The applicability of natural colorants in papermaking

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ABSTRACT: Natural colorant extracts from norbixin, curcumin, and copper chlorophyll were studied for their potential as paper dyes. Higher consistencies in stock preparation and higher levels of refining were found to favor the retention of these three natural colorants, as evaluated by the saturation of the color. For both norbixin and curcumin, color saturation was higher in the acidic range of pH than in the alkaline range. The copper chlorophyllin exhibited a higher color saturation at pH 6.0, with values falling below pH 5.0 and above pH 7.0. Generally, aluminum sulfate and cationic starch contributed to the retention of the natural colorants. The addition of precipitated calcium carbonate fillers reduced the color saturation of the three colorants as a result of the tendency of the PCC fillers to mask the color of the papers.

Application: Natural colorants are a viable and ecologically favorable alternative to synthetic colorants.

The paper industry usually adopts artificial colorants because of their high stability, purity, availability, dyeing capacity, and low cost. The indiscriminate use of these colorants and their toxicity has been questioned by some, and this criticism has led to several synthetic colorants being forbidden in many European countries [1].

Natural colorants derived from vegetal origins represent good potential substitutes for the artificial colorants in foods, cosmetics, and textiles [2]. Natural colorants may be used in the coloration of the absorbent papers (napkins, paper towels, paper handkerchiefs, toilet paper), wrappings for foods and medicines, and papers for graphic works (folders, cards, coverings, advertisements in magazines). Natural colorants are already being used for adding color to craft papers.

BACKGROUND

After the rise of synthetic colorants, the paper industry did not have an incentive to use natural colorants for technological and economic reasons. In the last years, however, the extraction and processing techniques of natural colorants have been improving. New technologies have been studied to obtain those colorants that have high pigment concentrations. Among the techniques, supercritical fluid extraction is especially promising, since it offers the advantages of less thermal degradation, high quality of recovered products, a low energy requirement in recovering the solvent, and high selectivity in the separation process [3,4].

The annatto colorants represent more than 80% of the natural colorant market. Norbixin is a component of the hydrosoluble fraction extracted from the orange-colored seeds of annatto. Curcumin, the main chromophore in *Curcuma longa L.*, gives the substrate a golden-yellow color, and it is the second most highly marketed natural colorant. Copper chlorophyllin is obtained from chlorophyll extracts, which are taken from natural or dried vegetation, with the magnesium atom replaced by a copper atom to make the products more stable. Copper chlorophyllin imparts a green color to the substrate [5–7].

How well cellulosic pulp adsorbs the coloring molecules depends on the characteristics of the coloring molecules and fibers, as well as the chemical conditions of the medium, such as pH, conductivity, interfering substances, and anionic polymers. The absorption also depends on the physical operating conditions, such as the turbulence, temperature, stock consistency, and the addition sequence [2,8].

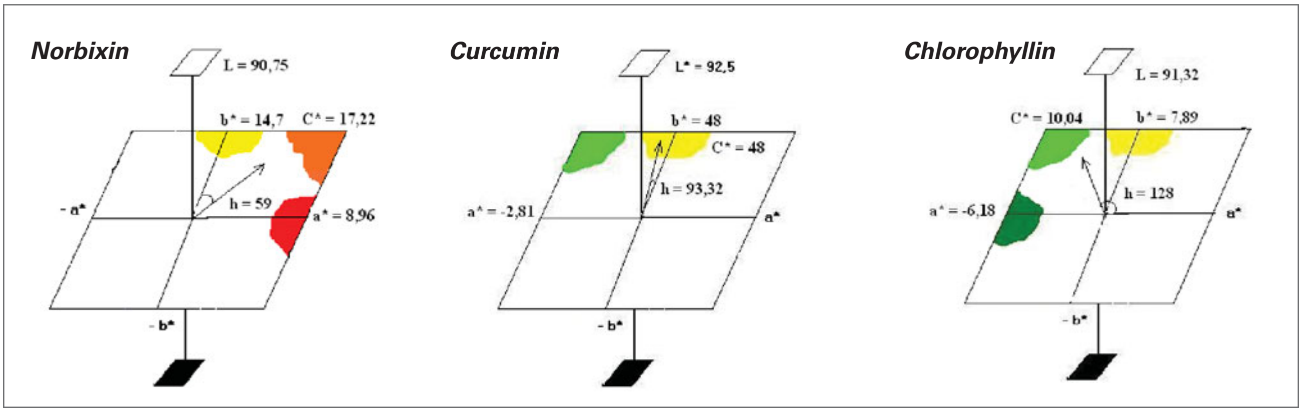
The use of natural colorant by the papermaking industry requires the study of the physiochemical interactions between the coloring molecules and the cellulosic fiber, the interactions among the colorants and other additives, and the behavior of those colorants in the papermaking process. We must also study the influence of these colorants on the properties of the final product and on the characteristics of the generated effluent.

MATERIALS AND METHODS

We used an industrial kraft pulp of *Eucalyptus spp.* bleached by an ECF sequence (i.e, free of elemental chlorine). For the natural colorants, we use norbixin extracted from the annatto seeds, hydrosoluble curcumin extracted from *Curcuma longa*, and hydrosoluble copper chlorophyllin extracted from green spinach sheets.

The extracts were diluted with water before being added to the refined pulp, which was beaten at 10,000 revolutions in a laboratory hydrapulper. The concentration of the dye extracts was 0.5% on o.d. pulp. Aluminum sulfate was added to the copper chlorophyllin extract at the same concentration (0.5% on o.d. pulp).

Different conditions of stock preparation and sheet formation were evaluated beforehand, for the purpose of optimizing the retention of the colors. We used a Datacolor Elrepho 2000 to evaluate the dyeing power of the colorants as indicated by the CIE L*a*b* color coordinates. Tests were



1. Chromaticity system CIE L*a*b* for the colored bleached pulp, colored with 0.5% dye extracts (norbixin, curcumin, and copper chlorophyllin).

conducted for the following parameters: four consistencies of stock preparation (0.2%, 0.4%, 1.0%, and 1.5%); four consistency levels of papermaking (0.02%, 0.03%, 0.045%, and 0.06%); four pH values for stock (4, 6, 7, and 8); and four refining levels. We evaluated the pulp in the unrefined state (0°SR) and at three refiner levels: 1000 revolutions (24°SR), 2750 revolutions (30°SR), and 4000 revolutions (38°SR) in a PFI mill.

Colored alkaline handsheets were made with the extracts from natural colorants. The additives were used in the following concentrations (as a percent on o.d. pulp) in the following order of addition: (a) 0.6% cationic starch, (b) 0.5% natural colorant extract, (c) 0.5% aluminum sulfate, (d) 0.5% alkaline sizing agent (ASA), and (e) 15% precipitated calcium carbonate (PCC). All additives, except calcium carbonate, were added to the hydrapulper at 1% consistency and were individually homogenized at 10,000 revolutions after refining (30°SR).

After the AKD glue was added, the pulp was transferred to a homogenizer containing the calcium carbonate suspended in water (pH 8.0), and the consistency was adjusted to 0.4%.

The handsheets were made at a basis weight of 60 g/m^2 in a TAPPI-type handsheet former and were pressed for 7 min at 400 kPa. The handsheets were dried at 105°C for 10 min.

RESULTS AND DISCUSSION

The process of making colored papers has a number of variables. Besides color type and the choice of the dyeing process, the results are also determined by the type of pulp used, the stock consistency, the degree of refining, drying and finishing, the water quality, the machine characteristics, the fiber–colorant contact time, and the additives used and their addition sequence.

We evaluated the retention of the natural colorants by measuring the CIE L*a*b* color coordinates, giving special attention to the saturation, or chrome (C*). The chrome is the intensity of the color, the quality by which one can distinguish a pale color from a lively one. In this study, increases in the values of chrome correlated to better color retention, or, in more technical terms, to increases in the tinctorial power capacity of the colors tested.

The angle *h*, expressed in degrees, represents the primary and compound colors. It is directly related to the absorption wavelength of the colorant. At the axes a* and b*, one may observe: +a* red, –a* green, +b* yellow, and –b* blue. The brightness of the color is represented by the L* axis, upon which there are all gray tonalities between white and black. It is the quality by which one may distinguish a clear color from a darker shade [9].

Figure 1 shows the chromaticity system CIE L*a*b* for colored pulp with 0.5% dye extracts consisting of norbixin (orange), curcumin (yellow), and copper chlorophyllin (green). The arrow represents the angle h that points out the color obtained in coloring the pulp.

Stock consistency

As commonly known, the consistency of the stock significantly affects the reactive performance of the cellulosic fibers in the aqueous suspension. For the three colorants under study, the best retentions were obtained when relatively high consistencies (1.5%) were used.

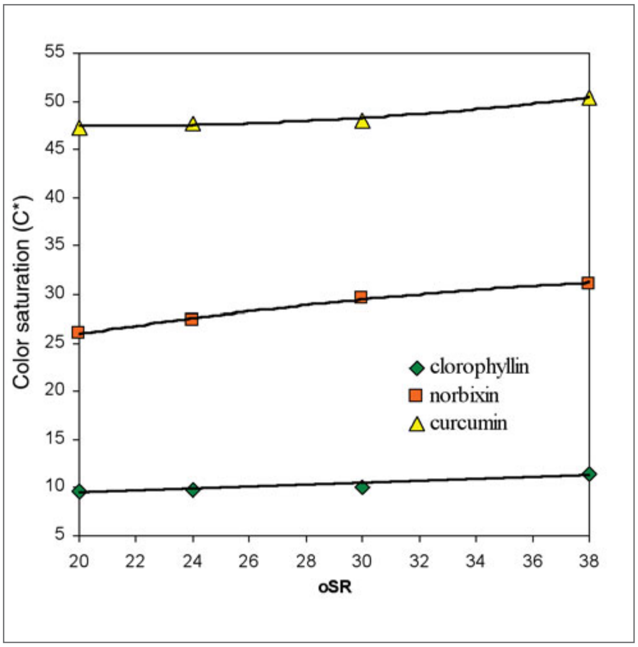
Sheet formation

The consistency during sheet formation is an important factor in papermaking. It is controlled by adding water and creating turbulence to disperse the fibers and prevent the formation of flocks. The highest formation consistency possible for us to test in this study, 0.06%, proved to be the most favorable to the retention of the three natural colorants under the laboratory conditions.

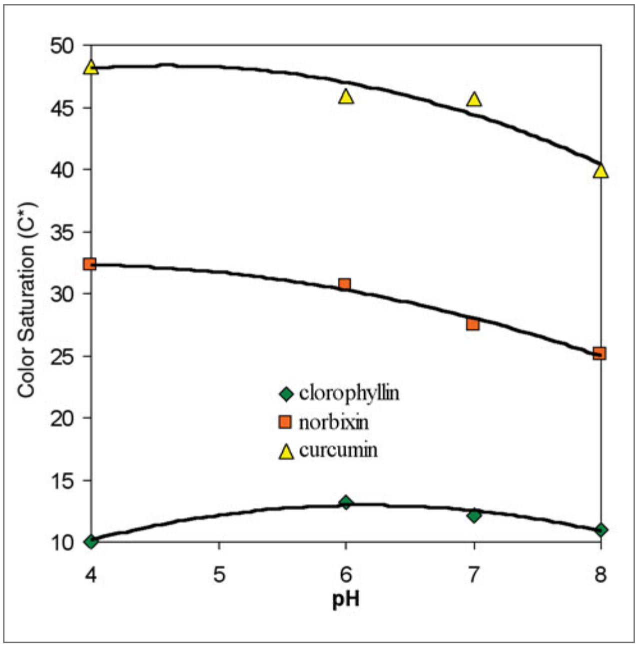
At this consistency, at which three times less water is used than at 0.02% consistency, we obtained adequate dispersion of the fibers and satisfactory sheet formation. Although the consistencies of formation are higher in industrial manufacturing, the behavior is expected to be similar to that observed in this study.

Degree of refining

The physical and chemical characteristics of the pulps are influenced by the action of refining, which also affects the papermaking process. Refining affects the drainage and the drying of paper, which influences the retention of the additives and their interactions with the functional-groups of the cellulosic fiber.



2. Color saturation, C*, in the papers colored the dye extracts norbixin, curcumin and copper chlorophyllin as a function of different refining levels.



3. Color saturation, C*, of the papers colored with the dye extracts norbixin, curcumin, and copper chlorophyllin as a function of different pH values.

As Fig. 2 shows, the retention of colorants increases with the degree of refining. The colorant most affected by refining was chlorophyllin, followed by norbixin, and finally curcumin. This outcome is shown by the percent increase in the saturation of the color.

As to the role of refining, there are two possibilities. One hypothesis is that higher refining increases the area for the adsorption of additives and exposes the functional groups of the cellulosic pulp that interact with the coloring molecules. In other words, the retention of the color depends on the presence of fines, which tend to adsorb color [8].

Stock pH

The stability, tonality, saturation, and retention of the color are variables that depend on the pH of the system. In the process of paper coloration, operators must control the pH strictly because colorants are inherently unstable under pH variations, especially the natural colorants.

Figure 3 shows the color saturation (C*) of the papers dyed with the coloring extracts of norbixin, curcumin, and copper chlorophyllin as a function of different stock pH values. According to the regression analysis, the saturation in the color as a function of the variation in pH follows a polynomial tendency.

The norbixin extract, for which the carrier is potassium hydroxide, is found in the pH range of 7–8 in the form of potassium norbixinate. In spite of norbixin showing a higher stability in the alkaline range, the acid range guarantees a higher retention of the coloring molecule in the fibers. Precipitation in the acid range avoids the leaching of the color and guarantees an evenly colored product. The decrease in the saturation of the color (C*) with the increased pH is probably caused by the increase in the solubility of norbixin.

According to Rusig and Martins [11], the highest stability for the dye extract from curcumin at 7°C is attained over a pH range from 4.0 to 7.0. However, at 37°C, the highest stability is from 4.0 to 5.0. For our experiments, the papers were formed at room temperature (23°C) and were dried at 105±3°C for 10 min. The saturation of the color decreased above pH 5.0. In pH 8,0, the loss in the saturation was about 17%, when compared with pH 4,0.

The copper chlorophyllin shows high saturation of the color at pH 6.0. The same saturation (12.0) is shown at pH 5.0 and 7.0, but the color retention declines at values immediately below pH 5.0 and above pH 7.0.

Retention of the natural colorants

Many types of paper contain noncellulosic additives that are meant to improve the final properties of the product and eliminate or control some operational problems. The colorants show different affinities for these additives.

Table I shows the CIE L*a*b* values of the papers colored with the dye extracts of norbixin, curcumin, and chlorophyllin. The reference papers consisted of pulp alone plus the colorant. The other additives were cationic starch (CS), aluminum sulfate, alkaline sizing agent (AKD), and precipitated calcium carbonate (PCC). The addition was cumulative, and the

Colorants	Additives	(L*)	a*	b*	C*	h*
Norbixin	Ref.	90.75	8.96	14.71	17.22	58.65
	CS	86.31	7.64	18.81	20.31	63.93
	Sulfate	85.85	14.55	26.96	30.64	61.64
	AKD	80.22	20.13	31.45	37.34	60.68
	PCC	82.23	18.66	31.29	36.43	59.20
Curcumin	Ref.	92.40	–2.81	48.00	48.08	93.37
	CS	91.26	–2.92	50.35	50.36	91.04
	Sulfate	89.09	–4.92	52.67	52.90	95.34
	AKD	91.12	–1.93	45.32	45.36	92.44
	PCC	92.50	–2.31	35.42	35.70	93.73
Chlorophyllin	Ref.	94.42	–0.80	3.36	3.46	103.49
	CS	91.32	–6.18	7.89	10.04	128.05
	Sulfate	87.18	–12.8	10.34	16.46	141.05
	AKD	83.21	–11.85	11.77	16.71	135.21
	PCC	87.39	–9.34	9.40	13.25	134.84

CS = cationic starch. AKD = alkyl ketene dimer. PCC = precipitated calcium carbonate.

I. Average values of the color coordinates CIE L*a*b* for papers dyed with norbixin, curcumin, and chlorophyllin

order of addition was CS + colorant + sulfate + AKD + PCC.

Cationic starch. The presence of the starch provided a favorable effect in the retention of the three colorants, especially copper chlorophyllin. The copper chlorophyllin, which presents no natural affinity for the cellulosic fiber, shows its coordinate a* (the green characteristic) increased from –0.80 to –6.18 for the sheets without additives.

The table also shows a significantly increased saturation of the color. The addition of starch gave the paper a green tone. The tonality angle h changed from 105° to 128°. According to Scott [8], the cationic starch also gives the system a positive charge, which supports the retention of the copper chlorophyllin.

The addition of starch increased the saturation of the norbixin color from 17.22 in the papers without additive to 20.31 after the addition of the cationic starch. The tonality increased from 58.65 to 64, because of a greater contribution of the yellow coordinate but a minor contribution of the red one. The properties of the starch are related to the abundance of hydroxyl groups in its molecular composition [10], which form hydrogen bonds with water. The water molecules disappear during the drying process, whereas hydrogen bonds are formed between starch and fiber.

Cationic starch had the least influence on curcumin. The tonality angle changed from 93.37 to 91.04 with a major contribution of the yellow coordinate but an insignificant contribution of the green coordinate. The angle *h* is close to the angle of the yellow coordinate in the CIE L*a*b* diagram (90°), which shows the purity of the yellow color of the dye extract from curcumin.

Aluminum sulfate. The addition of the aluminum sulfate, after the addition of the cationic starch and dye extract, intensified the retention of the three colorants. This outcome is observed in the increased saturation of the color (C*). The highest retention was observed for the copper chlorophyllin, followed by norbixin, and finally curcumin, as observed by comparing values with those of the reference papers in the table.

The tonality angle changed from 128° to 141° when aluminum sulfate was added to the stock preparation to dye the paper with chlorophyllin. This change in the angle arises from the increased contribution of the green color and the reduced contribution of the yellow one. The addition of aluminum sulfate practically doubled the contribution of the coordinate a*, the red color, for norbixin, which reduced the tonality angle to 61.64°. The aluminum sulfate provides the highest retention for the green-colored compounds found in the curcumin extract, which changed the angle *h* from 91.04° to 95.34°.

According to Neimo [10] and Marton [12], the retention of the low-affinity colorants will be increased if the aluminum sulfate is added after the colorant is added. This increase was noticeable with the copper chlorophyllin, which showed little affinity for the cellulosic pulp. The addition of aluminum sulfate before the introduction of the colorant may reduce the color strength and brightness, which could generate double-face characteristics.

AKD. The addition of the AKD reduced the saturation by about 14% for the papers dyed with curcumin. For chlorophyllin, there was a small reduction of the coordinate a* but no change in the saturation of the color. Norbixin was the only color that showed an increase in saturation when the sizing agent was added. An explanation for the reduced saturation in the papers dyed with curcumin could be the competition of the sizing agent for reactive sites on the fibers.

PCC. As expected, the addition of the PCC mineral reduced the of saturation for all three colors. This filler has a tendency to mask the color of the papers because of its pronounced affinity to the colorants. As a result, the color of the paper becomes weaker than it would be in the absence of the filler [10]. Curcumin was the colorant most affected by the addition of calcium carbonate, as a result of the alkalinity (pH 8.0).

The retention of the mineral filler is evaluated by the content of ashes. The handsheets showed average contents of 10.47%, 10.39%, and 10.56% for norbixin, curcumin, and chlorophyllin, respectively.

Natural and synthetic colorants

On February 2002, the magazine *O Papel* announced that Arjo Wiggins, Cia Suzano, and Ripasa were testing vegetal colorants for the coloration of papers [13]. In August 2004, Arjo Wiggins introduced into the market a graphic paper line called "Natural" in green, brown, blue, or yellow, with the colors extracted from natural and water-based colorants. This development corroborated the viability of using natural colorants in the paper industry [14].

The cost of the natural colorant varies according to the manufacturer. When the average prices are compared by kilogram with the prices for the synthetic colorants, colorants made from urucum (a commonly-grown Brazilian tree) are found to be two to four times cheaper, depending on the manufacturer. Curcumin costs 1.5 times more. Chlorophyll presents the highest difference in price, since it costs ten times more than the synthetic colorants.

With regard to the dosage of colorant, the dosage we used for the three colorants was equivalent to 5 kg of colorant per ton of pulp. This dosage is not much different from the dosage used commercially for artificial colorant counterparts. To date, no data have been published about the natural colorant dosages used in the industrial tests, which limits a comparison of costs between the papers dyed with natural colorants and papers dyed with the artificial colorants.

CONCLUSIONS

The dye extracts studied are easily hydrated, are soluble in cold water, and are easily manipulated. We evaluated the retention of the three natural colorants according to the color saturation. Under the laboratory conditions, increases in consistency and refining increased the retention of the natural colorants.

To dye paper with natural colorants requires strict control of the pH in stock preparation. The curcumin showed high stability in the pH range of 4.0–5.0 but a degradation in the color above pH 7.0, with the formation of brownish-colored compounds. For norbixin, the acidic condition guaranteed a higher retention of the coloring molecule of the fibers. The copper chlorophyllin presents a high saturation of the color at pH 6.0, with reduced values for saturation below pH 5.0 and above pH 7.0.

The addition of cationic starch supported the retention of the three extracts from natural colorants. The addition of the PCC mineral filler reduced the saturation as a result of the tendency of the fillers to mask the color of papers. When calcium carbonate and mineral filler were added, the colorant most affected was curcumin, because of the alkalinity.

Under the test conditions, the natural colorants showed good interaction with the others additives and may be considered an ecologically attractive alternative for dyeing paper products. Papers dyed with vegetal colorants are products tailored the demands of a public attuned to social and environmental needs. **TJ**

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