mg/L or higher. In addition, this study showed that ethanol inhibits the 440 nm absorbance intensity during the oxidation of a catechin-based model wine, and the pigments are identified as xanthylum cations. Similarly, Fe(II) enhances the concentration of xanthylum cations [26]. Another study by Guo et al. [27] showed that different metal ions such as Cu(II), Fe(II), Fe(III), and Mn(II) can influence the generation of xanthylum cation pigments from catechin and tartaric acid at various steps of the reaction mechanism, as well as the isomeric distribution of the resulting pigments. Furthermore, it has been demonstrated that the oxidative coloration of white wine exhibits a greater consistency with respect to absorbance enhancements at both yellow (420 nm) and red (500 nm) wavelengths [28]. The browning of white wines typically follows zero-order kinetics, and the rate constants (k) can be determined by graphically analyzing the slopes of regression lines [29–31].

This study was undertaken to investigate the kinetic aspects of browning development (measured as A_{420 nm}) and its relationship with the reducing in ethanol concentration to simulate the condition of dealcoholized/alcohol free wines. In addition, the behavior of Cu and Fe in both ethanol and aqueous solutions was explored. Notably, existing studies have yielded conflicting results regarding the behavior of these metals in wine-like solutions. A study by Danilewicz [32] suggested a synergistic effect between Cu and Fe on the reaction rate of SO₂, while Berg and Akiyoshi's

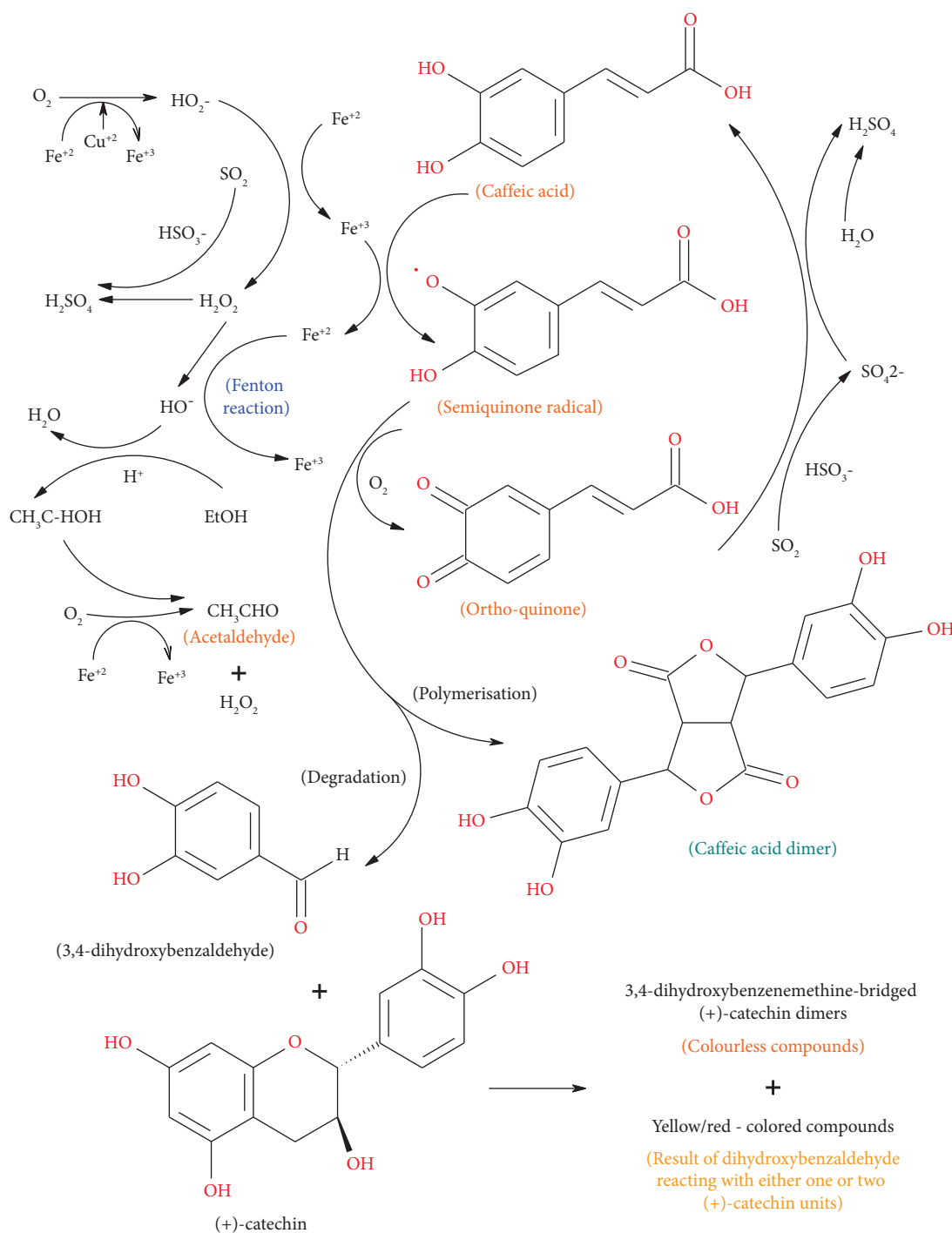
[33] research indicated an additive relationship between Fe and Cu. This study seeks to validate the individual efficacy of Cu and Fe, both when employed separately and in tandem when both metals are present concurrently. Through a comprehensive examination of their independent and combined effects, this research aims to elucidate the intricate interplay between Cu and Fe. Furthermore, kinetic analysis was done to provide deeper insights into how the copresence of Cu and Fe affects their respective efficiencies, contrasting with their individual applications in both ethanol and aqueous solutions. In alignment with the research objectives outlined earlier, we hypothesized that reducing the ethanol concentration leads to an increase in browning kinetic rates. Furthermore, the addition of Cu and Fe together leads to a synergistic effect on the browning rate and absorbance value (420 nm). Overall, this study can provide useful insights to understand the browning phenomenon and oxidation processes in low-alcohol wines during storage.

2. Materials and Methods

2.1. Chemicals and Reagents. Deionized water (11.1 MΩ cm) was produced from a Milli-Q Plus purification system and used for preparation of all solutions. Caffeic acid, (+)-catechin monohydrate, Fe(II) sulfate heptahydrate (FeSO₄•7 H₂O), Cu(II) sulfate pentahydrate (CuSO₄•5 H₂O) and potassium metabisulfite (K₂S₂O₅) for SO₂ solution, absolute ethanol (96.6% v/v), tartaric acid, and 1 M NaOH were obtained from Sigma-Aldrich.

2.2. Model Wine Preparation. Model wines were prepared, following the procedure by Danilewicz and Wallbridge [8], with minor modifications. To achieve this, 6 g/L of tartaric acid was dissolved in deionized water, and ethanol was subsequently introduced to attain a final ethanol concentration ranging from 0% to 12% (v/v). The final pH was adjusted to 3.60 (using 1 M NaOH) for all model wines. The concentrations of caffeic acid and catechin were standardized at 4 mg/L each, according to the average amount present in chardonnay wine (collected data from literature are summarized in Supporting Table 1). The concentrations of Cu and Fe were maintained at 0.3 and 3 mg/L, respectively. In addition, the concentration of SO₂ in model wine was maintained at 45 mg/L by adding K₂S₂O₅ (refer Supporting File “preparation of the working solutions”).

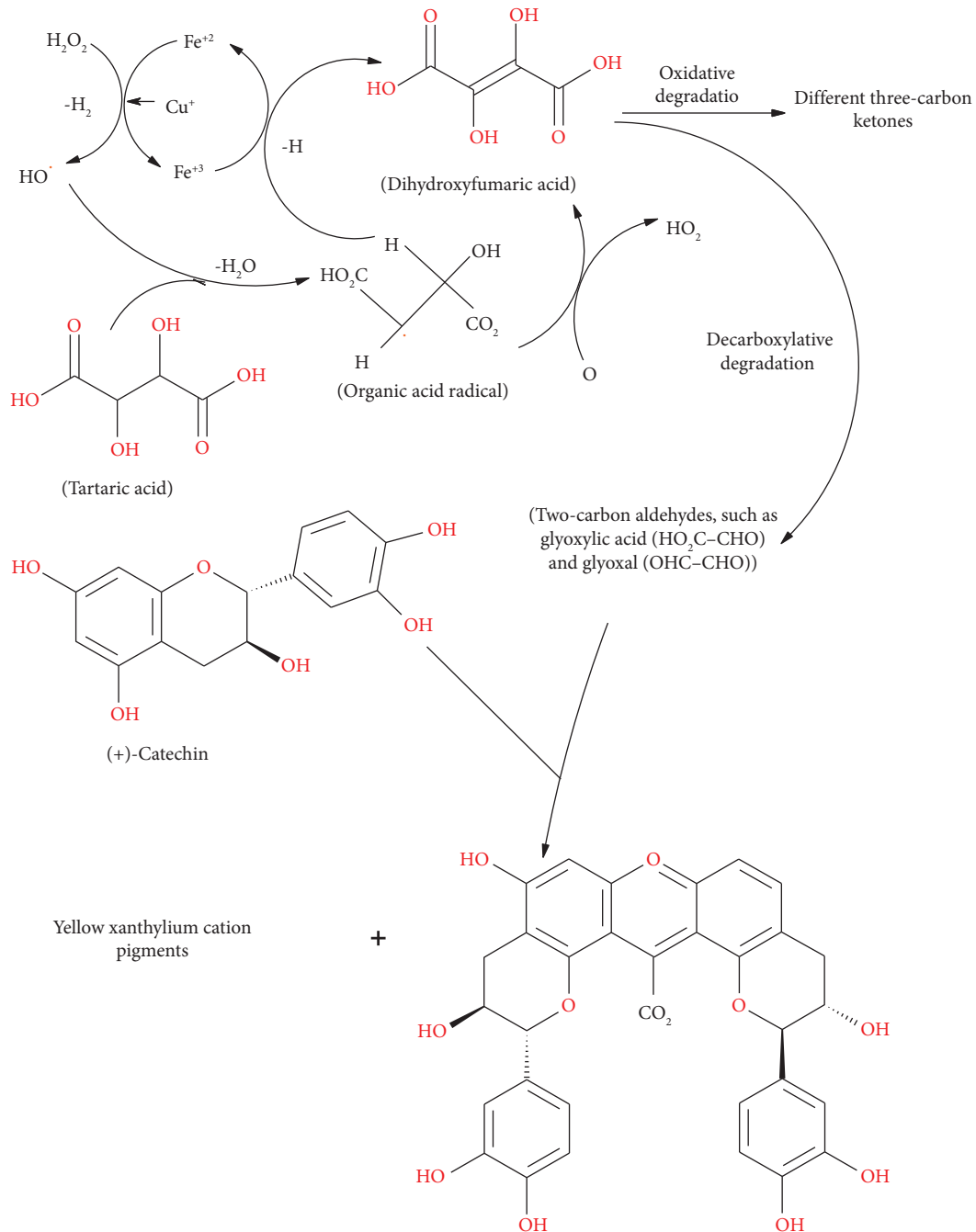
2.3. Storage and Browning Measurement. Model wine aliquots of 30 mL were introduced into 40 mL glass vials sealed with screw caps. These glass vials measured 8 cm in length and possessed an outer diameter of 2.5 cm, with a headspace of 2 cm (equivalent to 10 mL) above the samples. Model wines were vigorously shaken in air for 10 s to saturation, and this operation was repeated three times. Subsequently, the samples underwent controlled heating at a constant temperature of 35 ± 1°C in the Climatic Hood 810 thermostatic dome (Levanchimica srl, Bari, Italy), all under conditions of darkness.



SCHEME 1: Oxidation of caffeic acid and subsequent reactions with (+)-catechin.

In addition, measurements of absorbance values were recorded at a wavelength of 420 nm, using as blank the model solution (12% ethanol, 6 g/L tartaric acid, and pH 3.6). Absorbance at 420 nm is used in the wine industry as a browning index of wine during storage thus is considered as a marker of white wine oxidation [34]. These absorbance measurements were conducted using a Cary 60 UV-Vis spectrophotometer (Agilent Technologies, Palo Alto, CA). The chosen experimental conditions

allowed for a timely assessment of samples although the endpoint was arbitrarily selected. It was recommended that the test period could be extended until maximum browning is achieved. To maintain a practical examination timeframe, days 24 (effect of ethanol on browning kinetics) and 35 (effect of Fe and Cu on browning) were selected as the endpoints for the study. After measurement, samples were vigorously shaken to maintain air saturation.



SCHEME 2: The production of yellow xanthylum cations from (+)-catechin and tartaric acid.

2.4. Statistics. The experiments were conducted in triplicate ($n=3$). Browning rate constants (k) were calculated by determining the slope of the regression line when plotting $A_{420\text{ nm}}$ against time (in days) and were subsequently expressed in units of days^{-1} . The coefficient of determination (R^2) was used to evaluate how well a linear regression model fits the data. A zero-order reaction model produced a good fit of the data.

$$A_{420\text{ nm}} = A_{420\text{ nm}}^0 + kt, \quad (1)$$

where $A_{420\text{ nm}}$ represents the browning value at time t , $A_{420\text{ nm}}^0$ represents the initial browning value, k represents the reaction rate constant (days^{-1}), and t represents time.

3. Results and Discussion

3.1. Effect of Ethanol on Browning Kinetics. The absorbance at 420 nm highlights distinct variations in values among wines with varying concentrations of ethanol. Figures 1(a) and 2(a) represent the change in browning value ($A_{420\text{ nm}}$) over time

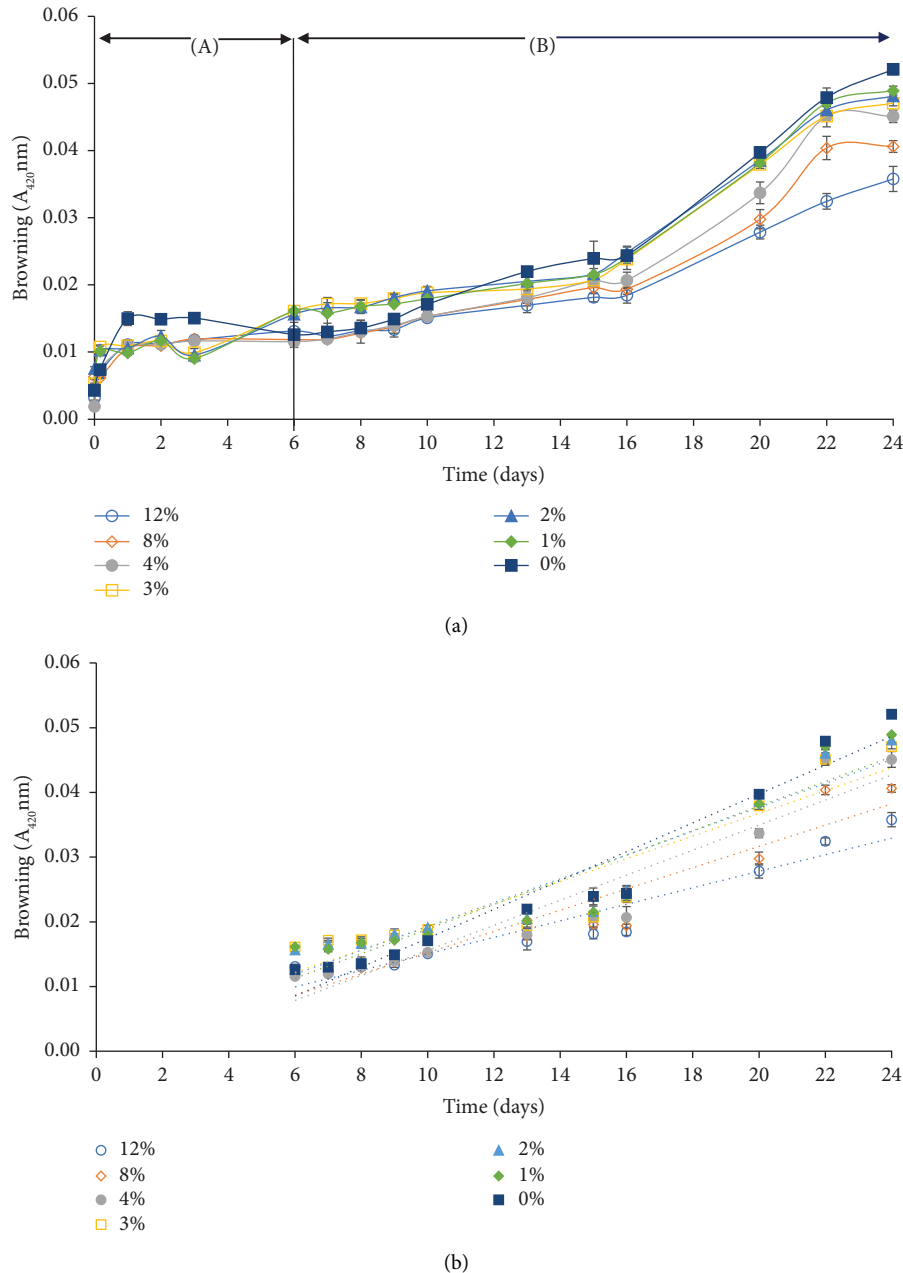


FIGURE 1: (a) The 420 nm absorbance of the model wine containing different concentrations of ethanol (with 6 g/L of tartaric acid, 4 mg/L of caffeic acid and catechin, 0.3 mg/L copper, and 3 mg/L of iron) in the presence of SO_2 (45 mg/L) during storage at 35°C , in the dark. Phase “A” exhibits an initial increase followed by a subsequent decline over the first six days, while phase “B” is characterized by a linear onset of $A_{420\text{ nm}}$ as a function of time for the remaining storage period. (b) The regression lines, derived from the correlation between browning values ($A_{420\text{ nm}}$) and time (days), yield slopes that signify the zero-order browning rate constant (k).

(days) in the presence (45 mg/L) and absence of SO_2 , respectively. The initial relevant finding was that the browning process showed two phases (biphasic course and linear increase). In the case of model wine, with added SO_2 , this biphasic pattern occurred over a span of 6 days while for model wine, without SO_2 addition, it took place over a period of 3 days, which was characterized by a rise and fall of browning (denoted as “A” in Figures 1(a) and 2(a)). Subsequently, after this initial biphasic phase, absorbance values at 420 nm exhibited a linear increase with time,

designated as “B” in Figures 1(a) and 2(a). Similarly, Sioumis et al. [30] noted a biphasic progression during the initial 3 days, followed by a subsequent linear increase over time in the browning values (at 420 nm) of white wines. The biphasic browning observed in wine may be attributed to several distinct reactions. First, in a model wine system, the combination of (+)-catechin and the oxidation product of tartaric acid, i.e., glyoxylic acid, leads to the formation of initially colorless compounds, subsequently evolving into yellowish compounds. Es-Safi et al. [15] noted that the latter

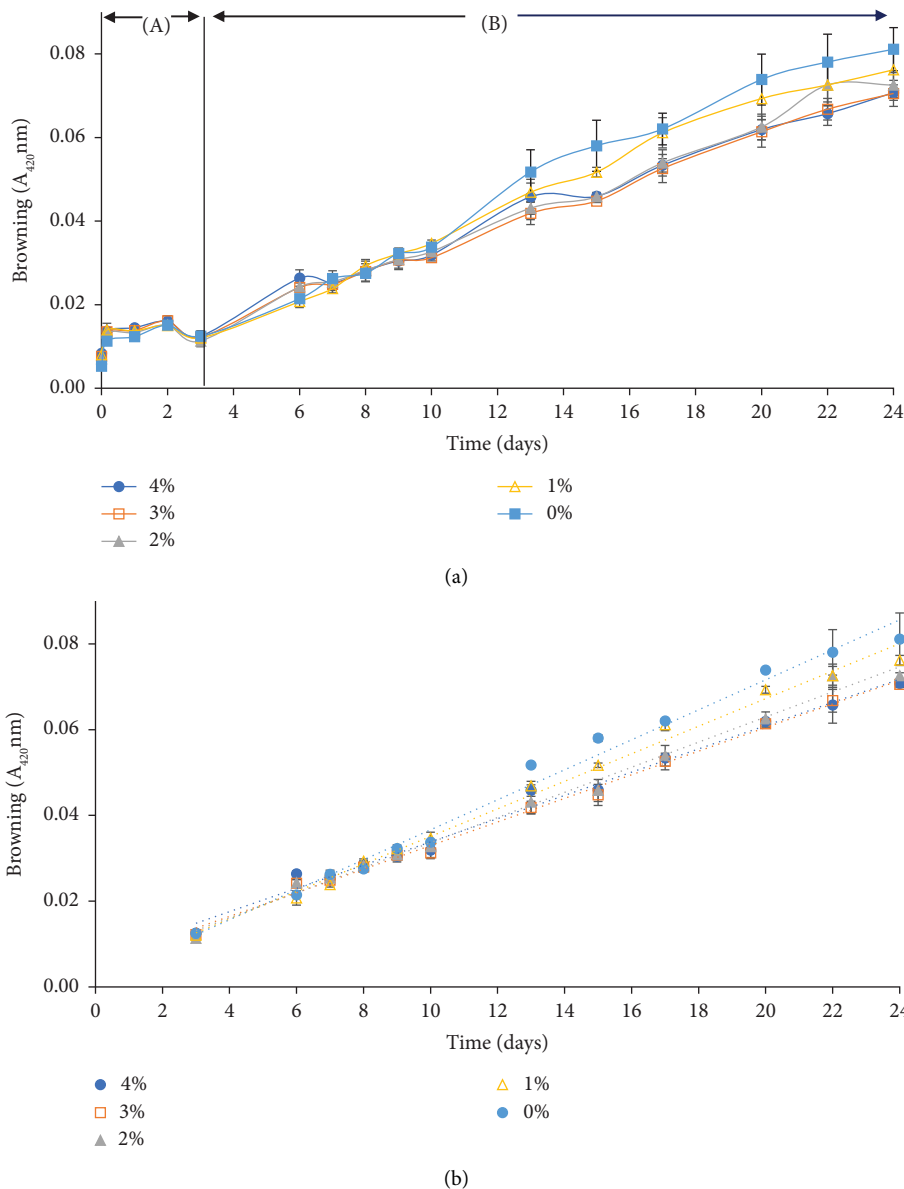


FIGURE 2: (a) The 420 nm absorbance of the model wines containing different concentrations of ethanol (with 6 g/L of tartaric acid, 4 mg/L of caffeic acid and catechin, 0.3 mg/L copper, and 3 mg/L of iron) in the absence of SO_2 during storage at 35°C , in the dark. Phase “A” exhibits an initial increase followed by a subsequent decline over the first six days, while phase “B” is characterized by a linear onset of $A_{420\text{ nm}}$ as a function of time for the remaining storage period. (b) The regression lines, derived from the correlation between browning values ($A_{420\text{ nm}}$) and time (days), yield slopes that signify the zero-order browning rate constant (k).

pathway predominates, with yellowish compounds consistently observed as minor peaks in LC/MS analysis. The colorless compounds are composed of (+)-catechin units linked by a methine carboxylic bridge. Second, when polyphenols undergo oxidation to generate quinone, the presence of SO_2 acts to reduce the quinone back to its phenolic form. In the case of catechin, Danilewicz and Wallbridge [8] reported that 96% of the quinone is effectively recycled back to polyphenol by SO_2 . Also, SO_2 will bind reactive aldehyde compounds, such as glyoxylic acid and glyoxal, and slow their reaction with catechin [35, 36]. The linear trend observed can be explained by the effective alignment of the data with a zero-order reaction model,

yielding a good fit ($R^2 = 0.8732\text{--}0.9956$). Furthermore, the rate constants (k) were graphically calculated from the slopes of regression lines for wines with SO_2 (Figure 1(b)) and wines without SO_2 (Figure 2(b)). Browning rate constants (k) of model white wines containing different concentrations of ethanol (with 6 g/L of tartaric acid, 4 mg/L of caffeic acid and catechin, 0.3 mg/L Cu, and 3 mg/L of Fe) in the absence and presence of SO_2 (45 mg/L) are presented in Table 1. In addition, it was observed that model wines without ethanol exhibited the highest rate of browning in both scenarios: in the presence of SO_2 ($k = 0.0022\text{ day}^{-1}$) and in the absence of SO_2 ($k = 0.0035\text{ day}^{-1}$). Notably, the kinetic rate decreased as ethanol concentration increased. Moreover, to ascertain the

TABLE 1: Browning rate constants (k) of model white wines containing different concentrations of ethanol (with 6 g/L of tartaric acid, 4 mg/L of caffeic acid and catechin, 0.3 mg/L copper, and 3 mg/L of iron) in the absence and presence of SO_2 (45 mg/L).

Model wine with SO_2 (45 mg/L)			
Ethanol (% v/v)	k (day^{-1}) $\times 10^{-4}$	R^2	Equation ($A_{420} = A_{420}^0 + kt$)
12	13	0.9186	$y = 0.0013x + 0.0023$
8	16	0.9101	$y = 0.0016x - 0.0012$
4	19	0.9119	$y = 0.0019x - 0.0037$
3	18	0.8732	$y = 0.0018x + 0.0016$
2	18	0.8987	$y = 0.0018x + 0.0008$
1	19	0.8875	$y = 0.0019x - 0.0001$
0	22	0.9443	$y = 0.0022x - 0.0048$
Model wine without SO_2			
Ethanol (% v/v)	k (day^{-1}) $\times 10^{-4}$	R^2	Equation
4	27	0.9890	$y = 0.0027x + 0.0067$
3	28	0.9956	$y = 0.0028x + 0.0054$
2	29	0.9918	$y = 0.0029x + 0.0043$
1	32	0.9916	$y = 0.0032x + 0.0030$
0	35	0.9875	$y = 0.0035x + 0.0016$

Note: A_{420} represents the browning value at time t , and A_{420}^0 represents the browning value (Day 6 for wine containing SO_2 and Day 3 for wine without SO_2).

potential relationship between reaction rates and ethanol concentration, a correlation analysis was conducted between ethanol concentration and the corresponding k -values. The correlation results revealed that ethanol concentration and kinetic rate are negatively correlated in both scenarios: in the presence of SO_2 ($r = -0.9317$) and in the absence of SO_2 ($r = -0.9667$). Various authors have conducted investigations into the browning kinetics of Chardonnay white wines, revealing differential kinetic rates (A_{420} nm) under distinct temperature conditions. Ricci, Parpinello, and Versari [29] reported a browning rate of $1.71 \times 10^{-4} \text{ day}^{-1}$ for Chardonnay white wine stored at 20°C for 10 months in glass bottles. Furthermore, Fu, Lim, and McNicholas [37] observed browning rates of $0.27 \times 10^{-3} \text{ day}^{-1}$, $0.73 \times 10^{-3} \text{ day}^{-1}$, and $2.87 \times 10^{-3} \text{ day}^{-1}$ for the same wine stored at 22, 35, and 45°C , respectively, for 30 days in bag-in-box. The difference in the browning rate at 35°C compared with the current study could be attributed to variations in wine composition and packaging materials. In addition, Sioumis et al. [30] documented a substantially higher rate of $74.5 \times 10^{-3} \text{ day}^{-1}$ for Chardonnay white wine stored at 55°C for days in glass vials. These variations in browning kinetics rate might be due to differences in wine composition, trace components, packaging types, and storage conditions.

Furthermore, the change in browning can be explained by rate of HO^\bullet reaction. Danilewicz [19] proposed that the HO^\bullet radical reacts promptly with the first potential substrate it encounters in close proximity to its site of production. This experimental setup involves ethanol present at a significantly higher molar excess (exceeding at least 30,855-fold in each case of 12%, 8%, and 4% ethanol wines) compared with catechin and caffeic acid. Consequently, from the concentration point of view, ethanol emerges as the preferred substrate, followed by tartaric acid, existing in an ~ 18 -fold molar excess (in each case). The higher reducing ability of catechin and caffeic acid does not necessarily enhance their reactivity. Considering the relative molar concentrations, as reactivity is dependent on this factor, the

probability of a HO^\bullet encountering a molecule of catechin or caffeic acid would be very low. Model wine that was produced without ethanol (0% v/v) exhibits the highest rate of browning compared with other wines. This may be explained by HO^\bullet directly reacting with tartaric acid, resulting in the formation of dihydroxy fumaric acid. Furthermore, the decarboxylative degradation of dihydroxy fumaric acid leads to the production of two carbon aldehydes, such as glyoxylic acid and glyoxal. These aldehydes then react with catechin, leading to the formation of a yellow xanthylum cation pigment (Scheme 2). At an ethanol concentration below 0.5% v/v, wine displays a molarity comparable with that of tartaric acid. Based on the observed results, it can be postulated that wines with the ethanol content below 0.5% v/v (dealcoholized/NoLo wines) had higher possibility to exhibit an oxidative pathway in accordance with Scheme 2, while wines with the ethanol content exceeding 0.5% v/v undergo oxidation following the pathway outlined in Scheme 1. Dihydroxybenzaldehyde was formed through the Fe-mediated oxidation of caffeic acid, and upon reacting with catechin, it led to the generation of both colorless and yellow/red-colored compounds. This distinction highlights the ethanol content-dependent divergence in oxidative mechanisms within wines. In addition, as anticipated, the absence of SO_2 in the wine led to higher absorbance values compared with wines containing SO_2 [38]. In this view, SO_2 acts as an antioxidant in two different ways: by reacting with hydrogen peroxide and carbonyl formed during oxidation [13, 36, 39]. The presence of SO_2 in wine results in wines with lower absorbance at 420 nm (yellow color). Coleman et al. [40] observed similar trends in the consumption of dissolved oxygen in a model wine system, where ethanol and SO_2 concentrations were varied. Their findings revealed that in an air saturated (8.5 mg/L oxygen) model solution containing 4 g/L tartaric acid, 15 mg/L Fe (II), the highest oxygen consumption occurred in the absence of ethanol (0% v/v). As the ethanol concentration increased, oxygen consumption exhibited

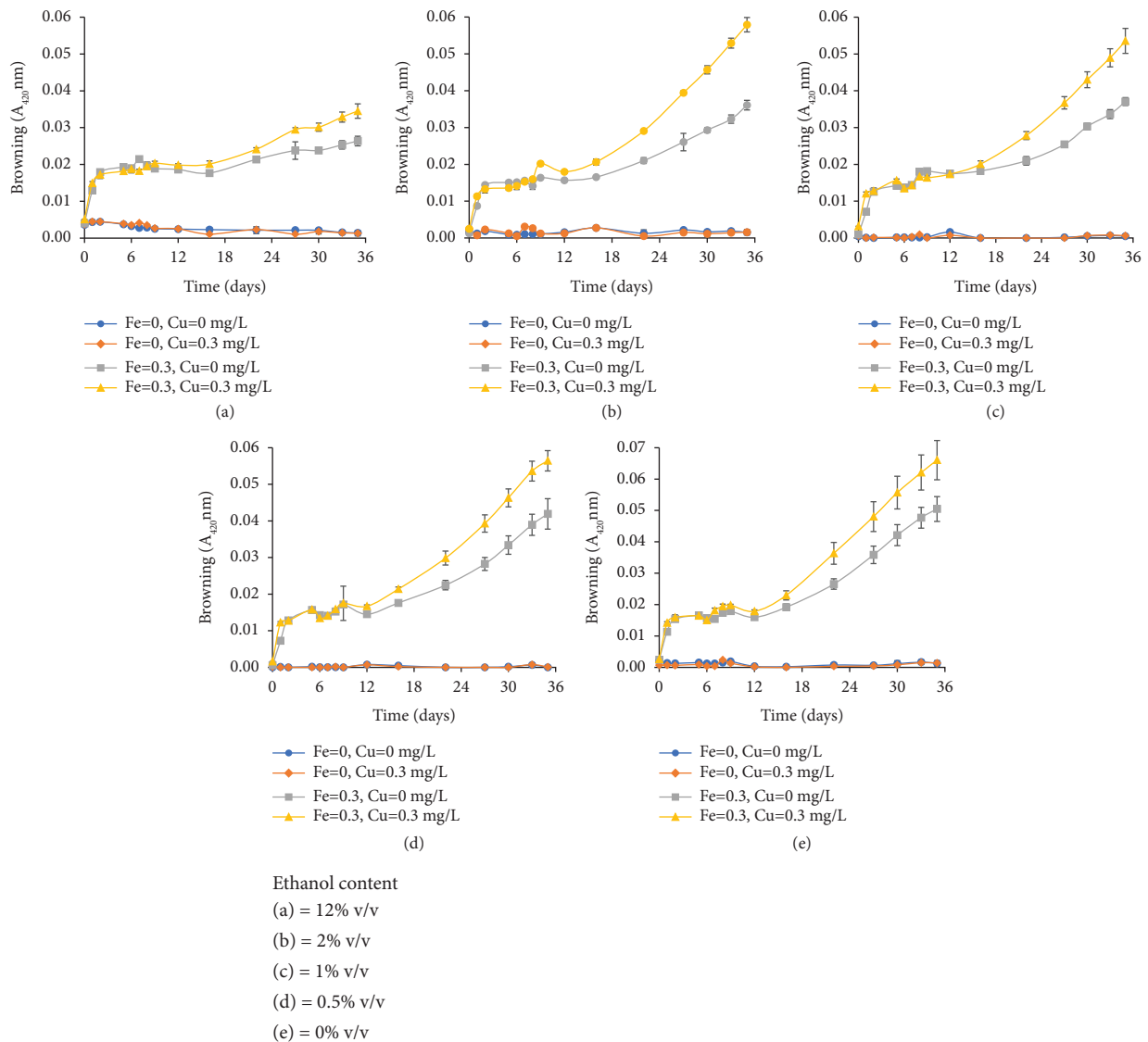


FIGURE 3: Effect of the Fe and Cu on the 420 nm absorbance of the model white wine containing different concentrations of ethanol (with 6 g/L of tartaric acid, 4 mg/L of caffeic acid and catechin, and 45 mg/L of SO₂) during storage at 35°C, in the dark.

a progressive decline, with values corresponding to 0.0015%, 0.015%, 0.15%, 1.5%, and 15% v/v, under conditions of pH 2.5 and 4.5. Notably, when hydrogen peroxide (H₂O₂) was introduced in the absence of ethanol, complete oxygen consumption occurred within 15 min. Importantly, this outcome was found to be independent of pH. Furthermore, the addition of SO₂ at a concentration of 30 mg/L effectively inhibited the significant advancement of the propagation stage of oxygen consumption, regardless of the pH conditions. In contrast, in samples without SO₂, all the dissolved oxygen was consumed within 1 hour.

In addition, 6 g/L tartaric acid (with 0.3 mg/L Cu and 3 mg/L Fe) without polyphenols had a minor statistically nonsignificant impact on browning (A₄₂₀ nm) in hydro-alcoholic and aqueous solutions during a 30 day storage period at 35°C (in dark and light), both in the absence and presence of SO₂ (45 mg/L) (data are not reported). These findings suggest that the oxidation of tartaric acid, even

when combined with Cu and Fe, does not significantly influence the browning value (A_{420nm}) without polyphenols under the specified storage conditions.

3.2. Effect of Fe and Cu on Browning. The effects of Cu and Fe on the browning (A₄₂₀ nm) in various ethanol concentrations (12%, 2%, 1%, and 0.5% v/v) and aqueous solutions were investigated. The concentrations of caffeic acid and catechin were standardized at 4 mg/L each, alongside a final pH value of 3.6 for all solutions. Figure 3 illustrates the effect of Fe and Cu on the 420 nm absorbance over time in model white wine containing 6 g/L tartaric acid, 4 mg/L caffeic acid and catechin, 0.3 mg/L Cu, and 3 mg/L Fe at different ethanol concentrations in the presence of 45 mg/L SO₂ during storage at 35°C in the dark. When caffeic acid and catechin were exposed to saturated air in the presence of SO₂ (45 mg/L), Fe (3 mg/L), and Cu (0.3 mg/L) within the model

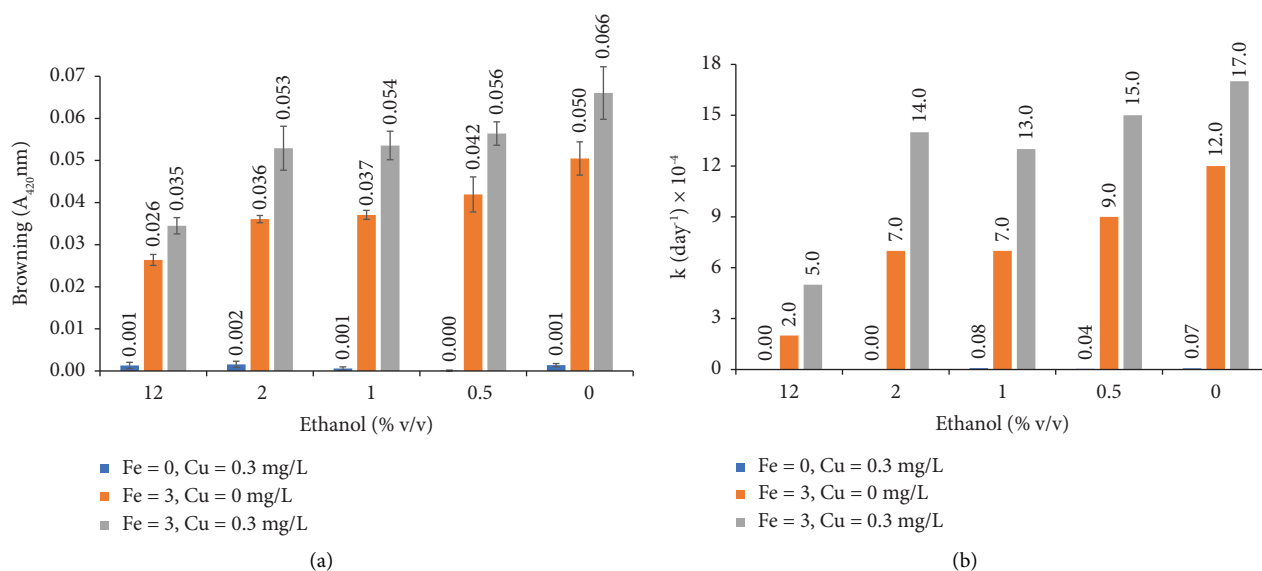


FIGURE 4: Absorbance values at day 35 and browning kinetic (k) rate as influenced by varying concentrations of iron and copper across different ethanol concentrations.

solution, the absorbance values rapidly increased over time. Subsequent experiments involving only 3 mg/L of Fe exhibited lower absorbance values compared with solutions containing both Fe and Cu. In contrast, when no metal (Fe and Cu = 0) and only Cu (Fe = 0 and Cu = 0.3 mg/L) was added, no significant change in absorbance values was observed, indicating an absence of reaction over the 35 day period in each solution. Similarly, Wu et al. [41] found that Fe causes significant color changes of wine, and this was confirmed by adding chitosan, which is a chelation of Fe [42].

The rate of browning was almost zero in the absence of transition metals, similar as what found by Eftihia et al. [43]. This could be explained by the fact that the reaction proceeds in violation of the Pauli's exclusion principle, which is due to the difference in electronic structure, being in the triplet and singlet ground states for oxygen and polyphenols, respectively [3]. Furthermore, the results indicated that a decrease in the ethanol concentration led to an increase in the absorbance value. The solution without ethanol exhibited the highest absorbance value ($A_{420\text{ nm}}$: 0.066) when Fe = 3 and Cu = 0.3 mg/L on the last day (35). Figure 4 shows the absorbance value on the last day (Day 35) and kinetic rate (k) as a function of Fe and Cu concentrations at different ethanol concentrations. In this study, a synergistic effect of Fe and Cu was observed. The addition of 0.3 mg/L Cu (with Fe at 3 mg/L and Cu at 0.3 mg/L) increased the absorbance values at 420 nm by 31%, 47%, 44%, 35%, and 31% for ethanol concentrations of 12%, 2%, 1%, 0.5%, and 0% v/v, respectively, compared with samples containing only 3 mg/L Fe. Furthermore, the kinetic rate increased by 2.5, 2.0, 1.86, 1.67, and 1.42 times for ethanol concentrations of 12%, 2%, 1%, 0.5%, and 0% v/v, respectively, compared with samples containing only 3 mg/L Fe. The contribution of Cu to wine color has been reviewed by Wang et al. [44]. Similarly, Danilewicz [32] reported a synergistic effect of Fe and Cu on

the rate of SO_2 concentration. The study revealed that when both metals were present together at concentrations of Fe = 5 mg/L and Cu = 0.5 mg/L, they collectively exhibited a significantly greater increase in the rate (SO_2 consumption) compared with the cumulative rates observed when each metal was individually tested. In a study, Balla, Kiss, and Jameson [45] observed that the oxidation rate of catechol was notably influenced by Cu concentration in the presence of Fe. The catalytic ability of Fe in catechol oxidation hinges upon redox cycling, where the conversion of ferric ions to ferrous ions by catechols must be followed by the restoration of ferrous ions to the ferric state to sustain the catalytic process. Cu likely aids this redox cycling, potentially acting as a facilitator that could be rate limiting, enhancing interaction with oxygen, and possibly forming a species such as CuO^{2+} [45]. Contrarily, Berg and Akiyoshi [33] observed an additive effect of Fe and Cu on the browning rate of white wines.

4. Conclusion

The present investigation elucidates the intricate kinetics of browning development, assessed via $A_{420\text{ nm}}$ measurement, and its interplay with ethanol content reduction to simulate low- and no-alcohol wines. Concurrently, it sheds light on the behavior of Cu and Fe within both ethanol and aqueous solutions. These findings collectively underscore the catalytic significance of Fe and Cu in polyphenol oxidation, elucidating their intricate relationship with SO_2 and ethanol concentrations.

The results notably demonstrate a direct correlation between the browning rate and ethanol concentration, showcasing a decrement in the browning rate with increasing ethanol concentration. Furthermore, samples devoid of SO_2 exhibited markedly higher browning rates compared with those containing SO_2 . Remarkably, the

absence of both ethanol and SO₂ yielded the highest observed browning rate ($35 \times 10^{-4} \text{ day}^{-1}$). In the exploration of Fe and Cu effects, this study underscores the heightened sensitivity of browning rate to Cu concentration, given the ubiquitous presence of Fe. This emphasizes the influential role of Cu in modulating browning kinetics, invariably tied to the presence of Fe. The results found provide a valuable conceptual basis for implementing wine preservation, especially new low-alcohol products.

Future research is required to bridge the gap between laboratory observations and large-scale wine production by considering multiwavelength measurements to elucidate oxidation-induced color changes, oxygen diffusion, and complex chemical interactions in real low and no alcohol wine matrices.

Data Availability Statement

The metadata will be made available and searchable on the AMS Acta repository (<https://amsacta.unibo.it/>) by recording the DOI of the article soon after publishing.

Conflicts of Interest

The authors declare no conflicts of interest.

Author Contributions

Yogesh Kumar: conceptualization, methodology, formal analysis, investigation, software, data curation, and writing the original draft. Guanghao Wang: methodology, formal analysis, investigation, data curation, writing, editing, and revising. Arianna Ricci: editing and revising. Giuseppina Paola Parpinello: supervision, editing, and revising. Andrea Versari: conceptualization, methodology, investigation, resources, supervision, visualization, editing, and funding acquisition.

Funding

No funding was received for this research.

Supporting Information

Additional supporting information can be found online in the Supporting Information section. (*Supporting Information*)

Supporting File includes Supporting Table 1 entitled “The concentration of phenols (catechin and caffeic acid) present in the chardonnay wine” and preparation of the working solutions of Fe²⁺, Cu²⁺, and SO₂.

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