Research Note

Discoloring Process in Sherry Wines Studied by Means of Chromatic Parameters

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The decolorizing effects of different quantities of activated carbon adsorbent on the color of sherry samples (Fino wine) were studied. The color change was measured through the use of chromatic parameters determined by the CIELAB 76 system, using transmittances taken at 1-nm intervals throughout the visible spectrum. The effect of the adsorbent on the color of the wine has been expressed by equations that relate the values of the chromatic parameters with the quality of the added adsorbent. These equations show that the discoloring process follows a Freundlich-type adsorption isotherm. Using these equations, it is possible to predict the amount of carbon adsorbent necessary to attain a desired color.

KEY WORDS: sherry, wine color

One of the traditional characteristics of sherry wines is their unique system of aging (6,7), during which several of the processes which take place cause an intensification of color. This color change is due to components in the wood of the butts extracted during the different stages of the solera system, as well as redox processes as a result of transferring.

Often, consumers associate an increase in a wine's color with lower quality, which has led to a tendency toward paler sherries. This has caused wine producers to use color-adsorbing products such as activated carbon with a partially graphitized structure, *i.e.*, with a large surface area and, hence, with a high specific adsorption.

The two relationships used to characterize the adsorption in enology are the Langmuir and Freundlich isotherms. For example, the adsorption with poly-N-vinyl pyrrolidone (PVPP) was characterized with the Freundlich equation (8). With the Langmuir equation, the adsorption of proteins in wines has been described using bentonite as adsorbent; also, proline adsorption by bentonite may be explained as special cases of the Langmuir and of the Freundlich equations (1).

The Langmuir adsorption isotherm may be written as

$$x = x_m \cdot \left(\frac{c}{K_L^{-1} + c} \right) \qquad \text{Eq. 1}$$

where x is the amount of solute that is adsorbed from solution per mass of adsorbent, x_m is the maximum amount of solute that can be adsorbed per mass of adsorbent at equilibrium for the formation of the first monolayer, K_L is a constant, and c is the concentration of the solute in the solution that is in equilibrium with the adsorbent. When the adsorption process is followed through absorbance measures, c is proportional to A_i and x is proportional to $(A_0 - A_i)/g_i$ where A_0 and A_i indicate the absorbance of the wine solution without activated carbon and with g_i mg/L of activated carbon respectively.

The Freundlich adsorption isotherm

$$x = K_F \cdot c^{(1/n)} \qquad \text{Eq. 2}$$

may be written as

$$\log x = \log K_F + \frac{1}{n} \cdot \log c \qquad \text{Eq. 3}$$

where K_F and n are constants and x and c have the same meaning and equivalents as in the Langmuir isotherm. The physical meaning of this index is that for $n > 1$ the adsorption is weakly dependent on the concentration; for the case $n = 1$, the amount of solute adsorbed per unit of adsorbent is proportional to the equilibrium concentration and for $n < 1$ the adsorption is strongly dependent on the concentration.

Traditionally, the absorbance value at one or several wavelengths was used to characterize a wine's color, but this is an inadequate description of the color of a sample. However the use of the CIELAB 1976 chromatic space - obtaining previously the tristimulus X, Y, Z, from the visible absorption spectra - allows for a more precise definition of the color expressed as components of the coordinates L^* (lightness), a^* and b^* and also with the parameters chroma C^* and hue H^* obtained when a^* and b^* are represented in a two-dimensional space (2,5). The chromatic magnitude L^* is related to the psychological impression of the lightness which makes it possible to distinguish samples with different degrees of transparency and opacity; the Chroma C^* is related to the coloring intensity.

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Using this method to define the color, we have studied the adsorption isotherms that best fit the wines' chromatic parameters, when varying the amount of adsorbent, by developing mathematical expressions that relate the chromatic parameter values with the amount of adsorbent added. It is assumed that c is proportional to u_i^*, and similarly, x is proportional to $(u_0^* - u_i^*)/g_i$ where u_i^* means the value i of chromatic parameters -- L^*, a^*, b^*, C^* or H^* -- obtained when the wine sample has g_i mg/L of adsorbent and u_0^* the value without adsorbent.

These mathematical equations makes it possible to predict, *a priori*, the effect of a given amount of adsorbent on the color of a wine before these operations are carried out leaving no possibility of rectification. We have found no prior work that uses such a methodology.

Material and Methods

After examining several types of sherry wine of the Jerez area, we chose a Fino wine ready for sale from a local company. We chose this type of wine because the other wines of this area such as Oloroso and Amontillado are not generally susceptible to discoloring processes.

The activated carbon used (called Decoran) was supplied by AEB Ibérica; its surface area varied from 900 to 1100 m^2/g (B.E.T.), with a particle diameter of 1 to 10 nm.

Wine samples were treated with accurately weighed amounts of activated carbon and mechanically shaken in a thermostatic bath at 25°C for one hour to reach equilibrium, then centrifuged at 5000 rpm for five minutes and filtered with a 0.45-μm membrane filter. After several tests, the time necessary to reach equilibrium was found to be a little less than one hour, yet we preferred to continue for a little longer to be absolutely certain. No differences were found in the spectra of the samples when stirring was continued mechanically after reaching the equilibrium. Samples that were not centrifuged nor filtered did not show different spectra from those that had been.

The UV/V spectrometer was a Lambda-5 by Perkin-Elmer, computer controlled, which enables storage of the digitalized spectra. The transmittances in the visible spectra (380 to 770 nm) were always in the interval of 20% to 80%. The cells were Suprasil of 10-mm width, using water in the reference beam. The optical system corresponded to a C illuminant with a foveal angle less than 4°; this illuminant is equivalent to the illuminant D_{65} in the visible region, since we were working with monochromatic radiations and both illuminants only exhibit differences in the ultraviolet region.

The chromatic parameters were obtained from a method developed at the Department of Physical Chemistry, University of Cadiz (4), which uses 391 transmittance values between 380 and 770 nm to calculate the tristimulus coordinates X, Y, Z.

Results and Discussion

The spectra of six of the samples using different amounts of adsorbent added and, therefore, showing different degrees of discoloration are shown in Figure 1. Visually, the color of the samples ranged from yellow (without adsorbent) to almost transparent, at which point a further increase in the amount of activated carbon did not significantly change the color.

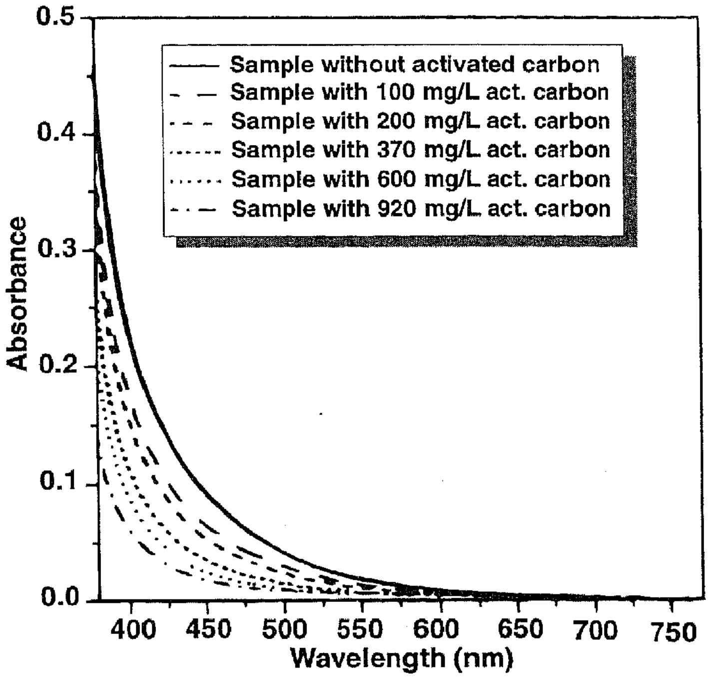

Fig. 1. Variation of a Fino wine as the proportion of activated carbon is increased.

The tristimulus X, Y, Z were calculated after converting the 391 absorbance measurements in each spectra into transmittances values; then, by means of the CIELAB chromatic space equations the results of Table I were obtained. The last two columns are the absorbance of the samples at two characteristic wavelengths (420 and 520 nm) used sometimes to describe, poorly and inadequately, the color of a sample. The data in Table I clearly show that during the discoloring process all the chromatic parameters varied, agreeing with the progressive disappearance of the color yellow due to the chemical adsorption of the coloring substances of Fino wine, since the graphitized structure of the adsorbent shows affinity for polyphenolic compounds responsible for the color. When the color of the wine changed toward high transparency, the lightness L^* and the a^* coordinate increased, whereas the coordinate b^* decreased. Furthermore, these main chromatic parameters, the chroma C^* and hue H^* parameters also changed during the discoloring process, since they are combinations of the a^* and b^* parameters; the hue tended towards higher angle and the chroma showed a decrease together with parameter b^*, since its contribution at the C^* value is larger than that of parameter a^*.

Figure 2 shows how the a^* and b^* coordinates evolved as a function of the activated carbon concentration used. Initially, for the b^* coordinate, a very rapid decrease in the color coordinate took place tending

Table 1. Values of the chromatic parameters and absorbance at 420 and 520 nm on increasing the concentration of activated Carbon in Fino wine.

Activated carbon (mg/L)	L*	a*	b*	C	H	A_{420}	A_{520}
0	98.19	-2.35	10.16	10.43	103.0	0.1516	0.0296
40	98.66	-1.81	7.24	7.46	104.0	0.1115	0.0215
60	98.88	-1.65	6.25	6.47	104.8	0.0975	0.0172
100	98.82	-1.64	6.08	6.30	105.1	0.0952	0.0170
160	99.25	-1.19	4.22	4.38	105.7	0.0688	0.0115
200	99.13	-1.12	4.12	4.27	105.3	0.0680	0.0113
270	99.27	-1.23	4.02	4.21	106.9	0.0658	0.0108
370	99.22	-0.98	3.39	3.53	106.1	0.0582	0.0113
430	99.42	-0.93	2.78	2.93	108.4	0.0493	0.0080
560	99.46	-0.80	2.44	2.57	108.2	0.0442	0.0072
600	99.51	-0.67	2.16	2.26	107.2	0.0395	0.0070
650	99.39	-0.72	2.36	2.47	106.9	0.0439	0.0084
760	99.39	-0.68	2.37	2.46	105.9	0.0434	0.0080
920	99.42	-0.62	2.08	2.17	106.7	0.0392	0.0078
1040	99.58	–0.58	1.71	1.81	108.8	0.0322	0.0054
1070	99.47	-0.56	1.87	1.95	106.7	0.0367	0.0073
1230	99.40	-0.51	1.73	1.80	106.6	0.0347	0.0078

towards a constant value beyond a certain concentration of added carbon, and no better results were then obtained in the discoloring whatever amount of activated carbon was added. A similar process can be observed for the a* coordinate that increased until it reached a constant value, although its absolute value also decreased. For the examined Fino wines the g_i value was of the order of 400 mg/L in both cases. Table 1 shows that the other chromatic parameters lead to the same conclusions.

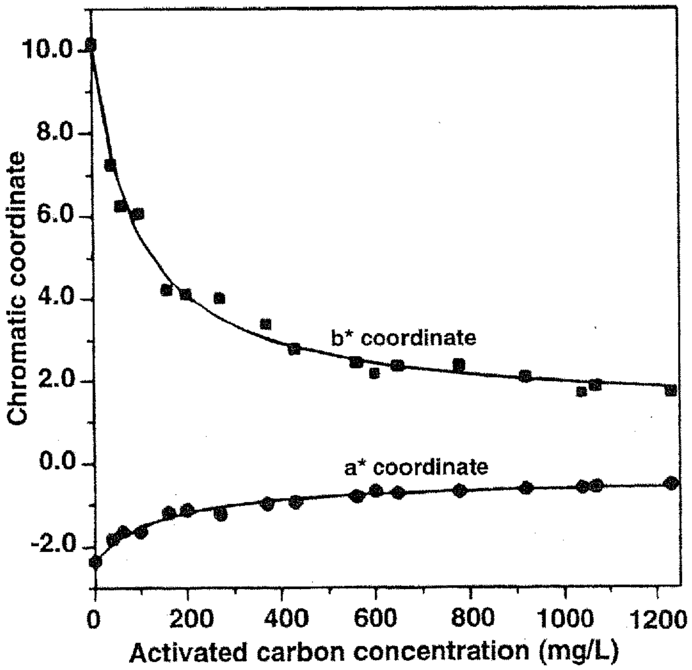

Fig. 2. Values of the a* and b* coordinates with respect to the concentration of carbon.

By means of a curve fitting programs (9), the curve that best fitted the experimental data for each of the chromatic parameters was of the type:

$$|u^*| = |u_0^*| - p \cdot \left(\frac{g}{g + q}\right) \qquad \text{Eq. 4}$$

where u^*_0, u^*, and g have the same meaning as above, and p and q are constants whose values are shown in Table 2, which also shows the correlation coefficients for each fit. Plotting the Equation 4 with the parameters in Table 2 gives the continuous lines that pass through the experimental data in Figure 2. The a*, b*, and C* parameters lead to the best correlation coefficients. This was to be expected given that L* is independent of the chromatic aspects and the discoloring that it underwent, even though there was an increase in its value when the sample became more transparent. The correlation coefficient of H* is quite low as discoloring hardly affects this parameter.

If for small concentrations of activated carbon, parameter b* were to undergo a lineal decrease with the adsorbent concentration this would mean according to

Table 2. Constants p and q and correlation coefficient r of the fitted equations that predict chromatic parameters for Sherry wines, depending on the concentration of activated carbon.

	a*	b*	L*	C	H
p	1.98	8.96	1.37	9.16	4.79
q	140.3	94.5	70.2	96.5	111.9
r	0.998	0.999	0.961	0.999	0.698

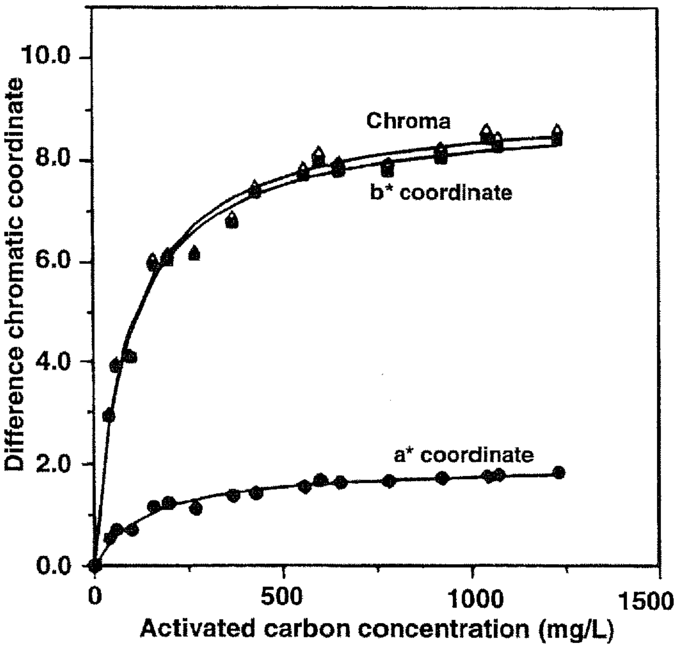

Fig. 3. Variation of the a*, b* coordinates and chroma C* with respect to their initial values as a function of the concentration of carbon.

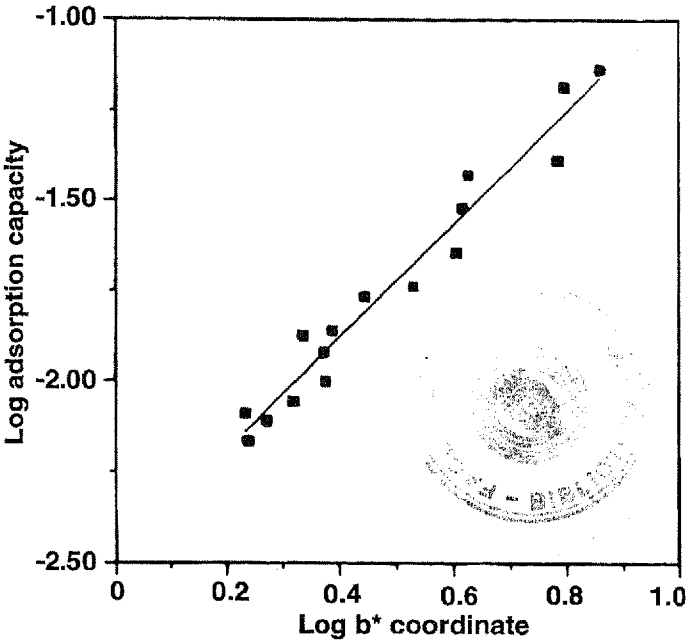

Fig. 4. Variation of the adsorption capacity as a function of the colored species in equilibrium, for the b* coordinate, according to the Freundlich model.

the Langmuir isotherm that the extent of adsorption had become independent of the concentration of the solute due to the saturation of the adsorbent. Figure 2 shows that the chromatic parameters varied appreciably - in a non-linear way - when the adsorbent concentration was small which would be more in agreement with the Freundlich model yet depending on the value of the *n* exponent.

Figure 3 shows the variation of the a^*, b^* and C^* with respect to its initials values for the sample with no activated carbon - a^*_0, b^*_0, and C^*_0 - against the concentration of activated carbon in the sample. Note that (mainly in curves b^* and C^*) for high $|u^*|$ and low g values it is true that $u^*_0 - u^* \approx K \bullet g$, which is obtained from Equation 4 when $g << q$. For the Langmuir adsorption isotherm this corresponds to the special case $c >> K_L^{-1}$ and hence the adsorbent is saturated and the adsorption capacity is independent of the adsorbent concentration.

In Figure 3, it can also be observed that above certain concentrations of carbon practically no discoloring of the wine occurs since the variations of the chromatic coordinates, $|u^*_0 - u^*|$, become insignificant. These differences tend towards the value p when g is very high as can be seen in Figure 3.

Equation 4 implies that it should correspond to one of the models for the adsorption isotherms when representing the adsorption capacity, expressed as the variation in the color coordinate per unit of adsorbent against the value of the concentration of colored species expressed in this case as the color coordinate. In Figure 4, the adsorption capacity is shown against the b^* chromatic coordinate value in equilibrium, expressed logarithmically. This linear plot means that the adsorption behavior of the colored compounds of Fino wine by activated carbon fits the Freundlich isotherm (Eq. 3). Table 3 shows the results of the least squares fit to the Freundlich adsorption model of the CIELAB system coordinates and Chroma C^*. The results exhibit a similar value of the Freundlich n index for the coordinates a^*, b^* and the Chroma, as $n < 1$ means that the adsorption was strongly dependent on the concentration. On the other hand for the Lightness a worse fit is obtained and the value n is different from those obtained for the other parameters, since it does not express chromatic aspects of the samples but indicates the degree of transparency.

As was indicated in the introduction, some authors use the absorbance value measured at a certain wavelength as an indication of a sample's color. An absorbance value is not a description of color; it can, however, be used in its determination due to the existence of a linear relationship between the absorbance value at certain wavelengths and the chromatic parameters. The results of a least squares fit to a Freundlich isotherm of the absorbance measurements of Table 1 are

Table 3. Statistical study of the CIELAB coordinates and certain wavelengths according to the Freundlich model.

	L*	a*	b*	C	A_{420}	A_{520}
Freundlich constant $K_F \bullet 10^2$	-1.0	0.42	0.30	0.29	5.9	15
Freundlich index n	0.96	0.61	0.64	0.63	0.54	0.59
Freundlich corr. coeff.	0.86	0.97	0.98	0.96	0.97	0.84

included in Table 3. The Freundlich n index values for A_{420} and A_{520} should be independent of the wavelength at which they are measured and be near those obtained with chromatic coordinates. Hence, in general, absorbance measurements do not serve as a description of color variations due to an adsorbent. Nevertheless for A_{420} an acceptable Freundlich correlation coefficient is obtained as exactly at this wavelength the absorbance measurement is proportional to the chromatic coordinate b^*.

A study similar to the one performed with the Freundlich model was carried out with the Langmuir model obtaining lower regression coefficients.

Conclusions

The amount of decolorant that has to be added to a Fino sherry wine to reach the desired color can be obtained from the equations that relate chromatic parameters with the carbon concentration. The adsorption process has been characterized by means of a Freundlich equation, which shows that the action on the adsorbent is strongly influenced by the adsorbate concentration. The color of wines should be characterized by means of the coordinates and chromatic parameters -- L^*, a^*, b^*, C^* and H^*; the time used in this is amply compensated by the good results achieved. The method used in the color characterization makes it possible to relate chromatic coordinates to other physico-chemical processes. Since a simple absorbance value is not really a characterization of color, but merely an indication, neither absorbance value should be used to characterize the adsorption of sherry wine, the more so as the results depend on the wavelength at which the absorbance value is measured.

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