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# Determination of Activation Energy from Decolorization Reactions of Synthetic Dyes by Fenton Processes Using the Behnajady–Modirshahla–Ghanbary Kinetic Model

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**Abstract:** The present work used the Behnajady–Modirshahla–Ghanbary (BMG) kinetic model to determine the initial reaction rates ($1/m$), which were used to calculate the activation energy ($Ea$) from the decolorization of synthetic dyes by Fenton processes ($Fe^{2+}/H_2O_2$, $Fe^{2+}/H_2O_2$/reducer and $Fe^{3+}/H_2O_2$/reducer). When increasing the temperature and adding $Fe^{3+}$-reducing compounds (3-Hydroxyanthranilic Acid, Hydroquinone, Gallic Acid, Cysteine or Ascorbic Acid), increases in the $1/m$ values were observed. When studying the classical Fenton reaction ($Fe^{2+}/H_2O_2$), almost all added reducers had decreased $Ea$. For example, 3-Hydroxyanthranilic Acid decreased the $Ea$ related to the decolorization of the Phenol Red dye by 39%, while Ascorbic Acid decreased the $Ea$ of Safranin T decolorization by 23%. These results demonstrate that the reducers increased the initial reaction rate and decreased the energy barrier to improve Fenton-based decolorization of dyes. When comparing the reaction systems in presence of reducers ($Fe^{n+}/H_2O_2$/reducer), the reactions initially containing $Fe^{2+}$ presented lower $Ea$ than reactions catalyzed by $Fe^{3+}$. That way, the activation energy obtained through the $1/m$ values of the BMG model highlighted the pro-oxidant effect of reducers in Fenton processes to degrade dyes.

**Keywords:** Fenton reaction; reducer; hydroxyl radical; kinetics; advanced oxidative process

## 1. Introduction

Several technologies have been evaluated to treat effluents from the textile industry, and processes based on the Fenton reaction have been standing out in removing more pollutants [1]. Conventional processes to treat these effluents do not properly remove or degrade the more complex structures of the dyes [2,3]. Furthermore, pollutants are generally transferred from the liquid phase to the form of sludge, which also needs to be treated and disposed of appropriately [4,5]. Advanced oxidation processes based on the Fenton reaction have demonstrated great efficiency in the degradation and mineralization of different classes of dyes [6–9]. The Fenton reaction is based on the catalytic degradation of hydrogen peroxide by ferrous ions (Reaction (1)) to generate hydroxyl radical ($HO^\bullet$). This free radical has a high standard reduction potential ($E° = 2.8$ V), and can degrade several recalcitrant pollutants, including dyes.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + HO^-, k = 50\text{–}80 \text{ mol}^{-1}\cdot L^{-1} \tag{1}$$
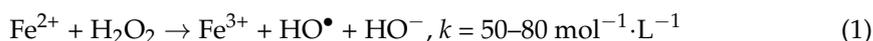
By adding $Fe^{3+}$ ions at the beginning, instead of $Fe^{2+}$, there is the Fenton-like reaction (Reaction (2)). However, the radical formed is hydroperoxyl ($HO_2^\bullet$), which has a lower standard reduction potential ($E° = 1.42$ V) and, consequently, less effectiveness when compared to $HO^\bullet$. Despite being very slow, the second reaction is important as it regenerates $Fe^{2+}$ from $Fe^{3+}$, allowing it to participate again in the first reaction [10–12].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+, k = 0.002\text{–}0.01 \text{ mol}^{-1}\cdot L^{-1} \tag{2}$$
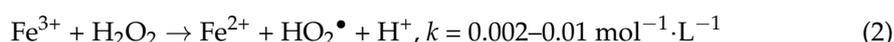
A limitation of processes based on the classical Fenton reaction is the low rate of reduction of $Fe^{3+}$ by Reaction (2) compared to the oxidation of $Fe^{2+}$ through Reaction (1). This promotes the accumulation of ferric ions that tend to precipitate as hydr(oxides), making the catalyst unavailable. An alternative to increasing the production of hydroxyl radicals in the reaction medium is to increase the concentrations of the reactants. However, when increasing the catalyst concentration, there is an increase in the formation of iron-containing sludge, while an excess of $H_2O_2$ or catalyst would reduce the degradation efficiency, as the $HO^\bullet$ also reacts with the $H_2O_2$ (Reaction (3)) and $Fe^{2+}$ (Reaction (4)), instead of reacting only with target pollutants [12,13].

$$H_2O_2 + HO^\bullet \rightarrow H_2O + HO_2^\bullet, k = 1.7\text{--}4.5 \times 10^7 \text{ mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1} \tag{3}$$

$$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + HO^-, k = 2.5\text{--}5.0 \times 10^8 \text{ mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1} \tag{4}$$
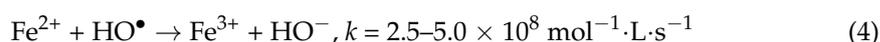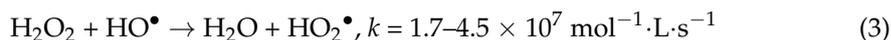
Certain organic compounds can minimize unwanted accumulation of $Fe^{3+}$ due to the constant regeneration of $Fe^{2+}$ (which is faster compared to $H_2O_2$), therefore enabling greater production of $HO^\bullet$ radicals in the treatments [10]. Several reducing compounds have been tested, many of which are phenolic. When reducing $Fe^{3+}$ to $Fe^{2+}$, phenolic reducers are converted to a semiquinone radical, which can also reduce $Fe^{3+}$ and convert into its respective quinone. The latter can be regenerated to the semiquinone radical or even be oxidized by $Fe^{3+}$ into smaller molecules, including $CO_2$ [14,15]. Therefore, the degradation and mineralization of the phenolic reducer and its intermediates may be desirable to minimize secondary pollution problems. The amino acid Cysteine and Ascorbic Acid present behavior very similar to phenols, considering the regeneration of $Fe^{2+}$ in Fenton processes [16–19]. Figure 1 presents some reactions involving Fenton reagents and a reducing compound to degrade a target dye.
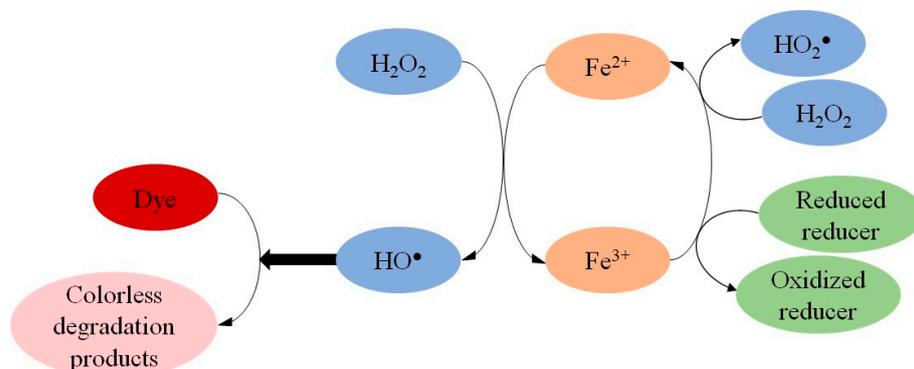


**Figure 1.** Reactions involved between Fe ions, $H_2O_2$, reducer, and a dye.

An appropriate way to evaluate the effect of a reducing compound on Fenton processes is to evaluate the reaction kinetics of experimental data. In several studies by our research group, it was found that the first-order reaction model has been the one that best fits data on dye decolorization reactions by Fenton/reducer processes [20–23]. In turn, the second-order kinetic model was the one that best adjusted the results of the decolorization of two dyes [21,24]. Another kinetic model that was used in these studies and that fitted well much of the experimental data was that first used by Chan and Chu [25], being more commonly known as Behnajady–Modirshahla–Ghanbary (BMG). It was developed as a way to evaluate the degradation of pollutants by classical Fenton reaction, which were not described by conventional reaction kinetics models [26].

The BMG model is expressed by Equation (5), and is shown in its linearized form by Equation (6).

$$\frac{C_t}{C_0} = 1 - \left[\frac{t}{(m + b\cdot t)}\right] \tag{5}$$

$$\frac{t}{\left[1 - \left(\frac{C_t}{C_0}\right)\right]} = m + b \cdot t \tag{6}$$

where $C_0$ and $C_t$ are the dye concentration values at the initial time and at a certain time t, respectively, while $m$ (intercept) and $b$ (slope) are the two intrinsic constants of the model. To interpret them, Equation (6) must be derived, as shown in Equation (7).

$$\frac{\mathrm{d}C/C_0}{\mathrm{d}t} = \frac{-m}{(m + b \cdot t)^2} \tag{7}$$

When time $t$ is small or close to zero, the slope obtained can be solved according to Equation (8). Therefore, the greater $1/m$, the greater the initial rate of degradation of the target pollutant. On the other hand, when the time is long and approaches infinity, it is possible to obtain the maximum theoretical oxidation capacity ($1/b$), according to Equation (9). This shows that the maximum value of $1/b$ is 1 when the final concentration is null.

$$\frac{\mathrm{d}C/C_0}{\mathrm{d}t} = -\frac{1}{m} \tag{8}$$

$$\frac{1}{b} = 1 - \frac{C_{t \to \infty}}{C_0} \tag{9}$$

Such mathematical observations can be better observed in Figure 2 with the extreme values of time ($t = 0$ and $t = \infty$).
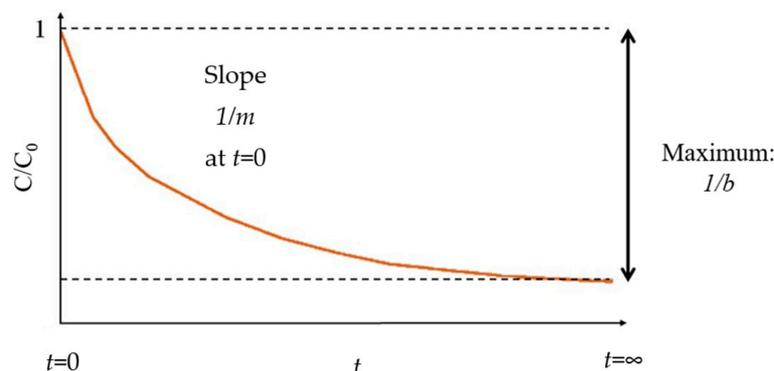


**Figure 2.** A linear way of representing the BMG model. This figure was reproduced from Behnajady et al. [26], with permission from Elsevier (license number 5735830415425).

The decolorization of some dyes by $Fe^{2+}/H_2O_2$ has been well described by the BMG model, particularly due to the two-stage reaction behavior: one first and faster, followed by another that is slower. The first stage has been attributed to the reaction between $Fe^{2+}$ and $H_2O_2$, resulting in $HO^{\bullet}$ radicals, and the second stage refers to the accumulation of $Fe^{3+}$ (or low regeneration of $Fe^{2+}$) that reacts with $H_2O_2$ to form weaker radicals (such as $HO_2^{\bullet}$) [8,26–31]. On the other hand, when using $Fe^{3+}$ as a catalyst at the beginning of reactions, decolorization does not usually have two stages, and the BMG model has been somewhat less adequate to describe them. When evaluating heterogeneous Fenton-like reaction, using natural schorl as catalyst, Xu et al. [32] also found that the BMG model did not fit the Methyl Orange decolorization data. From this perspective, previous studies by our research group corroborated these behaviors, as the BMG model fitted well to the decolorization reactions with $Fe^{2+}$, while those with $Fe^{3+}$ were not well described by this model. Interestingly, when Ascorbic Acid, Gallic Acid, 3-Hydroxyanthranilic Acid or Hydroquinone was added to the system $Fe^{3+}/H_2O_2$, the BMG model adjusted well to the experimental data, indicating that these compounds reduced $Fe^{3+}$ to $Fe^{2+}$ rapidly, causing the decolorization to present two phases [20,21,23,24].

Assessing the activation energy (*Ea*) of reactions involved in Fenton processes is an important way of analyzing the pro-oxidant effect of reducers. To do this, it is necessary to carry out the reaction at different temperatures, calculate the rate constants, and then obtain *Ea* [33]. In previous works by our research group, when *Ea* was calculated, the reaction rate constants obtained through classical kinetic models were generally used and best fit the majority of experimental data, being of first-order [20–23] or second-order [21,24]. As the BMG model also fitted well with much of the experimental data in these studies, the $1/m$ values could also be used to calculate *Ea*. When evaluating the degradation of an herbicide by $Fe^{2+}/H_2O_2$ at different temperatures, Santos et al. [34] used this kinetic model to interpret their results. The values of $1/m$ obtained replaced the reaction rate constant (*k*) in the Arrhenius equation, allowing them to find an *Ea* of 49.3 kJ·mol$^{-1}$. To the best of our knowledge, no studies have been conducted to calculate the *Ea* using $1/m$ values from the Fenton-based degradation of different dyes used as target pollutants.

Therefore, the present study aimed to continue studies of reaction kinetics based on the degradation of synthetic dyes via Fenton processes mediated by $Fe^{3+}$-reducing compounds. As a novelty, this work evaluated the activation energy (*Ea*) from the decolorization of various dyes by Fenton processes ($Fe^{2+}/H_2O_2$, $Fe^{2+}/H_2O_2$/reducer and $Fe^{3+}/H_2O_2$/reducer) using the values of $1/m$ from the BMG reaction kinetics model [34]. For this purpose, the values of $1/m$ obtained from previous studies developed by our research group [20–24] were used in the present work. In addition, comparisons were made between *Ea* values calculated using $1/m$ and those obtained from the rate constants ($k_1$, $k_2$) of conventional kinetic models.

## 2. Results and Discussion

### 2.1. Data for 1/m from Decolorization Reactions of Different Dyes Using Fenton Processes

Figure 3 shows the $1/m$ values obtained from previous studies by our research group. Only data referring to reactions that were well described by the BMG model ($R^2 > 0.9$) were used here; that is, all data related to the $Fe^{2+}/H_2O_2$ and $Fe^{2+}/H_2O_2$/reducer systems, in addition to specific ones from $Fe^{3+}/H_2O_2$/reducer in presence of 3-Hydroxyanthranilic Acid, Hydroquinone, Gallic Acid or Ascorbic Acid. In general, it was found that the $1/m$ values increased as a function of temperature, regardless of the target dye and the reaction system. This aspect can be explained by the increase in the number of collisions between reactant molecules with increasing temperature, promoting greater formation of free radicals [35,36]. For example, the value of $1/m$ referring to the $Fe^{2+}/H_2O_2$/3-Hydroxyanthranilic Acid system was 10 times higher at 50 °C than at 20 °C. The increase in the value of $1/m$ as a function of temperature has also been observed in other studies that evaluated the Fenton-based degradation of dyes [27,37], including Methyl Orange [32].

Furthermore, it was noted that the temperature differently influenced the decolorization of the dyes. For example, when varying it from 20 °C to 50 °C, the increase in the $1/m$ values was much greater with Chromotrope 2R than with Methyl Orange, both evaluated under the same reaction condition. When considering the Bismarck Brown Y dye, the increase in temperature had less influence on its decolorization in the presence of Salicylic Acid compared to the reducers Gallic Acid and Hydroquinone. On the other hand, the effect of temperature was more similar when comparing Cysteine and Ascorbic Acid to decolorize Safranin T.

When considering the different reaction systems, the following order was observed: $Fe^{3+}/H_2O_2$/reducer < $Fe^{2+}/H_2O_2$ < $Fe^{2+}/H_2O_2$/reducer. However, decolorization experiments involving Bismarck Brown Y dye and mediated by Gallic Acid or Hydroquinone did not follow this order, as the values of $1/m$ referring to the $Fe^{3+}/H_2O_2$/reducer system were greater than those found for $Fe^{2+}/H_2O_2$. For Chromotrope 2R, the three reaction systems had similar behavior.
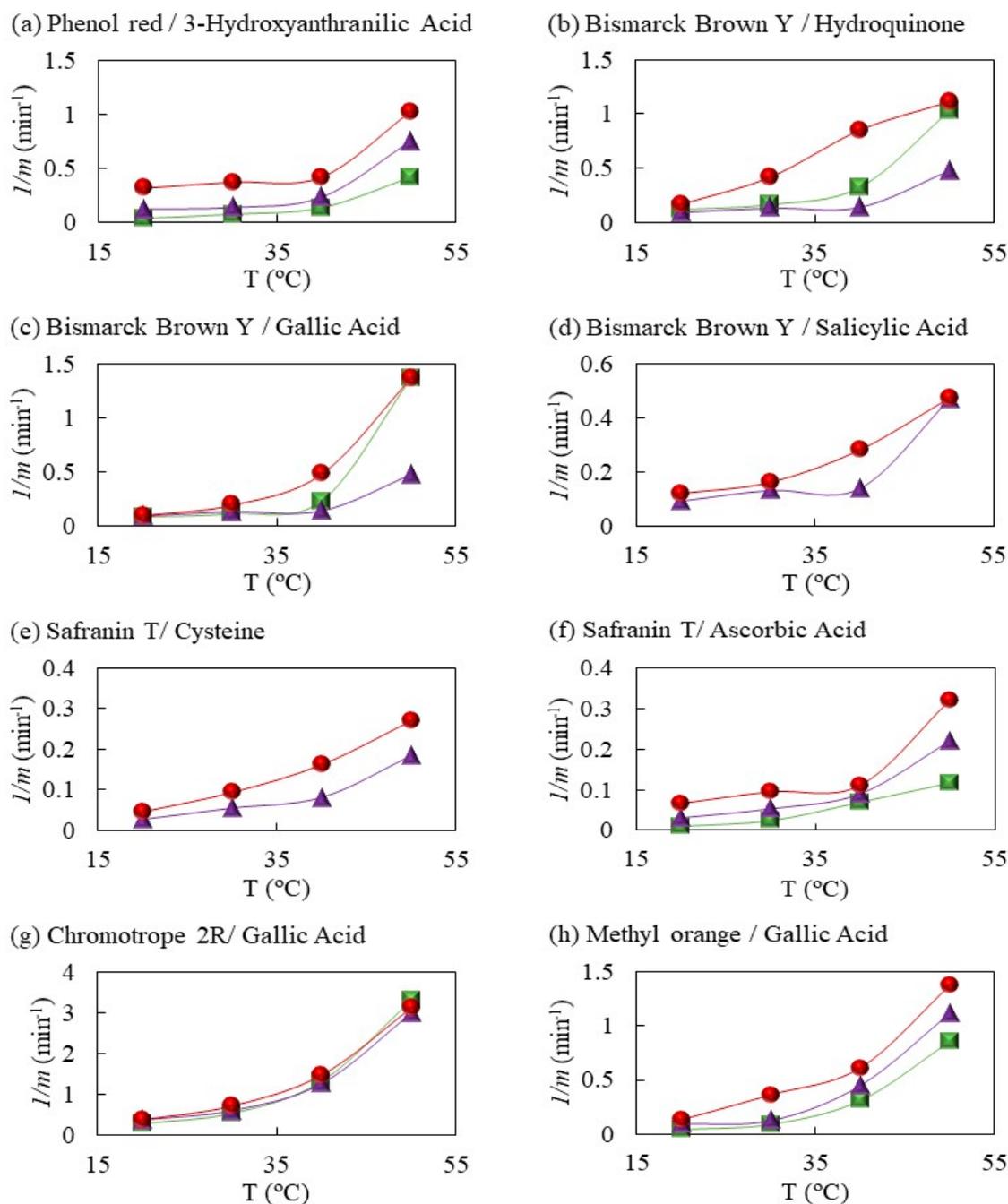
**Figure 3.** Effect of temperature on $1/m$ values from the decolorization of dyes by Fenton processes mediated by different reducing compounds. Reaction systems: $Fe^{2+}/H_2O_2$ (▲), $Fe^{2+}/H_2O_2$/reducer (●) and $Fe^{3+}/H_2O_2$/reducer (■).

The parity plot between the experimental and the predicted data can clarify if a kinetic model is suitable in describing a reaction system [38–40]. Figures S1–S5 (available in the Supplementary Materials) show the parity plots between the experimental data of decolorization at different temperatures and the results predicted through the equations obtained from the BMG kinetic model. For most of the reaction systems, the predictions of the models are in good agreement with the respective experimental results. Only one $R^2$ value was slightly lower than 0.8, which is the parity graph referring to Safranin T decolorization by $Fe^{2+}/H_2O_2$/Ascorbic Acid system. In this way, through the analysis of parity plots, the BMG model was adequate to describe the decolorization of the dyes by Fenton processes.

### 2.2. Ea Calculation

　　　Using Arrhenius plots (Figure 4), which relate the values of $1/m$ and the inverse of the temperatures, the *Ea* values of all reaction systems were calculated (Figures 5–9). It is noteworthy that four temperature values were evaluated, as this quantity is commonly used to calculate *Ea* in Fenton processes [6,7,34,41]. Almost all values of $R^2$ were high (most above 0.8), regardless of the dye and the reaction system. This indicates that, through Arrhenius plots, data from the BMG model can be used to calculate *Ea*. For comparison purposes, the *Ea* values obtained in previous our works, using first- or second-order kinetic constants, have been included in Figures 5–9.
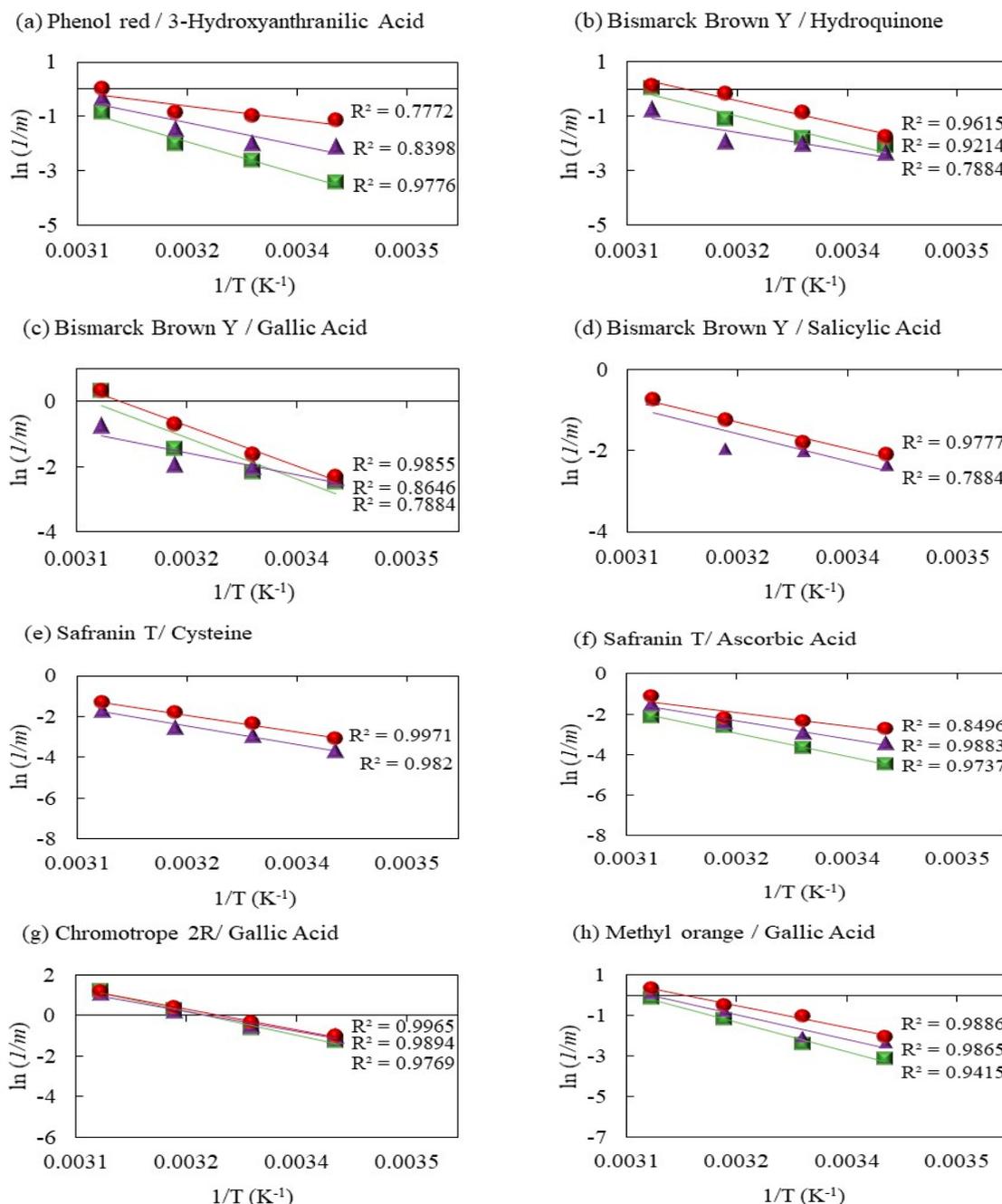


**Figure 4.** Arrhenius plots for the data of decolorization of different dyes by Fenton processes mediated by different reducing compounds. Systems: $Fe^{2+}/H_2O_2$ (▲), $Fe^{2+}/H_2O_2$/reducer (●) and $Fe^{3+}/H_2O_2$/reducer (■).
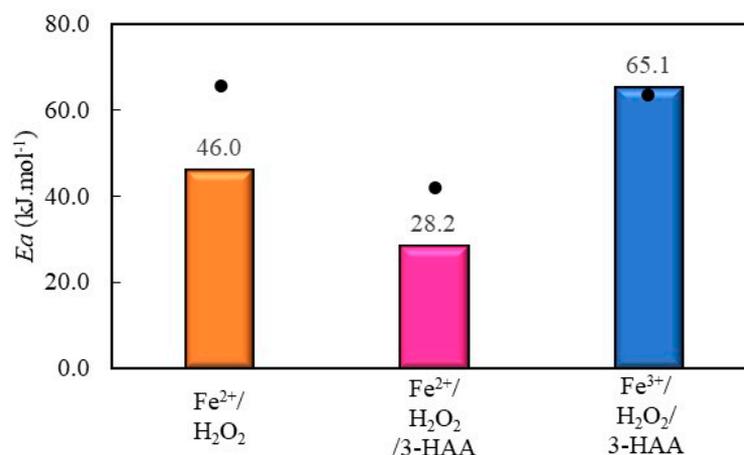
**Figure 5.** *Ea* values from Phenol Red decolorization via Fenton processes. Reaction conditions: [Fe] = 30 μmol L$^{-1}$; [H$_2$O$_2$] = 300 μmol L$^{-1}$; [dye] = 30 μmol L$^{-1}$; [3-HAA—3-Hydroxyanthranilic Acid] = 10 μmol L$^{-1}$; pH = 2.5–3.0. Bars: *Ea* values corresponding to the BMG model and calculated in the present study; dots: *Ea* values corresponding to the first-order reaction model based on past published data [20].
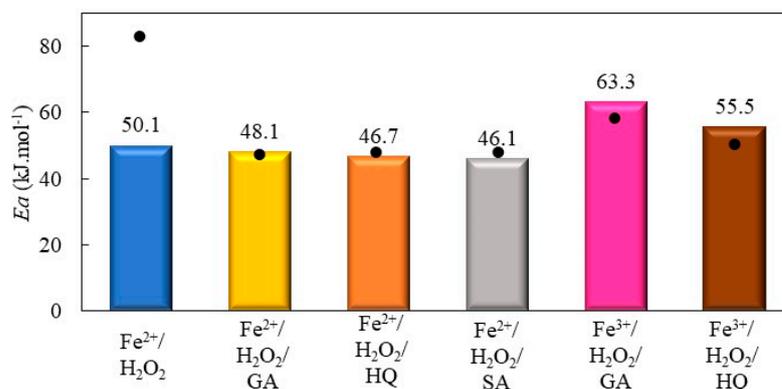


**Figure 6.** *Ea* values from Bismarck Brown Y decolorization via Fenton processes. Reaction conditions: [Fe] = 30 μmol L$^{-1}$; [H$_2$O$_2$] = 450 μmol L$^{-1}$; [dye] = 30 μmol L$^{-1}$; [reducer] = 10 μmol L$^{-1}$; pH = 2.5–3.0. Compounds evaluated: GA—Gallic Acid; HQ—Hydroquinone; SA—Salicylic Acid. Bars: *Ea* values corresponding to the BMG model and calculated in the present study; Dots: *Ea* values corresponding to the second-order reaction model based on past published data [24].
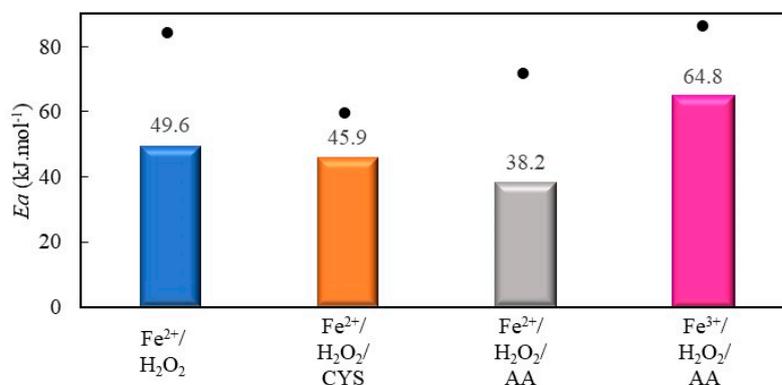


**Figure 7.** *Ea* values from Safranin T decolorization via Fenton processes. Reaction conditions: [Fe] = 30 μmol L$^{-1}$; [H$_2$O$_2$] = 300 μmol L$^{-1}$; [dye] = 40 μmol L$^{-1}$; [reducer] = 10 μmol L$^{-1}$; pH = 2.5–3.0. Reducers evaluated: CYS—Cysteine; AA—Ascorbic Acid. Bars: *Ea* values corresponding to the BMG model and calculated in the present study; dots: *Ea* values corresponding to the first-order reaction model based on past published data [22,23].
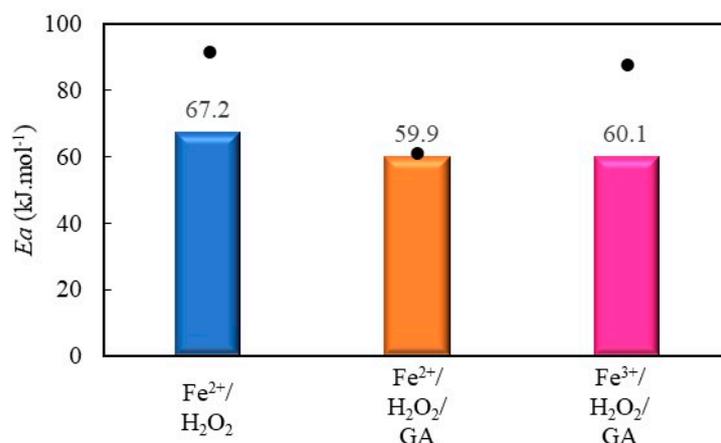
**Figure 8.** *Ea* values from decolorization of Methyl Orange via Fenton processes. Reaction conditions: [Fe] = 30 µmol L$^{-1}$; [H$_2$O$_2$] = 450 µmol L$^{-1}$; [dye] = 40 µmol L$^{-1}$; [GA—Gallic Acid] = 10 µmol L$^{-1}$; pH = 2.5–3.0. Bars: *Ea* values corresponding to the BMG model and calculated in the present study; dots: *Ea* values corresponding to the first-order reaction model based on past published data [21].
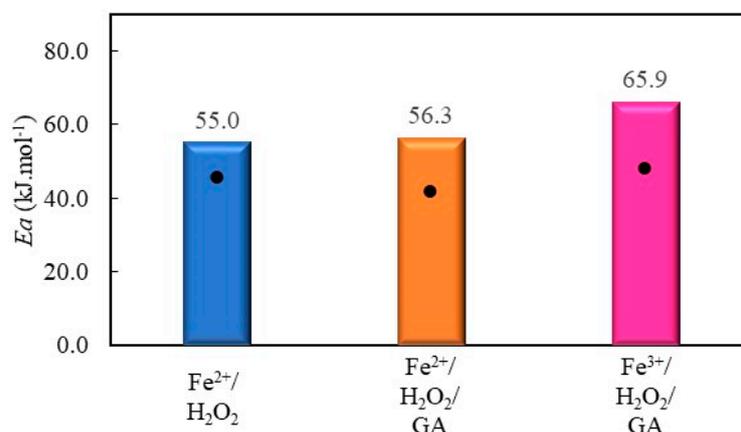


**Figure 9.** *Ea* values from Chromotrope 2R decolorization via Fenton processes. Reaction conditions: [Fe] = 30 µmol L$^{-1}$; [H$_2$O$_2$] = 450 µmol L$^{-1}$; [dye] = 40 µmol L$^{-1}$; [GA—Gallic Acid] = 10 µmol L$^{-1}$; pH = 2.5–3.0. Bars: *Ea* values corresponding to the BMG model and calculated in the present study; dots: *Ea* values corresponding to the second-order reaction model based on past published data [21].

### 2.2.1. Phenol Red Decolorization by Fenton Processes Mediated by 3 Hydroxyanthranilic Acid

The 3-Hydroxyanthranilic Acid (3-HAA) is a metabolite produced by the wood-decomposing fungus *Picnoporus cinnabarinus* [42]. Its pro-oxidant effect may be linked to its Fe$^{3+}$-reducing activity [10], consequently increasing the formation of hydroxyl radicals. When evaluating Phenol Red as a target pollutant, *Ea* values referring to Fenton processes are shown in Figure 5.

The *Ea* values from Phenol Red decolorization followed this order: Fe$^{3+}$/H$_2$O$_2$/3-HAA > Fe$^{2+}$/H$_2$O$_2$ > Fe$^{2+}$/H$_2$O$_2$/3-HAA. The addition of 3-HAA promoted a decrease in *Ea* by 39% when comparing the two last reaction systems. When considering data of *Ea* obtained with the first-order model [20], a lower difference was observed, 28%. Highlighting the contrast in *Ea* from $1/m$ values, the Fe$^{3+}$/H$_2$O$_2$/3-HAA system exhibited the highest one, surpassing the values for Fe$^{2+}$/H$_2$O$_2$ by 30% and Fe$^{2+}$/H$_2$O$_2$/3-HAA by 57%.

### 2.2.2. Decolorization of Bismarck Brown Y by Fenton Processes Mediated by Hydroquinone, Gallic Acid, and Salicylic Acid

When evaluating the decolorization of the Bismarck Brown Y dye by Fenton processes, three compounds were tested, namely Hydroquinone, Gallic Acid, or Salicylic Acid. It is important to mention that Salicylic Acid is not a reducer of Fe$^{3+}$, but it can be converted

into dihydroxylated reducers (2,5-dihydroxybenzoic acid, 2,3-dihydroxybenzoic acid, and catechol) by HO$^\bullet$ radicals during the reactions [14]. Figure S6 shows the Salicylic Acid being converted into intermediates, which react with $Fe^{3+}$ and then are converted into their respective quinones. The simplified mechanisms involving reactions between Fenton reagents and Hydroquinone or Gallic acid are shown in Figure S7 and Figure S8, respectively.

As shown in Figure 6, the three compounds decreased *Ea* when comparing $Fe^{2+}/H_2O_2$ and $Fe^{2+}/H_2O_2$/reducer systems. Salicylic Acid decreased the *Ea* by 8%, while Hydroquinone decreased by 7%. In turn, the addition of Gallic Acid reduced *Ea* by less than 5%. When the second-order rate constants were used in previous our study [24], this percentage decrease in *Ea* was much more evident. In the presence of Gallic Acid or Hydroquinone, $Fe^{3+}/H_2O_2$/reducer system exhibited higher *Ea* from $1/m$ values, surpassing $Fe^{2+}/H_2O_2$ and $Fe^{2+}/H_2O_2$/reducer by up to 24%.

### 2.2.3. Decolorization of Safranin T by Fenton Processes Mediated by Cysteine and Ascorbic Acid

The *Ea* values obtained from the decolorization of Safranin T are shown in Figure 7. Unlike other studies, two natural non-phenolic reducers were evaluated to decolorize this dye: Cysteine and Ascorbic Acid. Cysteine is an amino acid generally produced through the hydrolysis of keratin [43], and has the ability to reduce $Fe^{3+}$ due to the presence of a sulfhydryl group (-SH) in its molecule. The reaction between $Fe^{3+}$ and Cysteine results in $Fe^{2+}$ and Cystine. The latter may undergo reaction with HO$^\bullet$ to regenerate Cysteine or be converted into Cysteic acid [44]. Ascorbic Acid, also known as vitamin C, is found in many vegetables, although it is produced industrially from glucose [45]. At pH 3.0, Ascorbic Acid is partly found as ascorbate monoanion ($AA^-$), which undergoes a two-step oxidation to yield dehydroascorbic acid. Besides $AA^-$, other intermediates (ascorbyl radical; $AA^{-\bullet}$) actively reduce $Fe^{3+}$ to $Fe^{2+}$, catalyzing the conversion of $H_2O_2$ to HO$^\bullet$ radical through the Fenton reaction [46]. The simplified mechanisms involving reactions between the two reducers aforementioned and Fenton reagents are shown in Figure S9 and Figure S10, respectively.

As with other dyes, $Fe^{2+}/H_2O_2$/reducer system showed lower *Ea* than $Fe^{2+}/H_2O_2$. The Ascorbic Acid promoted a decrease in *Ea* by 23%, while the Cysteine only decreased by 7%. This suggests that there may be distinct interactions between Fe ions and the two reducing compounds studied. This explanation also applies to Bismarck Brown Y decolorization influenced by three compounds (Section 2.2.2). When comparing the systems in the presence of Ascorbic Acid, the *Ea* value for the $Fe^{3+}/H_2O_2$/reducer system was 69% higher than $Fe^{2+}/H_2O_2$/reducer. Similar to Phenol Red and Bismarck Brown Y (Sections 2.2.1 and 2.2.2, respectively), $Fe^{3+}/H_2O_2$/reducer system had the higher energy barrier to decolorize Safranin T.

In general, the *Ea* values previously calculated by the first-order reaction model were higher than those calculated by the BMG model. Furthermore, there was an inversion in the order of *Ea* values between the reaction systems with reducers. For example, the order of values of *Ea* from $k_1$ of the previous studies was $Fe^{3+}/H_2O_2$/Ascorbic Acid > $Fe^{2+}/H_2O_2$ > $Fe^{2+}/H_2O_2$/Ascorbic Acid > $Fe^{2+}/H_2O_2$/Cysteine, while when considering the $1/m$, the order was changed to $Fe^{3+}/H_2O_2$/Ascorbic Acid > $Fe^{2+}/H_2O_2$ > $Fe^{2+}/H_2O_2$/Cysteine > $Fe^{2+}/H_2O_2$/Ascorbic Acid.

### 2.2.4. Decolorization of Methyl Orange by Fenton Processes Mediated by Gallic Acid

Gallic Acid is a polyphenolic reducer extracted from plants and has been one of the most evaluated in the literature as a pro-oxidant in Fenton processes, as recently reviewed by Lima et al. [47]. In addition to the Bismarck Brown Y dye (Section 2.2.2), Gallic Acid was evaluated in the decolorization of two other azo dyes: Methyl Orange and Chromotrope 2R.

The *Ea* values for the decolorization of Methyl Orange are shown in Figure 8. Comparing the $Fe^{2+}/H_2O_2$ and $Fe^{2+}/H_2O_2$/reducer systems, the percentage of decrease in *Ea* was 11% due to the addition of Gallic Acid. Curiously, *Ea* values were similar for

the $Fe^{2+}/H_2O_2/GA$ and $Fe^{3+}/H_2O_2/GA$ systems. Notably, the reduction in *Ea* was more pronounced when employing the conventional first-order reaction model for the $Fe^{2+}/H_2O_2/GA$ system in relation to the others.

### 2.2.5. Decolorization of Chromotrope 2R by Gallic Acid-Mediated Fenton Processes

The *Ea* values for the decolorization of Chromotrope 2R are shown in Figure 9. Unlike other dyes, there was practically no significant change in *Ea* values regarding $Fe^{2+}/H_2O_2$ and $Fe^{2+}/H_2O_2/GA$. $Fe^{3+}/H_2O_2/GA$ exhibited the highest *Ea* value among the systems, surpassing $Fe^{2+}/H_2O_2$ and $Fe^{2+}/H_2O_2/GA$ by 17% and 15%, respectively. Except for Methyl Orange (Section 2.2.4), the $Fe^{3+}/H_2O_2$/reducer system had the higher energy barrier to decolorize the dyes.

It is important to mention that in the previous study, when calculating *Ea* using data from the second-order model [21], no variation in *Ea* was reported when Gallic Acid was added. This result can possibly be attributed to the greater susceptibility of Chromotrope 2R to being decolorized by free radicals, regardless of the presence of Gallic Acid.

Considering that the concentrations of the reagents in the experiments to decolorize each dye are not similar, the values of the $[Fe]:[H_2O_2]$ ratio are different. Consequently, the production of $HO^\bullet$ radical is influenced, interfering in the degradation of a target pollutant by Fenton processes [6,16]. In addition, dyes may exhibit different susceptibility to $HO^\bullet$ radicals. This aspect can be attributed to the different reactivity of its chromosphere groups and other non-chromophore sites present in their molecules [48,49]. Therefore, even if the dyes were evaluated under the same reaction condition, the *Ea* values would different between them. For example, regardless of the reaction kinetic model, *Ea* from decolorization of Chromotrope 2R was lower than Methyl Orange.

Comparing kinetic models and their constants used to calculate *Ea*, all $1/m$ values were greater than those for $k_1$ and $k_2$, when the three models fitted well the same experimental data in our previous works. Studies developed by other research groups also observed higher values of $1/m$ compared to $k_1$ [27,29,30]. Regardless of the *Ea* values being different based on the rate constants from three kinetic models, it was possible to verify that all $Fe^{3+}$-reducing compounds (in addition to Salicylic Acid) presented pro-oxidant behavior to degrade different dyes through Fenton processes.

## 3. Materials and Methods

Decolorization tests were carried out in triplicate, in the dark, and without agitation. The reactions were carried out in quartz cuvettes with a reaction volume of 2 mL containing a target dye, $H_2O_2$, $FeSO_4$ or $Fe(NO_3)_3$, $H_2SO_4$ (to adjust the pH in the ideal range between 2.5 and 3.0), and a reducer. The solutions were kept in a water bath for 10 min to reach the designed temperature (20, 30, 40, and 50 °C), and then Fe ions were added to start the reactions. This time interval also demonstrated that there was no decolorization of any of the dyes due to the unique effect of temperature. The different dyes and reducers, in addition to the concentrations of all reagents, are shown in Table 1 and additional details can be obtained from previous studies.

Dye decolorization was monitored on a spectrophotometer (NI 1800UV, Nova Instruments, Piracicaba, SP, Brazil) by decreasing absorbance at the characteristic maximum wavelength ($\lambda_{max}$) of each dye under the reaction conditions studied. The reference solution in the equipment contained all reagents except the dye and iron ions. Analytical curves were prepared to determine the residual concentration of the dyes. Controls involving the reagents separately (including only the reducers, Fe salts, or $H_2O_2$) were conducted in our previous studies, and did not present decolorization.

**Table 1.** Concentration of reagents evaluated in dye degradation tests via Fenton processes.

| [Dye] | Dye's Chemical Structure | $\lambda_{max}$ (nm) | [H$_2$O$_2$] ($\mu$mol·L$^{-1}$) | [FeSO$_4$] or [Fe(NO$_3$)$_3$] ($\mu$mol·L$^{-1}$) | [H$_2$SO$_4$] (mmol·L$^{-1}$) | [Reducer] | Reducer's Chemical Structure | Reference |
|---|---|---|---|---|---|---|---|---|
| 30 $\mu$mol·L$^{-1}$ Phenol red |  | 435 | 300 | 30 | 1 | 10 $\mu$mol·L$^{-1}$ 3-Hydroxyanthranilic Acid |  | [20] |
| 30 $\mu$mol·L$^{-1}$ Bismarck Brown Y |  | 450 | 450 | 30 | 1 | 10 $\mu$mol·L$^{-1}$ Hydroquinone |  | [24] |
| | | | | | | 10 $\mu$mol·L$^{-1}$ Gallic Acid |  | |
| | | | | | | 10 $\mu$mol·L$^{-1}$ Salicylic Acid |  | |
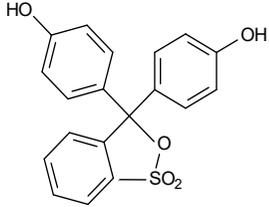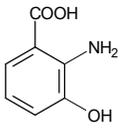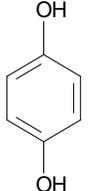
**Table 1.** *Cont.*
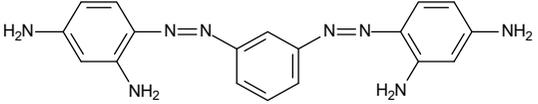
| [Dye] | Dye's Chemical Structure | $\lambda_{max}$ (nm) | [H$_2$O$_2$] ($\mu$mol·L$^{-1}$) | [FeSO$_4$] or [Fe(NO$_3$)$_3$] ($\mu$mol·L$^{-1}$) | [H$_2$SO$_4$] (mmol·L$^{-1}$) | [Reducer] | Reducer's Chemical Structure | Reference |
|---|---|---|---|---|---|---|---|---|
| 40 $\mu$mol·L$^{-1}$ Safranin T |  | 519 | 300 | 30 | 1 | 10 $\mu$mol·L$^{-1}$ Cysteine |  | [22] |
| | | | | | | 10 $\mu$mol·L$^{-1}$ Ascorbic Acid |  | [23] |
| 40 $\mu$mol·L$^{-1}$ Methyl Orange |  | 508 | | | | | | |
| 40 $\mu$mol·L$^{-1}$ Chromotrope 2R |  | 513 | 450 | 30 | 1 | 10 $\mu$mol·L$^{-1}$ Gallic Acid |  | [21] |
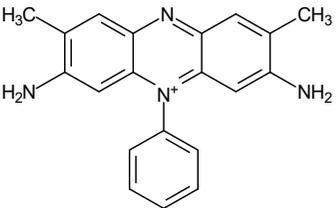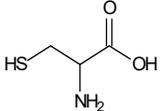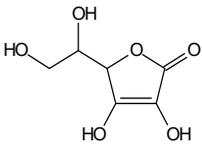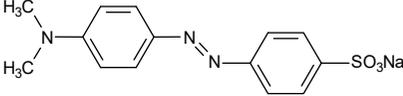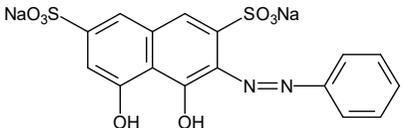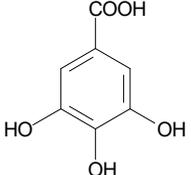
From the decolorization data over 60 min, a kinetic study was carried out based on the BMG model (Equation (6)) [23]. Using the values of $1/m$ at different temperatures, the *Ea* values were calculated for the decolorization reactions of the different dyes using the linearized Arrhenius equation (substituting $k$ for $1/m$), as shown in Equation (10) [33].

$$\ln\left(\frac{1}{m}\right) = \ln\left(A\right) - \frac{Ea}{R \cdot T} \tag{10}$$

where *A* is the frequency (min$^{-1}$); *Ea* is the activation energy (J·mol$^{-1}$); *R* is the ideal gas constant (8.314 J.mol$^{-1}$·K$^{-1}$); and *T* is the absolute temperature (*K*). The graph $\ln(1/m)$ vs. $1/T$ has allowed calculating the activation energy values from its slope.

## 4. Conclusions

Through the kinetic study using the BMG model, it can be noted that the values of the initial reaction rates $(1/m)$ obtained from the decolorization reactions of different dyes using Fenton processes ($Fe^{2+}/H_2O_2$, $Fe^{2+}/H_2O_2/$reducer, and $Fe^{3+}/H_2O_2/$reducer) were increased in the presence of $Fe^{3+}$-reducing organic compounds. For almost all dyes evaluated, the activation energy (*Ea*) calculated from the $1/m$ values showed that the energy barrier of reactions initially containing $Fe^{2+}$ was lower due to addition of reducers. Except for one of the dyes, Methyl Orange, the $Fe^{3+}/H_2O_2/$reducer system had the higher energy barrier to decolorize the dyes. Compared to *Ea* values from $k_1$ or $k_2$ data (from previous our works), the *Ea* values obtained from $1/m$ showed less differentiation between the reaction systems in the presence or absence of reducers. Although *Ea* values obtained from conventional kinetic models demonstrated more evident effect of reducers, the BMG model can be indicated as a complementary analysis to verify the pro-oxidant behavior of these compounds in Fenton processes.

**Conflicts of Interest:** The authors declare no conflict of interest.

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