ACS Sustainable Chemistry & Engineering
Research Article
pubs.acs.org/journal/ascecg

Ionic Liquids Can Significantly Improve Textile Dyeing: An Innovative Application Assuring Economic and Environmental Benefits

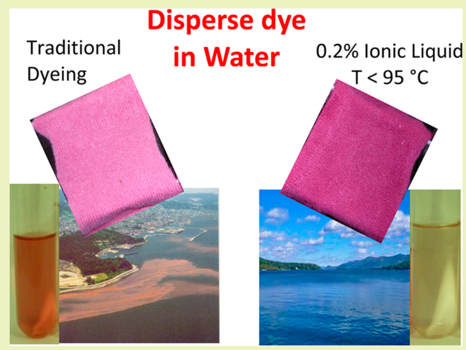
Roberto Bianchini,[†] Giorgio Cevasco,[*,‡] Cinzia Chiappe,[*,§] Christian Silvio Pomelli,[§] and María Jesús Rodríguez Douton[§]

[†]Dipartimento di Chimica "Ugo Schiff", Università di Firenze, Via della Lastruccia, 3-50019 Sesto Fiorentino, Italy

[‡]Dipartimento di Chimica e Chimica Industriale, Università di Genova, via Dodecaneso 31, 16146 Genova, IMC-CNR, 00100 Roma, Italy

[§]Dipartimento di Farmacia, Università di Pisa, via Bonanno 33, 56126 Pisa, Italy

ABSTRACT: Owing to economic reasons, the textile dyeing industry generally employs traditional and absolutely no-eco-friendly processes: very large quantities of water are indeed required together with a large number of added chemicals which represent dramatic environmental issues. In order to improve the sustainability of the process, we have investigated the dyeing of wool, polyester, and cotton with disperse Red 13 using ionic liquids as the sole additive. The results obtained in isothermal dyeing at 95 °C show an outstanding effect of the ionic liquid 1-(2-hydroxyethyl)-3-methylimidazolium chloride. This ionic liquid assures efficient dyeing of polyester and wool in open vessels, in the absence of whichever auxiliary agent with total dyebath exhaustion, thus allowing in principle the recycling of the dye bath! The environmental benefits arising from the substitution of a number of usually employed auxiliary agents with only an ionic liquid are highlighted together with the economic ones. This article reports for the first time, to the best of our knowledge, dyeing processes for several kinds of fibers (cotton, wool, and polyester) employing exclusively three components: pure disperse dye, water, and an appropriate ionic liquid.



KEYWORDS: *Textile dyeing, Ionic liquids and disperse dyes*

■ INTRODUCTION

Dyeing processes are extremely important for the marketing of textile products. They generally take place by fixing the dye molecules to the fibers with the aid of additives and dispersant agents with an incredibly large amount of water. In developed countries, dyeing and printing processes for one ton of fiber use up 100 tons of water, but larger amounts (up 300/400 tons) are employed in other vast areas of the planet. Indeed, several textile plants have been transferred to where labor costs less, and less stringent environmental regulations guarantee lower production costs. At the end of the process, the wastewater generally contains relevant amounts of dyes, dispersing agents, mordants, and surfactants (often "not explicitly declared" compounds present in the commercial dyes), and dumping untreated wastewater into local streams and rivers, although generally prohibited, represents an especially severe environmental threat.[1] Some of these compounds have a direct impact on the environment and/or human health: color brighteners, softeners, and sizing agents are not easily biodegradable, whereas other compounds (for example azo and nitro dyes) can be reduced in water sediments to potentially carcinogenic amines[2], and non-aromatic dyes, often carrying harmful heavy metals, require various toxic finishing processes.[3−7]

Although effluent treatment and water-recycling can reduce discharge pollution and prevent excessive water consumption, these treatments are very expensive. From this point of view, the better solution seems to be the innovation of both textile processing technologies and related chemistry to reduce the effluent pollution. In particular, it becomes important to find solutions for reducing water consumption and the discharge of polluting chemicals, as deeply and broadly discussed by Moore and Ausley.[8] Very recently, a review highlighting the significance and limitations of improving sustainability in reactive dyeing through the development of new dyes, the modification of dyeing machinery and processes, the chemical modification of cotton fiber prior to dyeing, and the use of biodegradable organic compounds in dye bath formulation with efficient effluent treatment processes has been published.[9] The modern textile industry's challenge is thus the development of more sustainable and water-friendly technologies to dye fibers, in particular cotton and polyester that represent the two most mass marketed textiles. Although in the last 20 years several procedures having minor environmental impact, such as those employing water-free processes (AirDye Technology) or supercritical CO_2,[10] have been proposed for dyeing textiles, traditional and absolutely non-eco-friendly processes are largely

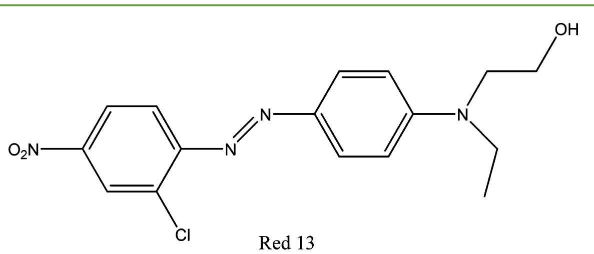
Received: June 25, 2015
Revised: July 15, 2015
Published: July 29, 2015

DOI: 10.1021/acssuschemeng.5b00578
ACS Sustainable Chem. Eng. 2015, 3, 2303−2308

employed worldwide, mainly due to economic reasons (investments for equipment are still very high).

In recent years, another approach to reduce the environmental impact of dyeing has been the substitution of one or more auxiliary agents with compounds having very small ecotoxicity and polluting strength. For instance, Ferrero et al.[11] reported the successful use of ethanol in the substitution of some auxiliary agents. Successively, Ferrero and Periolatto[12] have found that glycerol can efficiently replace ethanol and that moreover its low volatility, which implies low emission in air, is useful for industrial applications. Another example of the substitution principle has been recently offered by Pasquet et al.[13] with the use of vanillin for the chemical substitution of toxic carriers employed in low temperature dyeing of polyester fabrics. However, all these attempts aim at the substitution of only one (or few) of the multitude of auxiliary agents usually employed in the textile industry. Therefore, although very important from a scientific point of view, they cannot represent a global solution to the environmental question. Since we have been interested for a long time in ionic liquid (IL) chemistry,[14] investigating the synthesis, characterization, properties, and application, we have very recently explored also its potential role as a proper solution to current environmental challenges.[15] ILs are salts usually constituted by a large organic cation and an organic or inorganic anion and, as traditionally defined,[16] with melting temperatures below 100 °C. Because of their ionic character, ILs exhibit important properties such as a negligible vapor pressure, low flammability, high thermal and chemical stabilities, broad liquid temperature range, and high solvation ability for organic, inorganic, and polymeric compounds, including biopolymers such as cellulose, chitin, and keratin.[16] For these unique properties, which can be moreover tailored through an appropriate cation and anion selection, ILs have been proposed as "greener" solvents in several and diverse applications.[17−19] Despite the ongoing interest in ILs and their application in new and unexplored areas, the possibility to use this class of organic salts in dyeing processes has been only marginally investigated. In 2009, Queen's University researchers patented the dyeing of fibers in ionic liquids.[20] Subsequently, Yuan and Wang claimed[21] the possibility of improving the dyeing of wool using a specific IL, 1-butyl-3-methylimidazolium chloride ([bmim]Cl), and the same IL was applied by Chang et al.[22] as an accelerating agent in silk dyeing. Actually, in textile chemistry the peculiar solvent properties of ILs have been principally exploited to dissolve cellulose or other biopolymers[15,23−25] in order to prepare new fibers and tissues, such as IONCELL-F, or to remove textile dyes from wastewater.[26,27]

In this study, we report the use of a system constituted by only three components, namely, functionalized IL (in very small amounts), water, and disperse dye (Red 13) (Figure 1),



Red 13

Figure 1. Disperse Red 13.

for dyeing polyester and hydrophilic fibers at 95 °C in an open vessel (very mild conditions with respects to those usually employed, i.e., higher temperatures under pressure), thus avoiding the use of several other chemicals as is customary. To optimize the design of the process, the dyeing effects have been studied by changing IL structure and concentration.

■ RESULTS AND DISCUSSION

Cellulose, wool, and polyesters consist of linear macromolecules possessing 1,4-glucosidic, amide, and ester bonds, respectively. Cellulose in the solid state is able to form intra- and intermolecular hydrogen bonds, leading to organized chain structure. Intra- and intermolecular hydrogen bonds, together with polar and apolar interactions and disulfide cross-links, also determine the wool structure. In contrast, van der Waals interactions dominate in the synthetic polyester fibers (Dracon). Dye molecules cannot easily penetrate the highly ordered regions of most of the fibers, in the absence of proper additives, and at low temperature, dye adsorption normally takes place only in the less-ordered regions and on the surface of crystalline regions.

A pore model is usually used to describe the diffusion of dye molecules in textile fibers in aqueous baths: water and dye molecules diffuse through the fiber network and are simultaneously adsorbed on the surface of pores. Swelling of the fibers, when they are immersed in aqueous solutions at the appropriate temperature, favors dye diffusion into the fiber network (absorption), whereas the chemical affinity between polymer chains and dyes determines the anchoring of the dye molecules and the possibility to get the desired color.

In the case of disperse dyes, neutral organic compounds with a low water solubility and a high ability to give aggregates in this medium, the initial convectional diffusion of the dye to the fiber surface is preceded by the dissolution of the disperse particles. At the boiling temperature of water or even better under pressure at higher temperatures, the small amount of dye solubilized in the dyebath is transferred to the fiber, thus favoring meanwhile further dissolution of the dye in water. Disperse dyes have been initially developed for acetate rayon, although they can be used also for polyester: in both cases, van der Waals interactions between the dye and fiber determine the anchoring process. In the case of polyester, proper physicochemical treatments (e.g., chemical etching by strong acids, UV irradiation, corona discharge or low-temperature plasma treatments, etc.) can increase the number of dipoles on the fiber and favor the dyeing process with disperse dyes.[28] However, disperse dyes are rarely employed for cotton and wool. Direct, acid, or basic dyes able to give hydrogen bonds and dipole−dipole and electrostatic interactions are normally used for these hydrophilic fibers.

Since the possibility to use disperse dyes as "universal dyes" for all kinds of fibers can represent a significant innovation in textile chemistry, reducing both the complexity of the dyeing process and the waste streams,[29] we decided to use in this investigation Red 13 to dye cotton, wool, and polyester. Furthermore, to increase the sustainability of the process, dyeing was always carried out at atmospheric pressure and temperature lower than 100 °C (generally, at 95 °C) using a hydrophobic IL (1-butyl-3-methylimidazolium hexafluorophosphate, **1**) and seven water-soluble ILs (1-butyl-3-methylimidazolium tetrafluoroborate, **2**, 1-butyl-3-methylimidazolium chloride, **3**, 1-butyl-3-methylimidazolium dicyanamide, **4**, choline dihydrogen phosphate, **5**, choline chloride, **6**, 1-(2-hydrox-

DOI: 10.1021/acssuschemeng.5b00578
ACS Sustainable Chem. Eng. 2015, 3, 2303−2308

yethyl)-3-methylimidazolium chloride, 7, and 1-(2-hydroxyethyl)-3-methylimidazolium dicyanamide, **8**) as the sole additive (shown in Figure 2).

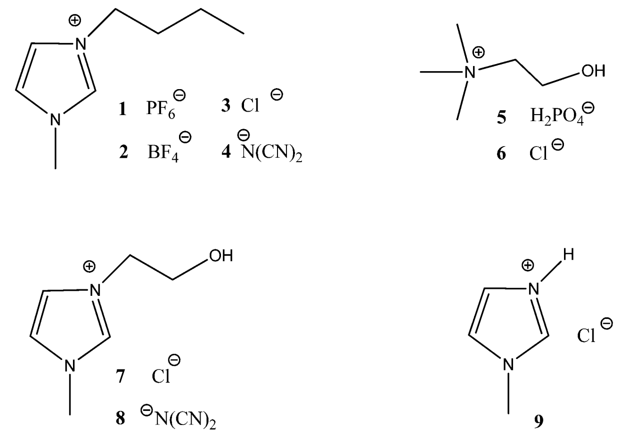


Figure 2. Tested ILs.

As expected, dyeing of cotton, wool, and polyester with Red 13 (0.5%) in water at a temperature of 95 °C and under atmospheric pressure in the absence of ionic liquid was unsuccessful. The fibers showed indeed a dull pink color, and part of the dye was easily removed by simple rinsing. Poor results were obtained also by adding 30 g/L of ILs **1** and **2** or **5** and **6**. At variance, bright and intense colored fibers were obtained using 1-butyl-3-methylimidazolium chloride, **3**, 1-(2-hydroxyethyl)-3-methylimidazolium chloride, **7**, 1-butyl-3-methylimidazolium dicyanamide, **4**, or 1-(2-hydroxyethyl)-3-methylimidazolium dicyanamide, **8**. However, taking into account the different costs (dicyanamide based IL synthesis requires two step processes involving expensive silver salts) and environmental impact of these salts (hydroxyl group on alkyl chain reduces ecotoxicity),[30] we decided to use exclusively **7** in the subsequent experiments aimed to determine the best conditions to perform an efficient dyeing process. Therefore, hereafter the term IL refers to compound **7** unless otherwise stated.

The color strength of wool fibers dyed with different amounts of ionic liquid from 2 to 15 g/L at 95 °C and atmospheric pressure is shown in Figure 3, whereas in Figure 4 is reported the wastewater at the end of the dyeing cycle. Similar results were also obtained using polyester microfibers or cotton. Figure 5 shows the different color tones of polyester microfiber fabrics dyed at 95 °C and atmospheric pressure, with and without IL. Control experiments clearly indicate that the use of conventional standard additives at 95 °C does not guarantee results comparable to those obtained in the presence of IL. Indeed, the dyeing of polyester is normally carried out at 130 °C and under pressure; therefore, our IL based approach deserves to be taken into consideration because much less energy consumption occurs here since the temperature does not exceed 95 °C.

Figure 6 reproduces, as is customary, a multifiber fabric containing strips of wool, acrylic, polyester, nylon, cotton, and acetate dyed with disperse Red13 (0.5%) at 95 °C (atmospheric pressure) in the presence of IL (2 g/L). It is noteworthy that also in this case dyeing occurs with bath exhaustion, and therefore, the different color intensities are due to the different color affinities of the constituting fibers.

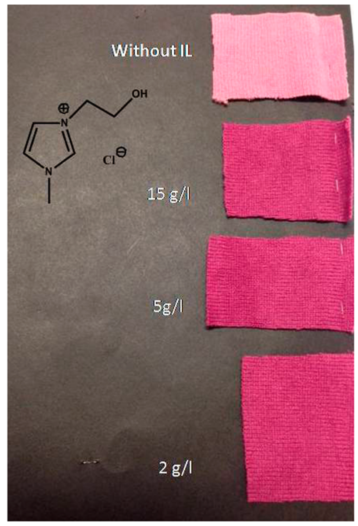


Figure 3. Color strength of wool fibers dyed with different amounts of ionic liquid from 2 to 15 g/L at 95 °C and atmospheric pressure (original unmodified photo).

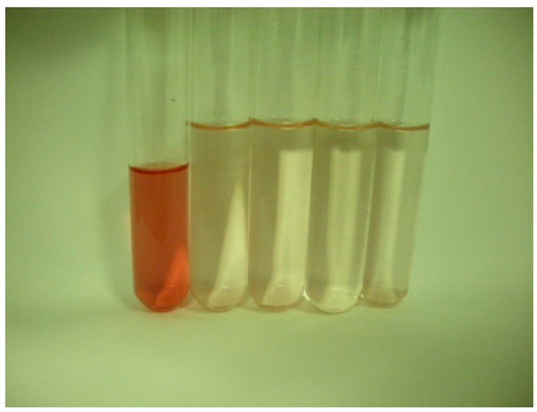


Figure 4. Wastewater arising from the dyeing of wool with Red 13. From left to right without IL and with decreasing amounts of IL (30, 15, 5, and 2 g/L) (original unmodified photo).

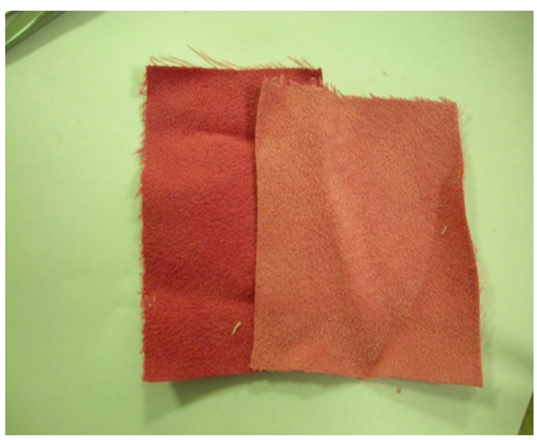


Figure 5. Different color tones of polyester microfibers, dyed at 95 °C under identical conditions with and without IL (left and right, respectively) (original unmodified photo).

It is noteworthy that only in the presence of IL the wastewater is uncolored (Figure 4) and that a concentration 2 g/L of IL appears to be sufficient to ensure that the dye is

DOI: 10.1021/acssuschemeng.5b00578
ACS Sustainable Chem. Eng. 2015, 3, 2303−2308

Figure 6. Multifiber fabric dyed with disperse Red 13 (0.5%) at 95 °C (atmospheric pressure) in the presence of IL (2 g/L) (original unmodified photo).

quantitatively absorbed by the fiber, giving bright and strong coloration, and an essentially colorless wastewater. The concentration of dye in the wastewater is indeed lower than 7×10^{-7} M, as judged by the absorbance at 499 nm. This aspect is extremely important since wastewater (containing therefore only the added IL) can be recycled, at least in principle, countless times with undeniable advantages from both economic and environmental standpoints. Although this aspect is at the moment beyond the scope of this work, we have repeated three cycles of dyeing reusing the same wastewater, replacing the dye but not the IL, obtaining excellent results in terms of dyeing. This of course suggest that the loss of IL is very small, if any, as expected taking into account the hydrophilic nature of **7** and its level of concentration in water.

Colorfastness to crocking test has been evaluated according to UNI EN ISO 105 X12/03, and crockmeter data show only a negligible transfer of color from the dyed surface of wool or polyester to either wet or dry rubbing. Furthermore, in agreement with the previous test, also the loss of color based on the gray change scale is negligible: values ranging from 4 to 5 on a 1−5 scale were generally obtained.

These preliminary results clearly show that IL structure dramatically affects the dyeing process. Although **3** and **7** are the sole ionic liquids, among the investigated ones, able to dissolve natural polymers, such as cellulose (ca. 15% w/w at 100 °C) under anhydrous conditions, this process surely cannot occur during dyeing (i.e., in the presence of large amounts of water). However, the ability of the IL anion to interact with cellulose or other macromolecules constituting the fabric fibers acting as a hydrogen bond acceptor probably positively affects the dye diffusion into the fiber and the subsequent anchoring of the dye onto the fiber. IL components, interacting with the fiber, might contemporaneously attract the polar groups of the disperse dye molecules thus increasing the substantiveness of the fiber to the disperse dye. Moreover, the swelling ability of the IL (it is indeed reasonable to hypothesize that IL anions and cations diffusing into the fiber pores produce a swelling effect) can reduce the degrees of crystallinity and/or orientation of the fiber polymers that greatly prevent the diffusion of disperse dye into fibers. Finally, other positive effects of the IL on dye solubility in water (for instance, acting as a dispersant) cannot be excluded.

Environmental Benefits and Economic Aspects. The use of only one additive (the IL) instead of a rather complex mixture of auxiliary agents (dispersants, carriers, mordants, antifoams, and deaerators, and swelling, wetting, retardant, and leveling agents) is surely one of the most convenient ways to reduce the number and concentration of pollutants in wastewater. The cost to substitute chemicals and products which are toxic pollutants is usually much less than the cost to remove the pollutants from the effluent via end-of-pipe treatments.[31]

The environmental concern of **7** is moderate: this IL can be classified as nontoxic to *Vibrio Fisheri* ($\log_{10}$ EC_{50} 3.89/μM),[30] harmless (EC_{50} 48 h: > 100 mg/L) toward fish (*D. rerio*) and crustaceans (*D. magna*), and only moderately toxic (EC_{50} 48 h: 10−100 mg/L) toward other species (*P. subcapitata*), in agreement with other imidazolium ILs bearing short hydroxylated side chains.[32] Unlike the dyes that are at least in part fixed onto textile fibers, the auxiliary agents remain in dyebaths and contribute significantly to the organic load of wastewater. Moreover, the use of retarders and levelers generally results in lower dyebath exhaustion and requires high water consumption to eliminate them from textiles. On the contrary, ionic compounds can be easily removed since they have high affinity for water. Reduction of water consumption is one of the principal targets to improve the efficiency of textile dyeing. In this regard, it is noteworthy that the proposed system allows the recycling of the dye-bath (water and ionic liquid).

From an economic point of view, the price of a commercial auxiliary agent is about 10 US$/kg. If such an auxiliary is employed at 1% over fiber weight, its cost for the recipe results in 0.1 US$/kg of fiber. Today, the price of simple chloride based ILs is about 20 US$/kg (ranging from 15 to 25 US$/kg); hence, if a concentration of 2 g/L is needed, the recipe cost depends on the material-to-liquor ratio. In industrial dyeing machinery, this ratio ranges from 1:20 to 1:5; hence, the IL cost could range from 0.8 to 0.2 US$/kg of fiber with a cost which could be significantly reduced using cheaper ILs, for example, Brønsted acidic ILs (price of about 2 US$/kg).

Preliminary experiments carried out using methylimidazolium chloride, **9**, evidence the possibility of using this very low cost IL (1g/L) at least for dyeing polyester at 100 °C, under the above-reported conditions. Finally, IL addition to a dyebath is able to significantly improve the dyeing procedure: IL allows the dyeing of multifiber fabrics in a single bath, at atmospheric pressure and lower process temperatures. This can add further economic advantages from an energy saving standpoint.

■ MATERIALS AND METHODS

The commercial dye used in this study, disperse Red 13, shown in Figure 1, was purchased from Sigma-Aldrich. Ionic liquids were prepared according to well-established synthetic procedures[33] and confirmed by NMR analysis and electrospray ionization mass spectrometry (ESI-MS).

Dyeing Procedure. Experimental tests were carried out in a small size apparatus routinely employed in laboratories of analysis and research in the textile sector. Stock solutions of Red 13 in IL were diluted with water to obtain dyebaths containing different concentrations of IL, ranging from 2 to 30 g/L, and 0.5% of dye (with respect to the fiber). The selected fiber (cotton, polyester, or wool fabrics, 5 g; multifiber test fabrics DW, 1 g) was immersed in the bath (250 mL) preheated at 80 °C and acidified at pH 4 with acetic acid (86%, 4g/L). The temperature was increased at 95 °C, and after 30 min, the bath was cooled down at 80 °C, and 0.5 g of acetic acid (86%) was added. Then, the bath temperature was reported again at 95 °C for a further 30 min. At the end of this second phase, the bath was cooled at 80 °C, and the dyed fiber was removed and sent to the conventional soaping phase. Blank experiments were carried out under identical conditions avoiding the addition of the IL.

■ CONCLUSIONS

Textile dyeing usually requires enormous amounts of water, a lot of chemicals, and has high energy demand. Therefore, a

DOI: 10.1021/acssuschemeng.5b00578
ACS Sustainable Chem. Eng. 2015, 3, 2303−2308

great effort has been made worldwide in order to depict a cleaner production framework to reduce the toxicity and environmental threat of textile chemicals.

In this article we describe, for the first time, the innovative use of a single IL for polyester, cotton, and wool dyeing as an efficient and valuable substitution to the usually employed multicomponent systems (containing indeed, often contemporaneously, dispersants, swelling agents, carriers, mordants, antifoams and deaerators, and others). In this regard, we emphasize that no direct comparison can be made with the results stemming from the papers cited in the Introduction since we employ a system completely different from those described in these papers. In this work, we indeed report for the first time, to the best of our knowledge, a process employing exclusively three components: pure dye, water, and an ionic liquid.

Dyeing of polyester in an open vessel with complete exhaustion of the dyebath is possible in the presence of suitable ILs. Polyester can be dyed at 95 °C without the aid of auxiliary agents at atmospheric pressure. Wool can be dyed with disperse dyes under identical conditions. Consequently, the use of IL allows the dyeing of multifiber fabrics in a single bath, at atmospheric pressure. The color yields and water-wash fastness are excellent. Moreover, the proposed process, being conducted at temperatures and pressures lower than those usually employed, assures significant energy savings.

Another key factor is provided by the complete exhaustion of the dyebath after dyeing is carried out with our method; thus, the residual dye baths can be obviously used again. Last but not least, the low environmental impact of IL **7**, which is harmless toward fish (*D. rerio*) and only moderately toxic toward other species (*D. magna* and *P. subcapitata*), significantly contributes to increase the sustainability of the process.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: giorgio.cevasco@unige.it.

*E-mail: cinziac@farm.unipi.it.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Regione Toscana who provided a grant for this investigation.

REFERENCES

(1) Christie, R. M. *Environmental Aspects of Textile Dyeing*, 1st ed; Woodhead Publishing Ltd.: Manchester, England, 2007.

(2) Chen, H. Recent advances in azo dye degrading enzyme research. *Curr. Protein Pept. Sci.* **2006**, *7*, 101.

(3) Ratna Padhi, B. S. Pollution due to synthetic dyes toxicity & carcinogenicity studies and remediation. *Int. J. Environ. Sci.* **2012**, *3*, 940.

(4) Verma, Y. Acute toxicity assessment of textile dyes and textile and dye industrial effluents using Daphnia magna bioassay. *Toxicol. Ind. Health* **2008**, *24*, 491.

(5) Verma, Y. Toxicity assessment of dye containing industrial effluents by acute toxicity test using Daphnia magna. *Toxicol. Ind. Health* **2011**, *27*, 41.

(6) Villegas-Navarro, A.; Ramírez, M. Y.; Salvador, S. M. S.; Gallardo, J. M. Determination of wastewater LC50 of the different process stages of the textile industry. *Ecotoxicol. Environ. Saf.* **2001**, *48*, 56.

(7) de Campos Ventura-Camargo, B.; Marin-Morales, M. A. Azo Dyes: Characterization and Toxicity− A Review. *Text. Light Ind. Sci. Technol.* **2013**, *2*, 85.

(8) Moore, S. B.; Ausley, L. W. Systems thinking and green chemistry in the textile industry: concepts, technologies and benefits. *J. Cleaner Prod.* **2004**, *12*, 585.

(9) Khatri, A.; Peerzada, M. H.; Mohsin, M.; White, M. A review on developments in dyeing cotton fabrics with reactive dyes for reducing effluent pollution. *J. Cleaner Prod.* **2015**, *87*, 50.

(10) DyeCoo Textile Systems B.V., **2010**. CO_2 Dyeing Gets Commercial Roll-out. Available from: http://www.dyecoo.com/pdfs/DyeCoo-stroy.pdf (accessed Apr 24, 2015). Gao, D.; Yang, D. Cui, H.; Huang, T. Lin J. Supercritical carbon dioxide dyeing for PET and cotton fabric with synthesized dyes by a modified apparatus *ACS Sustainable Chem. Eng.*, **2015**, *3*, 668 10.1021/sc500844d.

(11) Ferrero, F.; Periolatto, M.; Rovero, G.; Giansetti, M. Alcohol-assisted dyeing processes: a chemical substitution study. *J. Cleaner Prod.* **2011**, *19*, 1377.

(12) Ferrero, F.; Periolatto, M. Glycerol in comparison with ethanol in alcohol-assisted dyeing. *J. Cleaner Prod.* **2012**, *33*, 127.

(13) Pasquet, V.; Perwuelz, A.; Behary, N.; Isaad, J. Vanillin, a potential carrier for low temperature dyeing of polyester fabrics. *J. Cleaner Prod.* **2013**, *43*, 20.

(14) Chiappe, C.; Capraro, D.; Conte, V.; Pieraccini, D. Stereoselective halogenations of alkenes and alkynes in ionic liquids. *Org. Lett.* **2001**, *3*, 1061.

(15) Cevasco, G.; Chiappe, C. Are ionic liquids a proper solution to current environmental challenges? *Green Chem.* **2014**, *16*, 2375.

(16) Chiappe, C.; Pieraccini, D. Ionic liquids: solvent properties and organic reactivity. *J. Phys. Org. Chem.* **2005**, *18*, 275.

(17) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*, 2nd ed; Wiley-VCH: Weinheim, Germany, 2008.

(18) Hallett, J. P.; Welton, T. Room-temperature ionic liquids: solvents for synthesis and catalysis. 2. *Chem. Rev.* **2011**, *111*, 3508.

(19) Ohno, H. *Electrochemical Aspects of Ionic Liquids*, 2nd ed; John Wiley &Sons: Hoboken, NJ, 2011.

(20) Earle M. J.; Seddon, K. R. WO Patent 024766, 2009.

(21) Yuan, J.; Wang, Q.; Fan, X. Dyeing behaviors of ionic liquid treated wool. *J. Appl. Polym. Sci.* **2010**, *117*, 2278.

(22) Chang, D. H. *Adv. Mater. Res.* **2011**, *331*, 253.

(23) Wang, H.; Gurau, G.; Rogers, R. D. Ionic liquid processing of cellulose. *Chem. Soc. Rev.* **2012**, *41*, 1519.

(24) Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. Dissolution of cellulose with ionic liquids. *J. Am. Chem. Soc.* **2002**, *124*, 4974.

(25) Idris, A.; Vijayaraghavan, R.; Patti, A. F.; MacFarlane, D. R. Distillable Protic Ionic Liquids for Keratin Dissolution and Recovery. *ACS Sustainable Chem. Eng.* **2014**, *2*, 1888.

(26) Ferreira, A. M.; Coutinho, J. A. P.; Fernandes, A. M.; Freire, M. G. Complete removal of textile dyes from aqueous media using ionic-liquid-based aqueous two-phase systems. *Sep. Purif. Technol.* **2014**, *128*, 58.

(27) Sekar, S.; Surianarayanan, M.; Ranganathan, V.; MacFarlane, D. R.; Mandal, A. B. Choline-based ionic liquids-enhanced biodegradation of azo dyes. *Environ. Sci. Technol.* **2012**, *46*, 4902.

(28) Lehocký, M.; Mráček, A. Improvement of dye adsorption on synthetic polyester ¯bers by low temperature plasma pretreatment. *Czech. J. Phys.* **2006**, *56*, B1277.

(29) Fletcher, K. *Sustainable Fashion and Textiles: Design Journeys*; Routledge: New York, 2014.

(30) Bruzzone, S.; Chiappe, C.; Focardi, S. E.; Pretti, C.; Renzi, M. Theoretical descriptor for the correlation of aquatic toxicity of ionic liquids by quantitative structure−toxicity relationships. *Chem. Eng. J.* **2011**, *175*, 17.

(31) Kwok, W. Y.; Xin, J. H.; Chong, T. F. *Res. J. Text. Appar.* **1999**, *3*, 9.

(32) Pretti, C.; Chiappe, C.; Baldetti, I.; Brunini, S.; Monni, G.; Intorre, L. Acute toxicity of ionic liquids for three freshwater

DOI: 10.1021/acssuschemeng.5b00578
ACS Sustainable Chem. Eng. 2015, 3, 2303−2308

organisms: Pseudokirchneriella subcapitata, Daphnia magna and Danio rerio. *Ecotoxicol. Environ. Saf.* **2009**, *72*, 1170.
(33) Bini, R.; Bortolini, O.; Chiappe, C.; Pieraccini, D.; Siciliano, T. *J. Phys. Chem. B* **2007**, *111*, 598.

DOI: 10.1021/acssuschemeng.5b00578
ACS Sustainable Chem. Eng. 2015, 3, 2303−2308