Standard formulations for cold dyeing routes of agates: An energy-saving option for artisanal and small-scale producers

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Abstract

Artisanal and small-scale processes of dyeing of agates are usually non-standardized and often ineffective. In the Brazilian scenario, local arrangements need actions to improve the current processes and to minimize energy consumption and production of wastes. In this sense, the aim of this study was to investigate new standard dyeing procedures capable of producing a satisfactory color alteration using minimal quantities of inorganic dyes and heat. A so-called cold dyeing route was outlined and tested for the artificial colors black, red, blue and green. In all cases, experimental results showed a significant, and in some cases dramatic, improvement in the final color of agates dyed according to the proposed cold dyeing system in comparison to the conventional warm process. Most important, these improvements were achieved with an average reduction of heat energy and reactant consumption of 94.6% and 56.6%, respectively. Potential benefits obtained from applying the cold dyeing route include the reduction of operating costs and decrease in wastewater burden due to the use of dye solutions of low concentrations under optimized conditions.

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1. Introduction

Colored gemstones have been appreciated since ancient times as symbols of wealth and status. Nowadays, the global retail market of colored gemstones was estimated to be about US$ 10 billion in 2015 with favorable growth prospects in the near future (Shortell and Irwin, 2017). Gemstones comprise inorganic materials that are distinguished from other minerals due to their exclusive qualities, such as high unit value, unique characteristics, and complex processing. Prominent colored gemstones groups include jade, quartz, topaz, beryl, chrysoberyl, tourmaline, spinel, and corundum (Cartier, 2019). Despite the emergence of large-scale mechanized processes in recent years, the great majority (approximately 80%) of such gemstones is currently processed using artisanal and small-scale mining (ASM) techniques (Shortell and Irwin, 2017; IGF, 2017). This trend is likely to continue since many deposits are small-sized, short-lived, and thus not adapted to large-scale mining (Cartier, 2019). Nevertheless, colored gemstones ASM sector remains marked by challenges such as undervaluation of production, inadequate regulation, widespread illegal mining, and rudimentary, non-standard processing techniques (Shortell and Irwin, 2017; World Bank, 2019). It is no coincidence that the colored gemstone industry has been slow to respond to the sustainability challenge even when compared to other mining activities (Cartier, 2019).

Rio Grande do Sul State, in southern Brazil, is a major global supplier of agates, a gemstone represented by a mixture of different morphological quartz varieties (Flörke et al., 1982; Götz et al., 2001). Local productive arrangement accounts for about 300 companies and 4500 direct and indirect jobs (Villas Bôas et al., 2017), most of it composed of artisanal and small-scale producers distributed over many small communities. Agates are often used as ornamental gems and in jewelry so that gem’s color and appearance are fundamental issues associated with the gemstone quality. Dyeing, impregnation, and irradiation techniques are usual options for agates color enhancement, whose selection depends on the agate’s specific characteristics such as porosity and microcrystalline structure (Read, 2005). A distinctive feature of Brazilian agates is the high surface porosity of the geode crystals (with micropores up to 0.1 μm), which favors simpler coloring methods, such as dyeing. Not by chance is dyeing the main technique used to change the color and increase the banding contrast of Brazilian agates.
However, dyeing techniques applied have been largely unsatisfactory to date, since there is a lack of standard procedures, resulting in inefficient and time-consuming processing routes. To fill this gap and contribute to the development of vital economic activity in small communities, this study proposes replicable, optimized methods for agates dyeing focusing on the use of inorganic dyes.

1.1. Dyeing of Brazilian agates: state-of-the-art

A summary of local agate processing practices is here presented based on a survey performed by the authors, which included field visits and interviews with 15 local producers from the city of Sol-edade, one of the major poles of Brazil’s agate industry. The survey performed focused on collecting detailed information about three key features of dyeing processes: (a) chemical reagents used and their concentrations; (b) temperature of the dyeing bath; and (c) dyeing time, with particular attention to heating times. Secondarily, the survey allowed obtaining a general perception of the local agates processing scheme, which is briefly described as follows. It is worth noting that the survey performed was not intended to map the whole sector, which is composed of hundreds of manufacturers but to acquire relevant empirical information to serve as a starting point for the experimental work.

Most agates extraction activities are located at the Salto do Jacuí mining district, where occurs rich deposits that can be easily mined (Sampaio and Souza, 1999). Mining is conducted in open pits with the use of excavators or in swamp areas with basaltic outcrops, in which excavation can be carried out manually. The latter concentrates most of the local artisanal miners since the topography is not favorable to the use of excavators. Once extracted, agate geodes are directly transported to beneficiation facilities or sold by artisanal miners to local companies without any beneficiation. Agate beneficiation and distribution are held by these companies, from small family manufacturers to industrial factories.

Beneficiation involves a sequence of operations, which include sorting, shaping, dyeing, and polishing, most of these operations alternated by washing with different solvents (Fig. 1). Once extracted and sorted, agate geodes are usually cut using circular or diamond saws. Then, the geodes are washed in a detergent solution to remove the oil residue due to the cutting step. Occasionally, additional washing stages are carried out with caustic soda or muriatic acid to leach out the impregnated soil. At this stage, the agate slabs are ready to be dyed.

The dyeing process consists of the immersion of the pre-treated agate slabs in specific dyes to change their original color. It can be conducted by using organic or inorganic dyes and thermal treatment is commonly used to aid in dye acceptance (Götze and Mockle, 2012). Heating stages are usually conducted in wood or gas-fired ovens. A specific discussion on local agate dyeing techniques is presented here, but a comprehensive review of methods to enhance the appearance and color of gemstones can be found in Nassau (1984; 1994) while Tubino and Sampaio (2000) and Yazdi et al. (2016) present specific information about chemical treatments of agates.

In the local system, the dyeing process is divided into two main routes: an inorganic route, constituted by dye solutions obtained from inorganic acids, from which the colors black, red, blue and green can be obtained; and an organic route, based on aromatic anilines such as aniline and rhodamine B, from which the tones green, pink and purple are obtained. The inorganic route is generally more complex since it involves more intermediate steps of washing and heating.

A summary of the dyeing procedures currently used is shown in Table 1 based on the survey performed. In all cases, two main shortcomings were detected: (1) a lack of standardization in the concentration and amount of reactants used and so in the
concentration of the dye solution; (2) poor control over the time of dyeing. In some cases, such as for dyeing in green, even the control of temperature was deficient. Most such shortcomings derive from the use of inadequate work tools and the absence of protocols for material handling, mixing, storage and waste destination. Some of such issues are illustrated in Fig. 2. For example, the use by operators of “number of shovels” as a unit of measure of key reactants during the preparation of dye solutions is a common practice. Concerning the dye solutions themselves, all visited manufacturers use the same set of reactants (see Table 1 for details) which are based on the preponderance of observed quartz patterns in the agates (Vilasboas et al., 2017). It is recognized that processes standardization and optimization could reduce reactants and heat energy consumption during the dyeing step, thus aiding to overcome inadequate practices associated with the activity. Also, the adoption of standard procedures of dyeing provides a framework for studies involving the application of modern wastewater treatment technologies, such as photocatalytic degradation (Raza et al., 2020) and adsorption (da Rosa et al., 2018).

Seeking to develop more efficient processes for dyeing of agates, this work aimed to propose standardized dyeing routes targeting the minimum use of energy (heating stages) and reactants. For this purpose, standard formulations using inorganic dyes were defined and implemented, serving as the basis for subsequent process optimization. For the sake of conciseness, standardization and optimization of processes using organic dyes is not presented here, but future work on this topic is currently in progress.

2. Experimental setup

In order to test the assumption that agate dyeing processes could be more energy-efficient, a so-called cold route was outlined and tested. In this route, the dye bath was conducted without any external heating (with a punctual exception for the blue color as will be referred later) and the obtained coloring was then compared to that obtained when using the conventional, warm route, considering a laboratory scale set-up. For this purpose, the experimental work was divided into four components: (a) samples acquisition and preparation; (b) formulation of standard dye solutions for the colors black, red, blue and green; (c) dyeing tests with varying dye solution concentrations for each color; and (d) comparative dyeing analysis by UV-VIS spectrometry. These are described in detail as follows.

2.1. Samples preparation

Agate samples were obtained from different producers from the city of Soledade, southern Brazil. They were classified into four different classes, namely: massive agate, flocked agate, glazed agate, and salted agate. Such nomenclatures are used by local producers based on the preponderance of observed quartz patterns in the gems (Fig. 3). A total of 64 samples of agates were prepared for analysis, being 16 samples of each class. From these, 16 samples, 4 of each category, were constituted by agates already dyed according to the conventional process.

Laminated agate slabs with 3–5 mm thickness were prepared by using a circular saw. The slabs were subsequently washed in a detergent solution to remove any residual soil. To delimit the region for spectrometric analysis, each agate slab received two laser engravings (circles of 6 mm diameter) with a numerical code for identification and a paper mask to replicate the marked points.

2.2. Standardization of cold dyeing routes

The general dyeing procedure outlined is shown in Fig. 4. Agate slabs were arranged in layers and immersed inside a beaker containing the dye solution for 168 h at room temperature. After, the samples were removed, washed in water, and then placed in an acid bath (if required, depending on the desired color). Finally, the slabs were washed once more with water, disposed in alternate layers with sand and heated in a muffle furnace for a specified time. Information about dyeing conditions and reactants concentration for each color are detailed in Table 2.

Table 1

<table>
<thead>
<tr>
<th>Color</th>
<th>Dyeing procedure</th>
<th>Main issues</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black</td>
<td>Immersion in aqueous sugar syrup with a 2:1 dilute ratio followed by heating at 80–90 °C for 2–120 h. Then the slabs are washed in water and immersed in sulfuric acid (H2SO4) bath at 80 °C for 72–120 h. Finally, the agate slabs are again washed in water and heated at 220 °C for approximately 10 h.</td>
<td>In all visited factories, the concentration of the H2SO4 used was not known by the staff. Also, as a rule, heating times are poorly controlled.</td>
</tr>
<tr>
<td>Red</td>
<td>Immersion in aqueous solution containing iron perchlorate (Cl2FeO8), nitric acid (HNO3), and iron scrap. The method consists of adding 1 kg of iron scrap (usually steel nails) and 1.4 kg of perchlorate for 10 L of HNO3. The system is then heated at 60–70 °C for 72–96 h. Lastly, the agate slabs are washed in water and heated at 240 °C for approximately 10 h.</td>
<td>In all visited factories, the concentration of the HNO3 used was not known by the staff. Also, as a rule, heating times are poorly controlled.</td>
</tr>
<tr>
<td>Blue</td>
<td>Immersion in aqueous solution of potassium ferricyanide (C6N6FeK3) with a 0.16:1 proportion ratio (0.44 M). The system is then heated at 60 °C for a period between 120 and 192 h. After, the agate slabs are removed, washed in water, and immersed in H2SO4 bath at 80 °C for 12 h. The slabs are subsequently washed and immersed in water to boil at 80 °C for 24 h. Supplementary water must be continuously added to compensate for evaporation losses. Finally, the slabs are dried in an oven at 50 °C for 4 h.</td>
<td>In all visited factories, the concentration of the H2SO4 used was not known by the staff. Heating times and supplementary water added in the boiling step are both poorly controlled.</td>
</tr>
<tr>
<td>Green</td>
<td>Immersion in a solution of chromic acid (H2CrO4) and ammonium chloride (NH4Cl) in varying proportions, which was estimated in approximately 1:1.5 (acid:chloride). The system is then heated at about 70 °C for a period between 120 and 192 h. After, the slabs were removed, washed in water, and heated for 10–12 h at temperatures varying from 230 to 260 °C.</td>
<td>No producer was able to provide the exact proportion and concentration of components nor the oxidation state of chromium in the dye solution. In some cases, temperature control of the first heating step (70 °C) is virtually absent. Also, as a rule, heating times are poorly controlled.</td>
</tr>
</tbody>
</table>
Fig. 2. Some inadequacies observed during field visits to artisanal producers. (a) Worker washing agate slabs just after dyeing using toxic chemicals without using any protective device; wastewater goes directly to the sewer system. (b) Drums containing gems immersed in dye solution precariously heated by cooking gas. (c) A container with dyed agates being loaded into a rudimentary heating oven without the door.

Fig. 3. Macroscopic patterns of agate deposition in geodes. (a) Flocked agate – with concentric and plane-parallel bands; (b) Massive agate – absence of prominent bands at the macroscopic level; (c) Glazed agate – with vitreous aspect; (d) Salted agate – containing partial fillings of whitish quartz; (e) Laser identification in the points to be analyzed (10M1 = sample number 10, category massive agate, first analysis point).
Table 2

<table>
<thead>
<tr>
<th>Color</th>
<th>Dye solution</th>
<th>Acid bath</th>
<th>Heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black</td>
<td>Sugar syrup, prepared by dilution of melted refined sugar in water with a 1:1 dilute ratio.</td>
<td>Immersion in sulfuric acid 96% bath for 96 h at room temperature.</td>
<td>Heating in a muffle furnace for 10 h at 200 °C.</td>
</tr>
<tr>
<td>Red</td>
<td>0.5 L mixture of an aqueous solution of ferric chloride hexahydrate (FeCl₃.6H₂O) 2.6 M, nitric acid 42%, and 25 g of metallic iron.</td>
<td>—</td>
<td>Heating in a muffle furnace for 10 h at 240 °C.</td>
</tr>
<tr>
<td>Blue</td>
<td>Aqueous solution of potassium ferricyanide (K₃[Fe(CN)₆]) 0.7 M.</td>
<td>Immersion in sulfuric acid 96% bath for 24 h at room temperature. After, immersion in water for 4 h at 60 °C.</td>
<td>Heating in a muffle furnace for 2 h at 50 °C.</td>
</tr>
<tr>
<td>Green</td>
<td>Mixture of aqueous solution of chromium oxide (CrO₃) 3.5 M and ammonium chloride (NH₄Cl) 6.2 M in proportion 1:1.5 (oxide:chloride).</td>
<td>—</td>
<td>Heating in a muffle furnace for 10 h at 240 °C.</td>
</tr>
</tbody>
</table>

Fig. 4. General scheme of the adopted cold dyeing process.

Fig. 5. Variation in dye solution concentrations adopted for optimization of the cold dyeing. The numbers marked with an asterisk (*) indicate the standard formulations previously outlined.
2.3. Cold dyeing: preliminary optimization

The optimal dye concentration was defined as the one that resulted in color alterations better or at least comparable to that obtained from the conventional dyeing system but with minimal reactant consumption. On this basis, variations in the concentration of dye solutions were set to identify the minimal dye concentration range needed to ensure a sufficient color alteration. Fig. 5 illustrates the scheme adopted for optimization for each color. One agate slab of each category was used to test three distinct concentrations for each artificial color. Average room temperatures measured during the immersion into dye solutions were of: 14.2 °C (±4.3 °C) for black color; 8.8 °C (±6.6 °C) for red color; 11.4 °C (±4.5 °C) for blue color; and 8.5 °C (±4.1 °C) for green color. In the case of black and blue colors, the measured room temperatures for the additional acid immersion stage were of 8.9 °C (±6.1 °C) and 7.5 °C (±5.0 °C), respectively.

2.4. Dyeing quality analysis

All samples were submitted to spectrometric analysis in three distinct stages: (1) before dyeing; (2) after dyeing, before polishing; and (3) after the final polishing. The readings were collected in a UV-VIS spectrophotometer Minolta CM-2600 d using the illuminant D65, which portrays standard daylight illumination conditions (wavelength between 400 nm and 700 nm). Reflectance capture simulated an observer at 10°. Calibration was executed at the beginning of readings having two reference points, the black measurement (zero) and the white standard. The readings were carried out inside the area of the points signaled by the laser engravings (see Fig. 3). The evaluated points were those which better represented the main feature of each sample (massive, salted, flocked, or glazed) selected before dyeing. On the basis of the collected data, spectral distribution curves were built for the four colors, represented by the average measures of each category. The obtained spectra of the different procedures for each color (warm versus cold dyeing) were then compared and analyzed. The distinctive effects of each dyeing process were also evaluated in terms of the visual aspects of the pieces through the different stages of treatment. A compilation of pictures of agates used in the current study is shown in Appendix A to D.

3. Results

In all cases, agate pieces dyed through the proposed cold dyeing route yielded better results in terms of color alteration and final color intensity than agate pieces dyed through the conventional route. The following section presents in detail the influence of dye solution concentration on color alteration for each artificial color as well as a comparative analysis of the dyeing routes.

3.1. Dyeing in black

Fig. 6 shows the spectral reflectance curves obtained for artificial black coloring, in which the reflectance values indicate the percentage of visible spectral range (400–700 nm) reflected by the samples. Black color surfaces have a radiation reflectance near to 0%, thus absorbing most of the incident light. In this sense, the overall effect of black dyeing and polishing operations was the decrease in light reflectance values in comparison to the initial, untreated state, as detailed in Fig. 5. On the whole, both reflectance spectra and visual results of the samples submitted to cold processing were superior to those obtained from conventional processing. Agates dyed by the traditional warm process exhibited shades closer to reddish-brown, whereas all samples dyed through the cold route showed a more prominent darkening, as can be seen in Fig. 7 (pictures of agates treated with all black dye concentrations can be seen in Fig. S1, Appendix A).

Regardless of dye solution concentration, samples of the massive class treated according to the proposed cold dyeing process showed reflectance curves closest to 0% both after dyeing and polishing operations, surpassing even the black standard (yellow lines in Fig. 6). The sample of the massive class dyed with concentration 3 (C3) solution, i.e. sugar syrup 5.84 M, showed the best coloring results in terms of reflectance. On the other hand, the other classes demonstrated oscillations in the reflectance values, especially the flocked and salted ones. Also, it can be observed that better reflectance values after polishing (in the case, closer to 0%) were not necessarily associated with the use of more concentrated dye solutions, as exemplified by the salted and glazed classes (having C1 and C2 exhibited better results, respectively). The oscillations observed in reflectance data showed to be no significant in visual terms, as exhibited in Fig. 7. In short, the results indicated that a significantly better black coloring can be obtained by using the proposed cold dyeing process even when the dye solution concentration is four times lower (concentration C1, 1.46 mol.L⁻¹) than that conventionally used (5.84 mol.L⁻¹).

3.2. Dyeing in red

The reflectance curves obtained for dyeing in red can be observed in Fig. 8(a). A higher reflectance in the wavelength range comprised between 610 nm and 700 nm corresponds to the red color in the visible spectra. Comparing the curves after the polishing step shows that the samples of massive and flocked classes treated with concentration 3 (C3) of the red dye solution exhibited profiles closer to the red spectrum, i.e. with a reflectance of about 50% within the red wavelength range (55.6% and 45.3%, respectively). On the other hand, agates of the salted class showed a comparatively high reflectance level for all the considered wavelengths, whereas the glazed class demonstrated relatively low reflectance values. The data also indicated that samples treated with warm dyeing did not present meaningful alterations in the reflectance profile, with exception to the massive class, as confirmed by the pictures in Fig. 8(b). Visual observation of the dyed pieces also corroborated the reflectance data, which points to the greater ease of dyeing red of the massive and flocked classes. Although the coloring levels showed to be more intense for C3, the dye solution C2, which was prepared using the half of iron, proved to be sufficiently effective for dyeing in red, especially when visually compared to the conventional system (Fig. 8b). Pictures of all pieces dyed in red can be found in Fig. S2, Appendix B.

3.3. Dyeing in blue

Fig. 9 shows the reflectance curves and pictures of the samples before and after the treatment for dyeing in blue. In all cases, the color alteration was not considered satisfactory in terms of spectral profile modification, since none of the samples exhibited a clear spectrum of reflectance in the blue wavelength band (i.e. reflectance of about 25% in the wavelength band between 450 nm and 495 nm and significantly lower reflectance values in larger wavelengths). Notwithstanding, the pieces treated by the cold processing showed a more remarkable change in the visual aspect than those treated by the warm route (Fig. 9b; see Fig. S3 in Appendix C for more details), which in turn showed very few observable differences to the pre-dyeing state. Within the cold route, the dye solutions of concentrations C2 and C3 had a positive impact on the flocked class, which showed reflectance curves closest to the blue spectrum. On the other hand, the points signaled for evaluation in...
Fig. 6. Reflectance curves showing the average measures of reflectance of the samples submitted to dyeing in black, with emphasis to the lower reflectance levels. C1, C2 and C3 represent the three dye solution concentrations adopted for optimization (see Fig. 4).
the salted class did not show significant color alterations, thus indicating the ineffectiveness of the thermo-chemical treatment to such a class. Also, after polishing some pieces acquired dark tones, in special the massive class and, to a minor extent, the glazed class, showing reflectance values near to 5% and resulting in a final color closer to black than blue. This could be related to the reduction of pieces transparency due to the intense tones of blue obtained after the treatment, which can be ultimately linked to differences in surface porosity of the classes. Despite being difficult to define the better dye concentration based on the reflectance curves, the visual aspect of the pieces suggests that even the lowest dye concentration (C1) provoked a slightly more intense color alteration than that observed in the conventional system (Fig. 9b).

3.4. Dyeing in green

The wavelength band comprised between 500 and 565 nm, near the middle of the visible band, corresponds to the green color. The spectra obtained after different treatments with green dye are reported in Fig. 10(a). All samples, including those dyed through the warm route, showed satisfactory levels of color alteration, except for particularities of each agates category. Samples of the flocked class showed higher reflectance values for the green band in all dye concentrations tested in the cold route. The class massive also showed reflectance profiles as well as the visual aspect corresponding to the green color. By comparing the visual results, it is also noticeable that the glazed class underwent an appreciable color alteration, but showed darker tones and displayed reflectance spectra values far from green. For the salted class, the observed color alteration was generally limited to the outer zones of the pieces, and the reflectance curves were not related to green. On the whole, cold dyeing using the lowest concentration of dye (C1) showed a slight advantage in terms of visual aspect over the warm route, as can be observed in Fig. 10(b). From this, it can be seen that while the classes glazed and flocked experienced comparable pigmentation in both routes, the classes salted and massive showed a more intense color alteration for the cold route. Pictures of agates treated with green dye can be seen in Fig. S4, Appendix D).

4. Discussion

Considering the colors studied, the optimized cold dyeing system showed significantly better results both for agates color alteration and visual color quality of the treated pieces in comparison to the local commercial system. Even though the specific conditions of cold dyeing should have played an important role in this result, the influence of the identified operational shortcomings related to the local dyeing practices must be taken into account. Samples of agates treated through the conventional system may have been submitted to dye concentrations different from those informed in loco, or even the quality of reactants used for dye preparation may not have fulfilled minimum quality requirements, which ultimately resulted in insufficient pigmentation, as observed in the case of black and blue colors. In this sense, the setting of the
Fig. 8. Reflectance curves of samples submitted to dyeing in red and pictures of the pieces following the treatment sequence. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
Fig. 9. Reflectance curves of samples submitted to dyeing in blue and color alteration of pieces submitted to the treatment. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
Fig. 10. Reflectance curves of samples submitted to dyeing in green and color alteration of pieces submitted to the treatment. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
minimal dye concentrations is a positive achievement by indicating minimal reference values for controlling the quality of dye solutions. In the case of dyeing in red, for instance, the intermediate dye concentration (1 mol L\(^{-1}\)) proved to be sufficient to promote an appreciable color alteration in the gems, whereas the lowest concentration (0.5 mol L\(^{-1}\)) was not, thus defining a minimum concentration for efficient dyeing. Setting a minimal concentration of dye not only reduces operating costs but also can prevent overloading the wastewater. This is particularly important for dyeing in green due to the worrying presence of chromium (CrO\(_3\)) in the dye solution. A more detailed discussion about the effects of applying the cold route on heat energy and reactant consumption is presented below.

4.1. Comparative analysis

In this section, the overall impact on heat energy and reactant consumption from using the cold dyeing process is compared to operational data surveyed from producers using the conventional warm system (Table 1). Table 3 summarizes the processing time associated with each dyeing route and color, from which it can be noticed a striking reduction of heating times for all studied colors when using cold dyeing. The average decrease in heating time considering all colors was 94.6% (±4.0%). For comparison purposes, this reduction would represent an energy consumption of only 1.35 kWh per ton of agate if compared to the average value of 25 kWh described in previous studies (Vilasbós et al., 2017). Also important is the fact that some factories use wood-fired ovens so that saving energy would reduce deforestation, air pollution and costs associated with transport and storage of fuel.

In most cases, heating times during the cold dyeing are virtually negligible compared with those of the conventional dyeing, as exemplified in the case of the blue color (196 h versus 2 h). Also, the implementation of the cold dyeing route resulted in an average total process time reduction of 26.6 h (±3.0 h) for dyeing in black, blue, and green colors. On the other hand, it represented an increase of 72 h in the total processing time of dyeing in red. Discounting this exception, the results indicate that in addition to the reduction in heat energy consumption, the application of the developed cold dyeing route is an option for minimizing dyeing time and thus increase production capacity. In practice, it can benefit producers by providing greater operational flexibility and production rate, which can be economically decisive for the economic subsistence of business at the artisanal and small-scale level.

Table 4 shows the difference in key reactants’ consumption between the conventional and the optimized cold dyeing routes. As a rule, the use of cold dyeing resulted in considerably lower consumption of reactants with the advantage of achieving a better color alteration as discussed previously. Unfortunately, a definitive evaluation of consumption variation was not possible for dyeing in green since the exact concentration and proportions of reactants commercially used were not satisfactorily informed by local producers (see Table 1). In the main, the results demonstrate the potential of the optimized dyeing conditions in the reduction of operational costs and in the decrease of environmental impacts, since in most cases the optimum concentration of dye solutions was lower than those commercially used, diminishing contaminants content in the wastewater. This is particularly relevant for potassium ferrocyanide (C\(_6\)N\(_6\)FeK\(_3\)), which is not easily removed from wastewater (Wei-Chang et al., 2006), being convenient to keep its concentration in the dye solution as low as possible.

5. Conclusions

In this work, a new route for cold dyeing of agates with inorganic dyes in the colors black, red, blue, and green is proposed and optimized, involving a sequence of operations with minimal use of heat and reactants. It was found that in virtually all cases, the application of the developed cold dyeing process was associated with substantial increases in the color intensity when compared to the conventional warm dyeing system. In relation to the agates categories, samples of the massive and flocked classes exhibited greater ease to be dyed in any of the colors tested, whereas the behavior of the glazed class varied depending on the color. Conversely, the salted class did not show significant color variation in any of the dyeing processes studied.

Moreover, the improvements in color quality also were accompanied by a remarkable reduction in heat energy and reactant consumption. Specifically, energy consumption showed an average reduction of 94.6% (±4.0%) while reactants consumption decreased from 20.5% for the blue color to 75% for the black and red colors. Although the lack of reactant consumption data in conventional dyeing has not allowed comparing the variation for the green color, the obtained value for the optimized condition can be used as a reference for future studies. The obtained results, therefore, indicate that a potential benefit in terms of reduction of operating costs...
and wastewater burden could be obtained from using the cold dyeing process.

Most notably, this is the first study to the authors’ knowledge to map the state of the art of the local agates’ productive system and to establish relationships between color quality, agates classes and reagents concentrations to be used in order to achieve minimal standards of coloration. However, some limitations are worth noting. The color loss (color stability), an important factor for colored agates in the market, was not explored in this study as well as optimized routes using organic dyes. Future studies should therefore focus on the implementation of cold dyeing with organic dyes and consider the influence of different exposure conditions on the stability of colored agates.

**CRediT authorship contribution statement**

- **Cristiane Ericksson**: Conceptualization, Methodology, Validation, Investigation, Data curation.
- **Irineu A.S. de Brum**: Supervision, Project administration, Funding acquisition. **Weslei M. Ambrós**: Writing - original draft, Writing - review & editing, Visualization.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**Appendix A. Supplementary data**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2020.125387.

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