

Dyeing of solid wood mediated by scCO₂: Challenges and novel approaches

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ABSTRACT

Colour of wood is limited to a rather narrow gamut ranging from yellowish in the brighter species like poplar to dark brown as inherent to walnut or ironwood. Aiming to give more choice to both consumers and manufacturers of furniture and woody construction materials, much progress has been made to date with regard to improved dyeing techniques. This paper presents the first results of a study that investigates green dyeing approaches using the carrier medium supercritical carbon dioxide (scCO₂), in combination with compatible disperse dyes, co-solvents and hydrophobization agents.

Supercritical impregnation offers a series of advantages related to dyeing kinetics, separation of pollutants and energy demand for recovery. Carbon dioxide is particularly appealing as it is plentiful, non-flammable, chemically largely inert, and undergoes transition to supercritical state at mild conditions (7.38 MPa and 31.2°C). In supercritical state it effuses through solids like a gas but dissolves compounds as liquids do [1]. These intriguing properties have been employed in a multitude of industrial applications including extraction and loading of active compounds [2] or dyeing of polyester fibres with disperse dyes [3].

However, impregnation of natural fibres or massive wood with commercial disperse dyes is difficult as the latter typically have low affinity towards polar, hydrophilic interfaces [3] and low solubility in scCO₂. The use of volatile co-solvents, such as acetone or ethanol, was not considered a viable option to overcome this obstacle as they would counteract the supercritical loading process under the desired mild process conditions [4].

Based on preliminary results, this paper discusses the pros and cons of various dyeing strategies for massive wood and proposes measures to improve the dye uptake of both commercially available and new disperse dyes for different European wood species.

INTRODUCTION

Supercritical carbon dioxide (scCO₂) technologies have been greatly advanced over the past decades, serve today for a multitude of technical applications and are continuously further developed owing to their great potential in modern material sciences and process engineering. Intriguing features like gas-like viscosities ($\sim 10^{-5}$ Pa·s), liquid-like densities (up to 800 kg·m⁻³), very low surface tension, non-flammability and chemical inertness are appealing features that literally invites to be used in solid wood modification as well. Numerous studies on wood impregnation have been therefore conducted in the last two decades [2, 5-9] eventually resulting in the development of a full industrial process for impregnation of wood with biocides (Superwood®, Finland, [10-12]).

Loading of wood with other compounds, however, using scCO₂ as carrier medium received only little attention. Examples are acetylation [13, 14] and dyeing of wood [4]. Although the latter could be performed in supercritical CO₂ as well, it was hitherto not comprehensively studied as only some experiments were performed in sub-critical

conditions (2.5, 5.0 MPa) using volatile solvents (ethanol, hexane) and a pressure gradient indicating that working in supercritical state would be not required.

Interestingly, scCO₂ is already used at industrial scale to colour polyester (PET) fibers with disperse dyes [15, 16]. Dyeing of cellulosic fibers, at the contrary, turned out more challenging. This is, however, comprehensible looking at the two scCO₂-mediated impregnation mechanisms reported in the literature. The first one is based on the fact that scCO₂ can plasticise efficiently synthetic polymers allowing a high degree of impregnation. Here, the dye (or other modification agent) is deposited into the polymer matrix while CO₂ is quickly leaving the matrix during depressurisation. The second mechanism is based on the partition coefficient that imparts a higher affinity for the matrix to the solute instead of for the supercritical fluid [17]. In the case of natural polymers like cellulose, extensive intra- and intermolecular hydrogen bonding largely impedes swelling in scCO₂. Moreover, disperse dyes are hydrophobic, suggesting a low partition coefficient between them and the hydrophilic polysaccharides. Thus, dyeing of natural fibers might be limited due to both the poor affinity of hydrophilic surfaces for non-polar dyes and the lacking swelling capabilities for natural hydrophilic polymers.

Recently, it has been shown that the bark of the cork oak (*Quercus suber* L.) can be coloured with disperse blue 14 using scCO₂ [18]. This is in so far surprising that cork is a lightweight but entirely closed-porous material with thin walls separating the gas-filled voids [19, 20]. High contents of hydrophobic suberin render these cell walls and, hence, cork as such impermeable to liquids [21] which is commercially used for sealing of wine bottles.

Considering these properties, we hypothesized that the good colourability of cork with non-polar disperse dyes using CO₂ as carrier medium should be the result of the particular chemical composition of the (secondary) cell walls composed of alternating layers of suberin and waxes [19, 21]. Suberin itself constitutes up to 50% of these walls and forms two domains, a polyphenolic and a polyaliphatic one. It is therefore likely that scCO₂ has the capability to swell both the waxes and the polyaliphatic domains in suberin rendering thus cork permeable for scCO₂ and to provide a higher partition coefficient between the non-polar cell constituents and the non-polar disperse dyes. Following this hypothesis, we pre-modify solid wood with a waxy compound in an attempt to mimic the hydrophobic cell wall constituents of cork and to improve the scCO₂ colourability of wood. The first results of this study using representative wood species (birch, beech, oak, reference cork) are presented and comprehensively discussed.

MATERIALS AND METHODS

All specimens subjected to liquid wax pre-impregnation were dried before soaking in the respective molten wax (90°C, 2 hrs.) and submitted to alternating cycles of vacuum (8 kPa) and atmospheric pressure in order to accelerate the wax uptake.

Supercritical dyeing experiments were performed using high-pressure supercritical CO₂ equipment (Separex, Champigneulle, France) connected to a 200 mL-autoclave (internal diameter of 34.5 mm). Disperse blue 134, in excess (ca. 100 mg), was filled into an empty teabag which was placed at the bottom of a sample holder. The different small wood and cork specimens (20 x 10 x 10 mm) were randomly placed onto the different stages of the sample holder. After adjusting the temperature to 45°C the equipment was pressurized at a rate of approx. 0.43 MPa·min⁻¹ which was considered to be slowly enough to allow for pressure equilibration in the interior of the semi-porous samples. After reaching working pressure (20.0 ± 2.0 MPa) both pressure and temperature were kept constant for 25 h. Then the heating systems were switched off and the autoclave was slowly depressurised at 0.22 MPa·min⁻¹; the final temperature was typically around 32°C.

Colour measurements covering the wavelength range of 400-700 nm were performed on 12 (Ø 6 mm) spots for each sample, thereof 8 spots at the surface and 4 spots at the interior of longitudinally halved specimen using a Phyma CODEC 400

spectrophotometer. The reproducibility of the measurement through all the process steps was insured by a home-made specimen holder. The obtained absorption data were evaluated for their values in the CIELAB colour space as expressed by the parameters L^* (lightness, 0 to 100), a^* , varying from green (-50) to red (+50), b^* , comprising the range from blue (-50) to yellow (+50), and the Euclidean distance ΔE . The latter can be regarded as a summary of these measurements as ΔE reports the average colour change. It is generally agreed upon that the human eye can distinguish a colour change when ΔE is greater than 2. The colour of each sample was quantified for every step of the process to evaluate the respective influence on L^* , a^* , b^* and ΔE .

RESULTS

Loading of native wood samples with Disperse Blue 134 as intended to accomplish by precipitation of the dye from respective solutions in scCO₂ upon slow depressurization translated into very low dye uptake. The overall change of colour, estimated by the value of ΔE , was 24.8 (\pm 1.4) for the outside surface of birch only. Dye uptake was even lower for oak (ΔE 14.3 \pm 1.1) and beech (ΔE 16.2 \pm 1.4). The colour change for the interior of the halved samples was close to the limit of detection for the human eye; ΔE reached 6.6 (\pm 1.1) for oak and 5.5 (\pm 2.3) for beech only. These considerable differences between exterior and interior loading by scCO₂-based wood impregnation processes have been mentioned in previous studies, too, such as for the preservative tebuconazole where the gradient between outside/inside loading was between 2.2 and 8.7 [7].

Dyeing of birch was somewhat more successful, ΔE was here 18.4 (\pm 2.2). Astonishingly, during the same experiment, cork could be nicely dyed and a deep blue coloration was obtained for both the exterior (ΔE 55.2 \pm 0.9) and interior surfaces (ΔE 37.2 \pm 3.4). Even though this remarkably good colourability of cork had been anticipated to some extent from a recent report about dyeing of wood with disperse blue 14 using scCO₂ [18], is indeed surprising considering the closed-porous, suberin-rich cork structure. Therefore, we hypothesized that suberin, a non-polar major constituent of the cork cell walls, plays a key role in mediating the diffusion of dye-loaded CO₂ by plasticization. Following this hypothesis we impregnated different wood samples with lipophilic compounds – for confidential reasons referred to as “waxes” – using an liquid, vacuum assisted impregnation approach.

The results confirmed that implementation of a lipophilization step – such as by impregnation of wood samples with molten waxes – prior to scCO₂ dyeing with disperse dyes (e.g., disperse blue 134) significantly improves the colour uptake for both the exterior and interior of the samples. This is evident from the considerable gain in ΔE for the outside surfaces of the wax-pretreated samples which was 46.5 \pm 3.2 for birch, 33.1 \pm 3.4 for beech and 28.4 \pm 2.5 for oak. This is nearly twice the values obtained for the non-pretreated samples. The wax pre-treatment itself had a little impact only on ΔE .

Since ΔE is calculated from the changes of L^* , a^* and b^* - defined as variations from the initial state to the final; ΔL^* , Δa^* and Δb^* - it is possible to trace back precisely which of these CIELAB colour space components contribute to what extent to ΔE obtained after scCO₂ dyeing of wood with disperse blue 134.

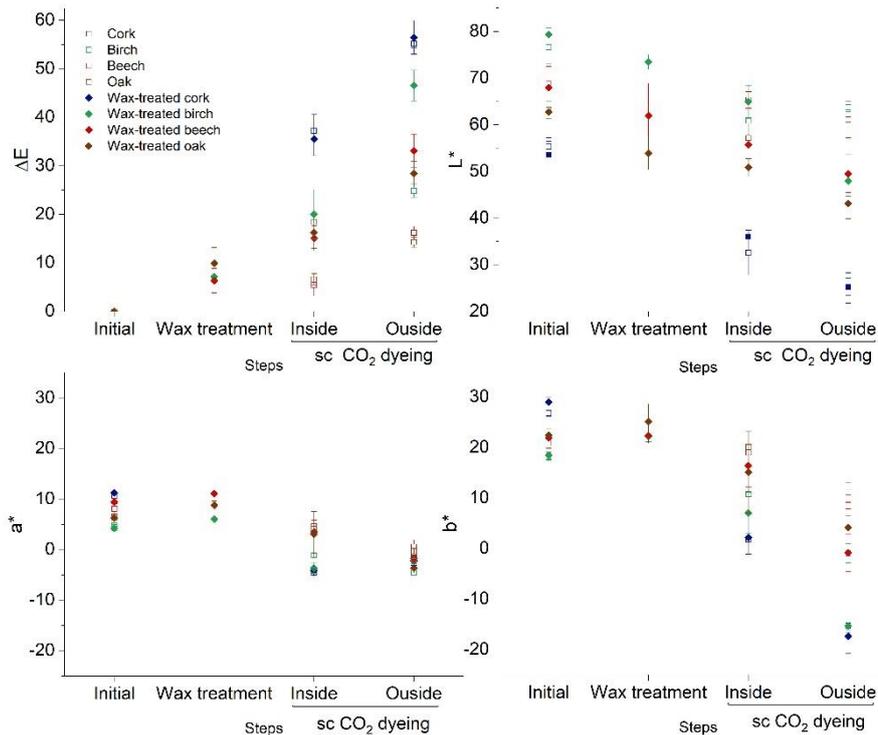


Figure 1: Characterisation of colour changes by CIELAB colour system of the considered specimens.

For non-wax pretreated samples it is evident that slight decreases in L^* (lightness) and in b^* are obtained only, confirming that a low amount of dyes had been loaded into the interior only. This is different for cork which has already relatively low values of L^* (55.3 ± 1.9 and reached a very low value of lightness on the outside surface (25 ± 3.3); resulting in a ΔL^* of 30.8. In comparison, oak, beech and birch featured a ΔL^* of 7.4, 7.6 and 12.9 respectively. The b^* values of cork were even more impressive and varied from 26.8 (± 0.7 ; exterior) to $-15.3 (\pm 5.5$; exterior). The resulting Δb^* is thus indicating that b^* , i.e. the blue component of the colour, is obviously the one which was most influenced by dyeing. Similarly, Δb^* of non-wax treated specimens was far lower than that with 9.9, 12.1 and 19.1 for treated oak, beech and birch respectively.

For wax-pretreated samples it was found that $scCO_2$ dyeing resulted in a significant decrease in both L^* and b^* . Most noteworthy is that for birch after dyeing reached nearly that of cork dyed in the same experiment (-15.3 ± 1.3 vs. -7.3 ± 1.3) which represents a significant shift into the blue range while a^* remained largely unaffected.

CONCLUSION

Pre-treatment of wood with certain waxes is a promising approach to improve the dyeing success of supercritical carbon dioxide assisted colourization with non-polar Disperse Dyes. This has been demonstrated for Disperse Blue 134 and selected wood samples (birch, oak, beech) representing a wide range wood species and colour. Even though the materials obtained still suffer from considerable colour inhomogeneities, i.e. colour gradients between exterior surface and core sections, there is promising evidence from current work that this obstacle can be overcome by synthesis of dyes of improved solubility in $scCO_2$ and use of certain co-solvents.

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