Modelling of Reaction Kinetics of Hibiscus Sabdariffa L. Juice Anthocyanins Degradation by Electrochemical Means

Ndiaye Khady1,2, Kane Cheikhou1,*, Ndoye Mouhamed1, Ayessou Nicolas2, Cisse Mady2, Diop Codou Mar1

1Laboratory of Electrochemistry and Membrane Processes ESP/UCAD, Dakar Senegal
2Laboratory of Continuing Education in Food Industry ESP/UCAD, Dakar Senegal

*Corresponding author: cheikhou.kane@ucad.edu.sn

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Abstract: The numerous benefits of anthocyanins from Hibiscus sabdariffa L on human health explain all the thermal and athermal preservation techniques undertaken so far. However, these methods result in considerable losses of anthocyanins, leading to a deterioration of the nutritional and organoleptic qualities of the product during storage. Platinum electrode oxygen reduction is a new athermal technique using a two-compartment electrolysis cell separated by a cationic membrane. The fruit juice is stabilized by passing the reduction current for a set time. The electrochemical approach is a new technique for cold juice without adding chemical molecules. Reaction kinetics in Hibiscus sabdariffa juice follows 1st order kinetics. The classical Arrhenius, Ball and Eyring models used showed the degradative effect of dissolved oxygen in the juice with a significant difference (Ea = 4000 J/mol) between the activation energy of the electroreduced extract and the control (untreated). This is corroborated by the values of the half-reaction time which are 24 S⁻¹ for the electrochemically treated extract and 20 S⁻¹ for the untreated control after 5 months of storage at 4°C. The value of the enthalpy of activation of the electroreduced juice is about 6 J/mol/K and that of the control 5.72 J/mol/K shows that the electrochemical process takes place at low energy, i.e. 0.28 J/mol/K for a volume of about 250 ml. The various kinetic models have also confirmed by the electrochemical approach that the temperature factor predominates over the dissolved oxygen factor. At 37°C, the half-reaction time is 1.3 s⁻¹ for the electroreduced Hibiscus juice as for the untreated extract after 5 months of conservation.

Keywords: Modelling, Hibiscus sabdariffa, Anthocyanins, Oxygen, conservation, Electroreduction, Kinetic


1. Introduction

The color of food products plays a key role in the food industry. It can be a fingerprint of the product to assess its overall quality. Anthocyanins are natural water-soluble pigments of the flavonoid family, and are secondary metabolites synthesized by plants [1-2].

Anthocyanins are present in a wide variety of vegetables, cereals, flowers and fruits. They are groups of molecules ranging from pink, red, purple to dark blue and have several medicinal interests. However, the presence of a flavylium cation makes them very unstable to factors such as temperature, light, oxygen among others [3-9].

Conventional food preservation processes usually involve the use of heat treatment in order to preserve food and its sensory properties. However, heat treatment has a negative influence on the stability of anthocyanins and their nutritional and organoleptic properties [1] [10] [13-15].

The negative impact of heat treatment on anthocyanins of Hibiscus sabdariffa L. has been studied by several authors [10] [14-15] by determining their kinetic parameters.

Dissolved oxygen in the juice is also a degradation factor that has been shown by several authors [16-20]. However, its removal has always been done by bubbling with an inert gas or by adding other molecules [21-22].

The reduction of dissolved oxygen in food products is a new electrochemical approach to stabilize cold juices without the addition of chemical molecules [23].

The modeling of reaction kinetics in Hibiscus sabdariffa juice will allow to better understanding the kinetic and thermodynamic parameters during hydrolysis.

The kinetic laws are basically based on the chemical reaction with a graphical approach. Chemical kinetics is the study of the evolution over time of a thermodynamically possible chemical reaction [24].

A model can be defined as an abstract and simplified representation of a real-world entity, phenomenon, process or system in order to describe, explain or predict it. In chemistry, models are used to describe the way a compound degrades or forms during a chemical reaction [25].
The influence of temperature variation on the reaction rate can be characterized by the activation energy \(E_a\). Reactions with low activation energy will be more sensitive to temperature than those with high activation energy [25].

Building a model therefore means translating simplifying hypotheses into mathematical equations. The modeling of reaction kinetics was carried out to develop a tool that could predict the degradation of anthocyanins after storage at different temperatures (4°C, 30°C and 37°C). Three models (Arrhenius, Eyring and Ball) were considered to describe anthocyanin degradation before and after electrochemical treatment.

Our objective is to show through the kinetic parameters (activation energy, rate constant, decimal reduction time, enthalpy and entropy) that anthocyanins from Hibiscus sabdariffa can be stabilized in the long term by electrochemical means and the rate of degradation predicted.

Figure 1. A) Electroreduction system B) Electrolysis cell with two compartments separated by a cationic membrane

2. Materials and Methods

2.1. Materials

\textit{Hibiscus sabdariffa} calyces were macerated with a ratio of 1/5 kg/kg (calyx/water).

The electrochemical equipment consisted of a two-compartment Plexiglas electrolysis cell separated by a cationic membrane. The electrochemical measurements carried out in this work use a three-electrode potentiostatic set-up. It comprises a working electrode, the site of the electrochemical reactions studied, an auxiliary electrode which closes the electrical circuit and a reference electrode, which makes it possible to control and measure the potential of the working electrode. The system used is a potentiostat connected to a computer equipped with cyclic voltammetry software (Figure 1).

The potential difference applied between the two electrodes, anode and cathode, is produced by an electric current generator, in potentiostatic mode, connected to a potentiostat that sets the potential between the anode and the reference electrode. The applied electrolysis potentials are fixed with respect to this reference.

The treatment was carried out on 250ml of \textit{Hibiscus sabdariffa} L juice placed in the cathode compartment using an equivalent volume of 0,1N hydrochloric acid in the anode compartment. The current intensities applied and the duration of the treatment were determined by following the voltammetric study.

3. Methods

3.1. Kinetic Models

The Arrhenius, Eyring and Ball models are used to study the kinetics of anthocyanin degradation. The reactions are described in terms of first order kinetics [14].

a. The Arrhenius model

The first order kinetic reaction is described by:

\[ C = C_0 \exp(-kt) \quad \text{avec} \quad k = k_\infty \exp\left(-\frac{E_a}{RT}\right) \]

\text{Equation 1}

- \(C\): Concentration at \(t\);
- \(C_0\): Concentration at to;
- \(K\): Rate constant in s\(^{-1}\);
- \(K_\infty\): Pre-exponential factor (value of \(k\) at infinity) in s\(^{-1}\);
- \(E_a\): Energy of activation in J.mol\(^{-1}\).k\(^{-1}\);
- \(R\): Perfect gas constant equal to 8,31 J.mol\(^{-1}\).k\(^{-1}\);
- \(T\): Temperature in kelvin (k);

We plot the variation of the concentration as a function of time: \(\ln(C) = f(t)\).

Thus, we obtain an affine line \(y = ax + b\);

By identification, \(a = \text{slope} = -k\) and \(b = \text{the intercept} = \ln(C_0)\)

To determine the parameters \(k_\infty\) and \(E_a\), the Arrhenius law is rewritten as follows:

\[ \ln k = \ln k_\infty - \frac{E_a}{RT} \]

Plotting the curve \(\ln(k) = f(1/T)\) gives a line whose slope represents \(-E_a / RT\) and the intercept is \(\ln k_\infty\). Thus, we obtain the two parameters \(E_a\) and \(k_\infty\) of the Arrhenius model.

b. The Eyring model

The first-order kinetics is based on the following equation:

\[ C = C_0 \exp(-kT) \quad \text{with} \quad k = \left(\frac{k_B}{h}\right) \frac{T}{\exp\left(-\frac{\Delta H^*/RT}\right) \exp\left(-\frac{\Delta S^*/R}\right)} \]

\text{Equation 2}

- \(k_B\): Bolzmann constant (1,381.10\(^{-23}\) J. K\(^{-1}\))
- \(h\): Planck constant (6,626.10\(^{-34}\) J.s)
Thus, by plotting the curve \( \ln(k/T) \) as a function of \( 1/T \), we obtain a straight line whose slope is \(-\Delta H^*/R\) and the intercept is \( \ln(K_B/h) + \Delta S^*/R \).

c. Ball's model

The Ball model expresses the thermoresistance of the compound under study by knowing the parameters \( D_0 \) and \( z \). The first order reaction of the model is given by the equation:

\[
C = C_0 \cdot 10^{-t/D_0} = D_0 \cdot 10^{\frac{-T}{z}} \tag{Equation 3}
\]

\( D_0 \): is the decimal reduction time at \( T = 0 \)°C in seconds (S);

\( z \): temperature difference for a change in \( D \) by a factor of ten in °C;

By introducing the decimal logarithm, we obtain:

\[
\log D = \log(D_0) - \frac{T}{z}
\]

Thus, by plotting the curve \( \log(D) = f(T) \), we obtain a straight line whose slope is \(-1/z\) and the intercept is \( \log(D_0) \).

4. Results and Discussion

The experimental study of the kinetics gives access to the reaction mechanisms, i.e. to understand the behaviour of the molecules at the infinitely small scale.

In this section, the results of the modeling of the electrochemically treated extract (sample) and the untreated extract (control) are presented.

The Arrhenius, Eyring and Ball models were used to study the kinetics of degradation of *Hibiscus sabdariffa* L. extracts after 5 months of storage at 4°C, 30°C and 37°C. The results presented in the following Figure 2 shows that the degradation follows first order kinetics.

**Sample 1** was treated with a peak reduction potential / treatment time pair (-125mV/30mn): this is the chronoamperometry.

**Sample 2** was treated by a reduction peak intensity / treatment time pair (-5mA/30mn): this is chronopotentiometry.
The control is the untreated extract electrochemically preserved under the same conditions as the samples. The curves are linear at all temperatures (4°C, 30°C and 37°C) with regression coefficients ranging from 0.96 to 0.99 for the control and from 0.98 to 0.99 for the samples. Thus, the Arrhenius, Eyring and Ball models are applicable.

4. Determination of Kinetic Parameters

The reactions were described in terms of first order kinetics:

\[
\frac{dX}{dt} = -K.X \quad \text{Equation 4}
\]

4.1. Arrhenius Model

The dependence of the reaction constant K on the absolute temperature of the system is expressed by the Arrhenius equation (Equation 1). K is given by \( \ln(C/Co) = f(t) \) figure2.

The following curve \( \ln (K) = f (1/T) \) figure3 allows us to determine the kinetic parameters (\( E_a \) and \( K_{\infty} \)).

The equations presented in figure3 (Arrhenius model) were used to establish the kinetic parameters in the following table1.

<table>
<thead>
<tr>
<th>Arrenius</th>
<th>K(( S^{-1} ))</th>
<th>Ea (KJ.mol(^{-1} ))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>5.92E+09a</td>
<td>59,58a'</td>
<td>0,998</td>
</tr>
<tr>
<td>Sample1</td>
<td>2.38E+10b</td>
<td>63,21b'</td>
<td>0,999</td>
</tr>
<tr>
<td>Sample2</td>
<td>1.82E+10c</td>
<td>62,44c'</td>
<td>0,999</td>
</tr>
</tbody>
</table>

Table 1 shows the kinetic parameters of the Arrhenius model: the rate constant \( K_{\infty} \), the activation energy \( E_a \) and the regression coefficient of the samples and the control.

The activation energy of the electrochemically treated extracts is significantly higher than that of the control. This could be explained by the fact that the degradation reactions of the untreated extract (Control \( E_a = 59,58 \) KJ.mol\(^{-1} \)) are partly due to the presence of dissolved oxygen compared to the Hibiscus extracts whose dissolved oxygen has been electroreduced (chronoamperometry and chronopotentiometry) respectively sample1 (\( E_a=63,21 \) KJ.mol\(^{-1} \)) and sample2 (\( E_a=62,44 \) KJ.mol\(^{-1} \)).

Referring to L. PIETRI's course [24], the activation energy is the energy barrier that the reactants must cross in order for the chemical transformation to take place, it can be said that the oxygen dissolved in the juice considerably reduces the activation energy barrier.

4.2. Eyring's Model

The Eyring model uses the enthalpy and entropy of activation (\( \Delta H^* \) and \( \Delta S^* \)). The representation of the curve \( \ln (K/T) \) as a function of \( 1/T \) gives the equations for determining the kinetic parameters \( \Delta H^* \) and \( \Delta S^* \).

The equations in Figure4 (Eyring model) were used to find the enthalpy and entropy of activation (\( \Delta H^* \) and \( \Delta S^* \)) of the samples and the control, recorded in Table2.

<table>
<thead>
<tr>
<th>Eyring</th>
<th>( \Delta H^* )(J/mol(^{-1} ))</th>
<th>( \Delta S^* )(J/mol(^{-1})K(^{-1} ))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>5.72E+04a</td>
<td>-65,95a'</td>
<td>0,997</td>
</tr>
<tr>
<td>Sample1</td>
<td>6.08E+04b</td>
<td>-54,37b'</td>
<td>0,998</td>
</tr>
<tr>
<td>Sample2</td>
<td>6.00E+04c</td>
<td>-56,64c'</td>
<td>0,999</td>
</tr>
</tbody>
</table>

Table 2 presents the enthalpy of activation (\( \Delta H^* \)), the entropy of activation (\( \Delta S^* \)) and the regression coefficient \( R^2 \) of the extracts treated with the \(-125mV/30mn \) couple (Sample1), the \(-5mA/30mn \) couple (Sample2) and of the extract not treated electrochemically (Control).
For processes carried out at constant pressure, the enthalpy change corresponds to the heat absorbed (or released) to remain at constant temperature [26].

Positive values for the samples and the control mean that the reactions in solution are endothermic. A significant difference of 3.6 kJ/mol was noted between the sample and the control showing the low energy consumption by the electrochemical treatment of bissap juice.

The negative values of the activation entropy $\Delta S^*$ of the samples (-54.3 and -56.64 J/mol/K) as well as the control (-65.95 J/mol/K) attest to the very low degree of disorder of the system at the microscopic level [26]. However, the significant difference noted between the samples and the control would be due to the reaction of reduction of oxygen to water carried out by chronopotentiometry (-125mV/30mn) or by chronoamperometry (-5mA/30mn) in the cathodic compartment of the electrochemical cell thus creating a certain disorder for the electroreduced extract (Sample).

### 4.2. Ball's Model

Ball's approach characterises the thermo-resistance of the compound by determining the decimal reduction time $D$ and the temperature difference $z$.

Ball's model is used in chemistry to study the degradation of compounds but also to study the thermal destruction of bacteria [25].

The graphical representation of $\log(D)$ as a function of $T$ (Figure 5) allows the equation characterising the decimal reduction time $D_0$ and the temperature difference $z$ to be determined.

The following table presents the kinetic parameters ($D_0$ and $z$) of Ball's model.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$D_0 (S)$</th>
<th>$Z (°C)$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>1.43E+11a</td>
<td>28.65a</td>
<td>0.991</td>
</tr>
<tr>
<td>Sample1</td>
<td>6.47E+11b</td>
<td>27.03b</td>
<td>0.989</td>
</tr>
<tr>
<td>Sample2</td>
<td>4.48E+11c</td>
<td>27.40c</td>
<td>0.988</td>
</tr>
</tbody>
</table>

The $\log(D) = f(T)$ curve in Figure 5 was used to determine the kinetic parameters: decimal reduction time $D_0$ and the temperature difference $z$.

The Bigelow-Ball law characterises the thermo-resistance of the product (microbial destruction) while the Arrhenius law characterises the thermosensitivity of the compound.

The $z$-factor is directly related to the activation energy in the Arrhenius law [25].

The results obtained on the Arrhenius and Ball models confirm the hydrolysis reaction carried out in bissap juice which allowed the reduction of dissolved oxygen to water.

Indeed, according to Hallstrom et al, when $z$ is between 25 and 50°C and $Ea$ between 60 and 110 KJ/mol, a hydrolysis reaction occurs [27].

Dye destruction can also be controlled by the relationship between $z$ and $Ea$. According to Hallstrom, when $z$ is between 38 and 80 °C and $Ea$ between 30 and 90 KJ/mol, dye destruction occurs. Thus, compared to our results, the juice keeps its red colour.

Similarly, the *Hibiscus sabdariffa* extract does not undergo non-enzymatic browning because the values of $z$ (Table 3) are not between 17 and 39 °C, and those of $Ea$ (Table 1) are not between 100 and 250 KJ/mol [27].

The results in Table 3 show the advantage of electrochemical treatment on the conservation of anthocyanins in *Hibiscus sabdariffa* L.

Indeed, the decimal reduction time $D_0$ is $6.47.10^{11}$ and $4.48.10^{11}$ for the samples against $1.43.10^{11}$ for the control, which means that the electroreduced extract is more resistant to degradation factors compared to the non-electroreduced extract (control).

The rate of destruction $D$ is related by the Arrhenius thermal activation law [25].

The half-reaction time $t_{1/2}$ is the time required to consume half of the limiting reagent initially present.

After 5 months of storage, we have a significant difference between the half-reaction times of the samples and the control at all storage temperatures (4°C, 30°C and 37°C) as well as for the destruction rate $D$.  

![Figure 5](image_url)  

**Figure 5.** Ball curve representing log (D) versus temperature (T) of: A) untreated *Hibiscus sabdariffa* extract, B) extract treated by chronoamperometry (-125mV/30mn), C) extract treated by chronopotentiometry (-5mA/30mn)
Thus, the limiting reagent of the juice with dissolved oxygen disappears faster than the one with reduced dissolved oxygen.

The results in Table 4 shows the predominance of the temperature factor over the dissolved oxygen factor. Indeed, the value of the half-reaction time \( t_{1/2} \) at 4°C is much higher than the values at 30°C and 37°C for both the sample and the control. Nevertheless, at 4°C the speed of the degradation reaction of the control is higher than that of the sample as shown by the values of the rate constant 3.4.10^{-2} S^{-1}(Control) and 2.84.10^{-2} S^{-1}(Sample2). This is corroborated by the difference in the values of the half-reaction times: 24.45 and 23.08 S^{-1} for the samples and 20.39 S^{-1} for the control. The electrochemical treatment therefore reduces the degradation rate of Hibiscus sabdariffa juice.

On the other hand, the results in Table 4 show that the two methods, namely chronooamperometry -125mV/30mn (Sample1) and chronopotentiometry -5mA/30mn (Sample2), are practically equivalent for the electrochemical treatment of the juice.

5. Conclusion

In general, the modeling of the reaction kinetics of Hibiscus sabdariffa L juice allowed us to see the effect of electrochemical treatment on the conservation of anthocyanins after 5 months of storage. The Arrhenius and Ball models characterizing respectively the thermo-sensitivity and thermo-resistance of the food product allow us to say that the reduction of dissolved oxygen in Hibiscus sabdariffa juice by electrochemical means significantly slows down the rate of degradation of anthocyanins, in particular a difference in activation energy of 4 KJ/mol between the sample and the control. This is corroborated by the difference of 4 S^{-1} noted between the half-reaction times of the electroreduced extract and the control.

Moreover, the parameters activation energy \( Ea \) of the Arrhenius model and temperature difference \( z \) of the Ball model show that the electrochemical treatment can contribute to a better preservation of the juice.

Furthermore, the low energy used to electrochemically treat 250 ml of Hibiscus sabdariffa juice is confirmed by the enthalpy of activation 5.72.10^{44} J/mol for the control against 6.00.10^{44} J/mol for the electroreduced Hibiscus extract.

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