Upgrading biomass wastes in chemical technology. Humic acid-like matter isolated from compost as chemical auxiliary for textile dyeing

Piero Savarino, Enzo Montoneri,* Miriam Biasizzo, Pierluigi Quagliotto, Guido Viscardi and Vittorio Boffa

Dipartimento di Chimica Generale ed Organica Applicata, Università di Torino, C. M. D'Azeglio 48, 10125 Torino, Italy

Abstract

BACKGROUND: In the context of the modern concern regarding rapid consumption and low availability of fossil sources of energy and chemicals, urban and agro-industrial sources of chemicals represent interesting environmentally friendly alternatives. A recent paper has shown that a humic acid-like material extracted from urban and green wastes compost exhibits very good surfactant properties. A large number of technological applications could possibly use this material as a chemical auxiliary. This paper reports on the performance of the material as a chemical auxiliary in textile dyeing.

RESULTS: The compost-isolated humic acid-like bio-surfactant is shown to perform in nylon 6 microfiber dyeing by water soluble and insoluble dyes as well as and more conveniently than commercial sodium dodecylsulfate (SDS) and sodium dodecylbenzenesulfonate (SDBS). With both types of dye the bio-surfactant allows the same quality of dyed product as the synthetic surfactants do, but at lower additive concentration. From process cost and environmental impact points of view, the bio-surfactant has the advantages of operating at much lower additive concentrations and should be available at significantly lower cost than the synthetic surfactants.

CONCLUSION: The results suggest that biomass wastes may be a low cost renewable source of chemicals with friendly environmental impact. Such a perspective implies economic and environmental benefits deriving from a new waste management technology that considers biomass waste as a source of chemicals, and from lower oil consumption in the manufacture of synthetic surfactants.
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Keywords: bio-surfactant; textile dyeing; humic acids; biomass

INTRODUCTION

The progressive increase in environmental awareness and in petroleum cost has raised the issue of renewable versus non-renewable sources of energy and chemicals. In this context, the development of new materials, techniques and processes aimed at exploiting renewable sources with a low environmental impact relies greatly on lignocellulosic materials, which contain the two most abundant organic compounds present in nature: lignin and cellulose. Thus, the valorization of wood components constitutes a new frontier of economically sustainable and environmentally friendly processes. Wood components are in fact a readily renewable source of great importance in the development of new chemical and biotechnological procedures for the production of commodities, specialties, fine chemicals and fuels. Plants and vegetables are the main sources of lignin and cellulose, and contain also a wide variety of other chemical compounds. On a quantitative basis these sources could be used to meet most of the modern energy demand and to provide a large variety of chemicals. However, they suffer from being high entropy systems since they are spread over relatively large land surfaces and contain mostly water. Also, cultivation of plants for chemical purposes would reduce the available land for food production.

Waste from urban activities and agro-industrial productions are also an important source of lignocellulosic materials. Composted waste, in particular, are interesting low entropy systems. They are available in a confined space and contain less water (35–55%) and more organic matter (26–50%) than fresh vegetable matter.[1,2] Composting is carried out nowadays in public and private facilities throughout the world.[2–4] This process is run after separate source collection of wastes and does not demand any external energy

supply. It occurs with heat release due to micro-biological reactions leading to some mineralization of organic C and N and to chemical modifications of the remaining organic residue. Compared to the starting biomass waste, the composted waste is generally characterized by a lower content of proteins and polysaccharides, and by a relatively higher concentration of lignin material.[5] Changes also involve chemical identities. Native lignin is modified to lignin-humus. The latter material, although not well defined, is usually characterized by its aliphatic/aromatic C ratio and by its content of carboxylic and phenolic functional groups. Lignin-humus contains an alkali soluble fraction (humic and fulvic acids)[6,7] and an insoluble fraction (humin).[8] Structural information allows forecasting good properties for these compounds as complexing agents, ion exchangers and anionic surfactants. Humic and fulvic acids, and humin are also constituents of soil[9] and the organic matter in natural waters.[10] For these reasons, composts are currently considered for soil fertilization and soil amending purposes.[2–4,6,7,11] It is unfortunate that in spite of the potential of these waste components for uses in chemical technology, compost as a source of chemicals to be used in place of synthetic chemicals has received almost no attention so far.

To our knowledge very few papers considering compost for uses other than agriculture have been published in the literature. In 1993 Marzotto *et al.* reported the performance of compost as an ion exchanger for sea water uranium extraction.[12] In 2003 Montoneri *et al.*[13–15] reported the sulfonation of humin isolated from compost to yield polyalkylphenyl-sulphonic acid with acid groups of variable strength, and proposed these compounds for the same chemical uses as for commercial lignosulphonates isolated from the exhausted liquor of pulp and paper production processes. Most recently, two other papers have been published on the use of the water-soluble fractions of composts for the photodegradation of organic pollutants in solar light,[16] and on the surfactant properties of a humic acid-like (cHAL) compound[1] isolated from food and green waste compost. The data obtained for cHAL suggest that this compound, by its anionic surfactant structural features (Fig. 1) and properties, might perform as a chemical auxiliary in many technological applications where synthetic surfactants are used. The cHAL critical micelle concentration (cmc) = $0.403\,\mathrm{g\,L^{-1}}$ and surface tension at cmc (γ_{cmc}) = $36.1\,\mathrm{mN\,m^{-1}}$ in aqueous solution at pH 7 appeared quite remarkable when compared with values for major commercial anionic surfactans.[1] Also, a phenanthrene (PHE) solubility study[1] pointed out the capacity of cHAL to incorporate large hydrophobic molecules into its micellar core, without change of its cmc value determined in the absence of other organic molecules, and to enhance the hydrocarbon water solubility more than other major commercial surfactants.
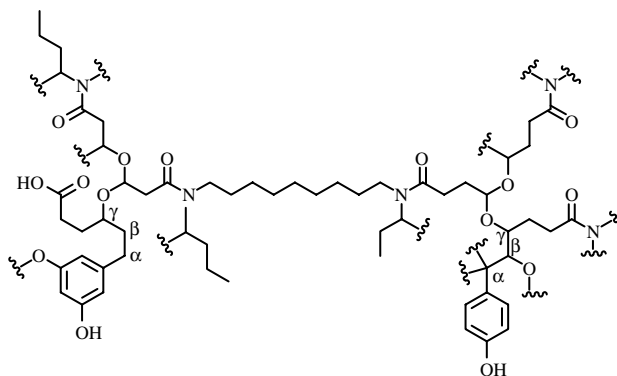

Figure 1. Proposed molecular fragment for cHAL.[1] H bonded to C omitted; sinusoidal bold lines indicate other fragments C, O, N atoms.

The property of a surfactant to enhance the water solubility of hydrophobic molecules gives the potential for an enormous number of technological applications. Given the widespread use of surfactants in modern life and their market value,[17] the likely economic benefit of waste treatment processes derived from the valorization of biowaste organic matter in the chemical market is sufficient incentive to continue a project to upgrade compost as a source of chemical auxiliaries for chemical technology. In this context, the fairest way to assess the value of compost biosurfactants is to directly compare the performance of the biosurfactants with the performance of major commercial synthetic surfactants in a typical application. Here the performance of the cHAL compound when used in textile dyeing is compared with the performance of two major commercial anionic synthetic surfactants, sodium dodecyl-sulfate (SDS) and sodium dodecylbenzenesulphonate (SDBS).

Fabric dyeing is quite challenging for chemists in terms of product quality, process cost and from the environmental point of view due the disposal of high process effluent volumes.[18–20] Important parameters for process energy and material cost and for handling the exhausted bath are the liquor to good volume/weight (V/w) ratio (LGR), and the type and concentration of the dye and of the additive in the dyeing bath. The aim in the present work was to determine whether the compost-derived cHAL surfactant might perform as well as or better than the two synthetic surfactants in textile dyeing. For this purpose, microfiber nylon 6 was chosen since this fabric, because of its morphological specification, is known to yield bad colour uniformity and is therefore particularly challenging for additives. As two main types of dye are generally used in this technology, i.e. water soluble and water insoluble, and these dyes act using different mechanisms, both dye types were included in the experimental plan.

It has already been pointed out that the range of potential applications of surfactants is very wide and multidisciplinary. Highly technical specialized

knowledge is required nowadays for the development of new products from laboratory to commercial scale. It is therefore stressed that in this work two typical textile dyes have been chosen as case studies, not as problems to solve, but rather as grounds for assessing the value of the new cHAL biosurfactant relative to that of commercially established SDS and SDBS. The specific aims in this work were twofold. First, to demonstrate that cHAL might perform as well as or better than the two commercial surfactants under the same experimental conditions. Second, to stimulate specialists in diversified technological applications to join in with efforts for assessing the level at which the organic fraction of municipal solid wastes could be a real alternative to synthetic commercial chemical auxiliaries, and to develop new processes and products from renewable sources.

EXPERIMENTAL

Microfiber nylon 6 supplied by Sniafibre (Italy) had the following specification: filling dtex 88/72, warp detx 167/30. Dyeing tests were carried out on a Linitest apparatus (Hanau, Germany) according to a previously reported procedure, at variable LGR and at variable pH using 0.1 mol L^{-1} acetate buffer at pH 4–5.4, and 0.1 mol L^{-1} Tris buffer at pH 7. The same procedure[19] was used for dyeing with the soluble and the insoluble dye. Previously wetted fabric was introduced into the dyebath at $40\,^\circ$C and the temperature raised to $80\,^\circ$C over 20 min and maintained for 1 h. The dyed fiber was then removed, rinsed, washed at $40\,^\circ$C with water solution containing soap ($2.5\,g\,L^{-1}$) and sodium carbonate ($2.5\,g\,L^{-1}$) at LGR 200:1, rinsed again and dried at room temperature. To evaluate colour uniformity tristimulous colorimetry was used.[19] Colour measurements were carried out with a Minolta CR200 instrument. This apparatus allows the determination of colour intensity (ΔE) and colour uniformity ($\sigma \Delta E$). The parameter ΔE is the mean of nine determinations of the colour difference between the dyed and undyed fabric performed over nine different sites of the specimen, while $\sigma \Delta E$ is the standard deviation around the mean ΔE value.

The water soluble dye, here named dye **1,** was a Clariant Chemical Company (Mutenz, Switzerland) product. This dye was used at LGR 5:1 or 10:1, pH 4 and 5.4 and 1% depth (percentage of dye related to the fiber weight). The water insoluble dye, here called dye **2,** was prepared as previously reported.[20] This dye was used at LGR 20, pH 5.4 and 7 and 1% depth. Dye dispersion was helped either by bath sonication using Vibra-cell 120 W apparatus or by mechanical IKA Ultra Turrax T25 dispersion tool (both supplied by LAISS Apparecchi Scientifici, Torino, Italy). The cHAL bio-surfactant was supplied by the Dipartimento di Produzione Vegetale of the Università di Milano (Italy). This material was isolated from a 15 day aged food residues–green waste compost by alkaline extraction followed by precipitation at pH <1.5 as previously reported.[1] Commercial SDS and SBDS were purchased from sigma Aldrich (St Louis, MO, USA).

RESULTS AND DISCUSSION
Technical problems and parameters in dyeing microfibers

Achieving good colour uniformity when dyeing microfibers is particularly challenging.[21] The polymeric monofilaments in ultra-fine fibers are only a few micrometers thick and give fabrics that are very light, have high texture density, and are porous to vapour but waterproof. These desirable properties come with the disadvantages of an enhanced specific surface. Compared to conventional fibers, ultra-fine fibers have a much greater surface area for interaction with dyes. This causes less uniform dyeing and an increased colorant demand to give comparable colour yield. While the higher dye uptake requirement may be remedied by increasing the dyeing depth (i.e. the percentage of dye related to the fibre weight), the achievement of good colour uniformity is accomplished using suitable additives. These compounds are supposed to act in different ways depending on the nature and solubility of the dye. As representatives of the two main types of dyes used in fabric dyeing technology, the water soluble dye **1** shown in Fig. 2 and the water insoluble dye **2** shown in Fig. 3, were selected. The former is an excellent test dye because of its tendency to give non-uniform dyeing, in particular at low temperature ($80\,^\circ$C) and when its uptake rate is fast. Optimized dyeing with the latter dye requires increasing the dye water solubility. The rationale for using cHAL and the synthetic surfactants SDS and SDBS in dyeing tests was based on the following different mechanisms by which the two types of dye are expected to act with respect to the polyamide fiber.
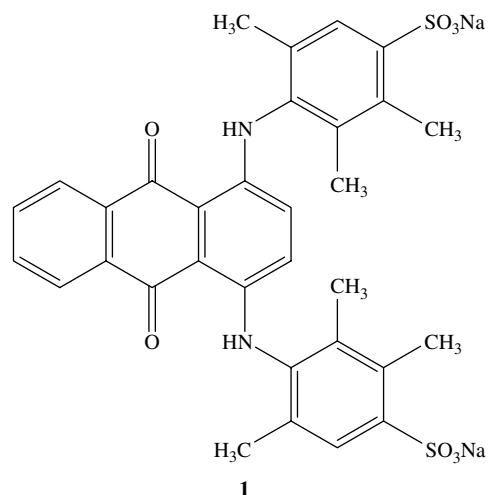

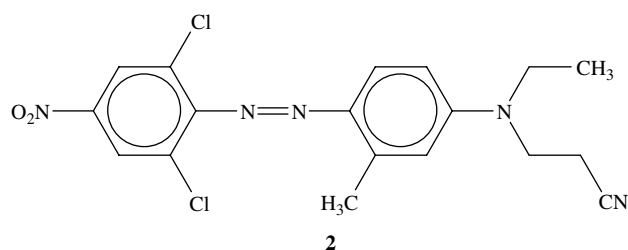**Figure 2.** Chemical structure of water soluble dye.

**Figure 3.** Chemical structure of water insoluble dispersive dye.

Dyeing with water soluble dye 1

Dyeing tests with sulfonated soluble dyes (Dye-SO$_3^-$), such as dye **1**, are usually carried out in acidic conditions.[21] The experiment conditions were pH 4 and 5.4 using acetate buffer. Under these conditions, the terminal NH$_2$ groups of the nylon fabric are protonated (Nyl-NH$_3^+$), and the dye uptake by the fabric occurs by the exchange reaction[22]

$$\text{Nyl-NH}_3^+\text{AcO}^- + \text{Dye-SO}_3^- \rightleftharpoons$$
$$\text{Nyl-NH}_3^+\text{Dye-SO}_3^- + \text{AcO}^- \quad (1)$$
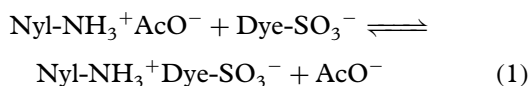
The fast rate of this dye uptake reaction may cause non-homogeneous dye distribution in the fabric solid phase.

The two sulfonated anionic surfactants are supposed to control the rate of the dye uptake in two ways. The surfactant anions (X-SO$_3^-$, X = RO for SDS and R-Ar for SDBS) may compete with the dye anion in the interaction with the nylon NH$_3^+$ sites, as in the following reaction:

$$\text{Nyl-NH}_3^+\text{AcO}^- + \text{X-SO}_3^- \rightleftharpoons$$
$$\text{Nyl-NH}_3^+\text{X-SO}_3^- + \text{AcO}^- \quad (2)$$
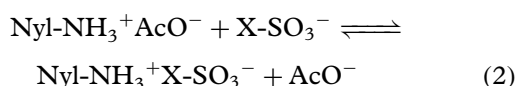
and therefore contribute to controlling the rate and the yield of the dye uptake by the fabric.

The second mechanism is based on the capacity of the surfactants molecules in solution to aggregate in micellar form:[23,24]

$$\text{n X-SO}_3^- \rightleftharpoons (\text{XSO}_3^-)_n \quad (3)$$

In this situation, diffusion of the dye into the surfactant's micellar core and formation of a complex by hydrophobic and/or polar interactions may occur:

$$\text{Dye-SO}_3^- + (\text{XSO}_3^-)_n \rightleftharpoons$$
$$[\text{Dye-SO}_3^- \cdots (\text{XSO}_3^-)_n] \quad (4)$$
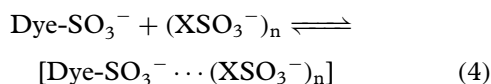
The complexation equilibrium in reaction (4) would allow control of the free dye concentration in solution and, therefore, of the rate and yield of dye uptake by the fabric according to reaction 1. With the strong acid dye **1**, it should, however, be considered that the mechanism involving reactions (1) and (2) is more likely than that involving reactions (1) and (4). Polar molecules are indeed known to hinder micellization of

anionic surfactants such as SDBS,[25] since they tend to interact with the surfactant polar groups, to substitute the water molecules at the outer micellar surface, and thus to increase the micelles solvation and decrease their aggregation number. By this interaction, dye **1** molecules would be unlikely to enter the interior of the micelles as required by reaction (4).

With the weakly acidic cHAL (Fig. 1) as additive in the dyeing bath at pH 4–5.4, competition between the surfactant anion and the dye anion for the nylon terminal NH$_3^+$ sites is less likely to occur since the concentration of the former is expected to be quite low. On the other hand, cHAL has been shown to yield micelles at lower critical micellar concentration (cmc) than the other two synthetic surfactants:[1]

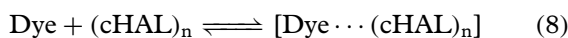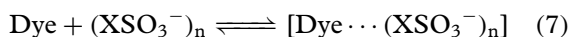$$\text{n cHAL} \rightleftharpoons (\text{cHAL})_n \quad (5)$$

Its chemical structure also contains aromatic rings. cHAL may, therefore, be expected to complex and include the dye into its micellar core as well as or better than the other two synthetic surfactants:

$$\text{Dye-SO}_3^- + (\text{cHAL})_n \rightleftharpoons$$
$$[\text{Dye-SO}_3^- \cdots (\text{cHAL})_n] \quad (6)$$
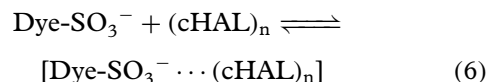
Dyeing with disperse dye 2

Uptake of dyes having poor water solubility by nylon 6 microfiber may occur by hydrophobic and hydrophilic interaction between the fabric and the dye.[21,22] However, the main problem is dye solubility. Poor water solubility of the dye causes non-homogenous distribution of dye throughout the fabric solid phase and the accumulation of dye preferentially on fiber surfaces. Under the specified operating conditions at pH 5.4 and 7, enhanced water solubility of dye **2** (Dye) by the above surfactants may occur by dye diffusion into the surfactants micellar core:

$$\text{Dye} + (\text{XSO}_3^-)_n \rightleftharpoons [\text{Dye} \cdots (\text{XSO}_3^-)_n] \quad (7)$$
$$\text{Dye} + (\text{cHAL})_n \rightleftharpoons [\text{Dye} \cdots (\text{cHAL})_n] \quad (8)$$

Therefore, the equilibria (7) or (8) are expected to control mainly the rate and yield of dye uptake by the fiber. Stronger interaction of the dye with cHAL than with the other two synthetic surfactants is expected, based on experimental results of previous work.[1] First, cHAL has been found capable of incorporating large molecules such as polycyclic aromatic hydrocarbon (PAH) molecules, into its micellar core, without change of its cmc value determined in the absence of other organic molecules. Second, cHAL has been shown to enhance PAH solubility significantly more than SBDS. These results seem to reflect the more polar nature of SDBS and the looser packing of the micelles due the coulombic repulsion between them.[25]

In controlling the uptake of both dye types by the fabric, pH under the specified experimental conditions is expected to be a fundamental parameter since it

influences both the ionization of acid groups and the cmc values[26] of the species involved.

Performance of surfactants when microfiber dyeing with water soluble dye

To determine the suitability of cHAL as an additive in dyeing nylon 6 microfiber with the water soluble dye **1** by comparison with SDS and SDBS, dyeing tests were performed in the absence and in the presence of the additives at the same experimental temperature (80 °C), dyeing time (1 h), pH (4 and 5.4) and LGR (5 and 10 V/w). The concentration of the additives (g L^{-1}) were chosen to include the published cmc value of each surfactant. These cmc values are 0.403 g L^{-1} for cHAL,[1] 2.33 g L^{-1} for SDS[23] and 0.7–1.4 g L^{-1} for SDBS,[24,25,27,28] all measured at pH 7. The indicators used for dyeing efficiency were the colour intensity (ΔE) and the colour uniformity ($\sigma \Delta E$), which were defined above. The results for each additive and parameter set are reported in Table 1 and Fig. 4. Analysis of the data in Table 1 indicates that the most statistically significant effect of the surfactants is on colour uniformity rather than on the colour intensity. The plots of $\sigma \Delta E$ values for SDS and SDBS (Fig. 4) show a clear trend of improving colour uniformity with increasing additive concentration at each pair of pH and LGR values. This trend seems consistent with control of the rate of fabric dye uptake reaction 1 by reactions 2 and/or 4. No definite pH effect can be picked out for both surfactants and no LGR effect is evident with SDS. In contrast, SDBS performs better at 10 LGR than at 5 LGR. For cHAL, the $\sigma \Delta E$ values do not show any definite trend of colour uniformity versus bio-surfactant concentration. At pH 4, no significant differences are seen in fabric colour homogeneity between the dyeing test performed in

the presence of cHAL and in the absence of any additive. Furthermore, at this pH the colour intensity in the presence of cHAL (Table 1) is lower than in the absence of additives. This means lower dye uptake in the presence of cHAL at pH 4, and indicates that the dye is strongly bonded to the bio-surfactant. An improvement in colour homogeneity in the presence of cHAL is observed at pH 5.4. For the bio-surfactant, the plot in Fig. 4 and the data in Table 1 show that over a narrow range of experimental conditions, i.e. 0.8 g L^{-1}, pH 5.4 and LGR 5–10, cHAL yields very good colour uniformity and colour intensity, whereas at lower and higher cHAL concentrations, both colour intensity and uniformity worsen. This behaviour suggests that the dye–cHAL interaction is different from that hypothesized for the two synthetic surfactants. Ionization of the weak acid COOH groups in cHAL is likely to be influenced by the pH change more than those of the XSO_3H groups, and therefore pH will influence, to a greater extent, the behaviour of the compost-isolated humic acid-like biosurfactant (cHAL) than that of the two synthetic surfactants. For soil humic acids,[25] cmc and ionization measurements have shown a continuous decrease in COOH ionization from 100% at pH 7, to 62% at pH 5.5 and to 31% at pH 4, in conjunction with an 80% decrease in cmc from the highest (7) to the lowest (4) pH value. Supposing a similar behaviour for the cHAL material, a lower cmc value at pH 4 than at pH 5.4 implies a higher number of micelles in solution by the equilibrium depicted in reaction 5 shifting to the right at the lower pH value. Consequently, the equilibrium in reaction 6 would also be shifted to the right. Thus, the free dye concentration availability for uptake by the fabric would be lower at pH 4 than at pH 5.4.
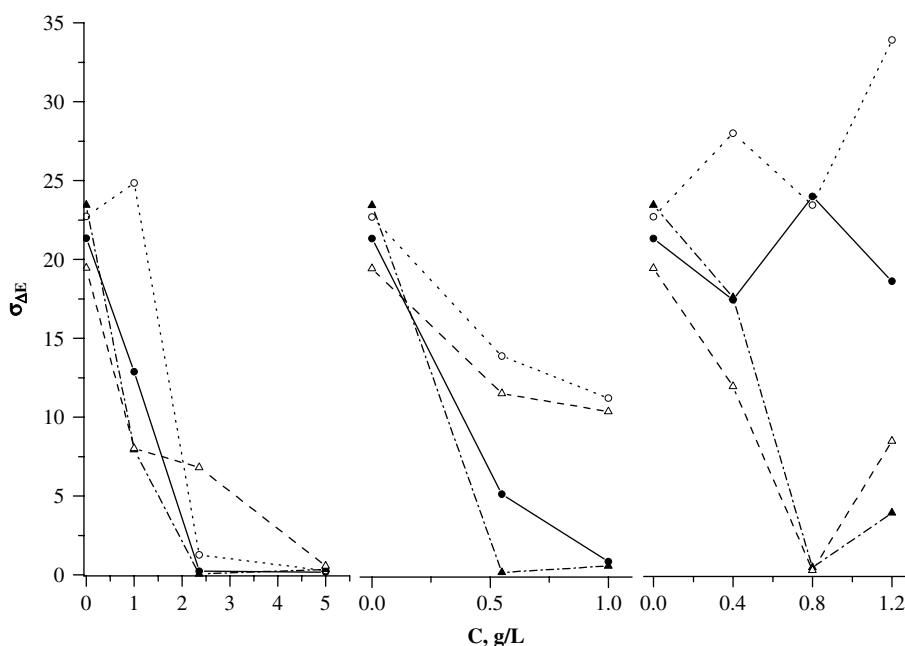

Figure 4. Colour homogeneity ($\sigma \Delta E$) versus concentration (C, g L^{-1}) of SDS ($0 \leq C \leq 5$), SDBS ($0 \leq C \leq 1$) and cHAL ($0 \leq C \leq 1.2$) for nylon 6 microfiber dyed by dye **1** under the following conditions: ●pH 4, LGR 10:1;○ pH 4, LGR 5:1; ▲pH 5.4, LGR 10:1; △pH 5.4, LGR 5:1.

Table 1. Colour intensity (ΔE) and uniformity ($\sigma \Delta E$) of nylon 6 microfiber dyed by dye **1** at 80 °C and 1 h dyeing time in the presence of cHAL, SDS and SDBS at variable additive concentration (C, g L^{-1}), pH and liquor to good ratio (*LGR*, V/w)

Additive	pH	*LGR*, V/w	C, g L^{-1}	ΔE	$\sigma \Delta E^{\text{a}}$
None	4	10		65.66	21.35 g
	4	5		63.46	22.72 g
	5.4	10		65.65	23.45 g
	5.4	5		69.35	19.45 g
SDBS	4	10	0.55	69.92	5.19 e,f
	4	5	0.55	66.79	13.93 f, g
	4	10	1.00	78.63	0.92 c,d
	4	5	1.00	69.80	11.26 f,g
	5.4	10	0.55	79.93	0.25 b,c
	5.4	5	0.55	74.39	11.56 f,g
	5.4	10	1.00	77.80	0.64 c,d
	5.4	5	1.00	74.45	10.41 f,g
SDS	4	10	1.00	62.63	12.89 f,g
	4	5	1.00	60.84	24.85 g
	4	10	2.36	60.18	0.24 b, c
	4	5	2.36	78.15	1.28 d
	4	10	5.00	62.51	0.19 b
	4	5	5.00	64.20	0.28 b, c
	5.4	10	1.00	69.66	7.95 f
	5.4	5	1.00	72.13	8.02 f
	5.4	10	2.36	68.02	0.07 a
	5.4	5	2.36	74.64	6.82 f
	5.4	10	5.00	55.69	0.35 b, c
	5.4	5	5.00	67.81	0.57 c
cHAL	4	10	0.40	59.72	17.46 g
	4	5	0.40	40.07	28.01 g
	4	10	0.80	59.66	24.01 g
	4	5	0.80	60.42	23.54 g
	4	10	1.20	50.75	18.64 g
	4	5	1.20	48.31	33.91 g
	5.4	10	0.40	62.73	17.62 g
	5.4	5	0.40	69.33	11.98 f,g
	5.4	10	0.80	77.41	0.51 c
	5.4	5	0.80	79.26	0.33 b, c
	5.4	10	1.20	76.83	3.98 e,f
	5.4	5	1.20	75.90	8.53 f,g

$^{\text{a}}$ Letters next to figures indicate variance inequalities by F test at 95% confidence level:[29] i.e., a < b < c < d < e < f < g.

The experimental data do not allow an assessment of which dye–surfactant interaction mechanism is active. From the practical point of view, however, the data indicate that under specific experimental conditions cHAL yields colour intensity and uniformity at the levels shown by the other two additives. Based on F test statistical significance,[29] the order of decreasing colour uniformity for $0.07 \leq \sigma \Delta E \leq 0.92$ is SDS (2.36 g L^{-1}, pH 5.4, LGR 10) > SDS (2.36–5 g L^{-1}, pH 4, LGR 10) = SDBS (0.55 g L^{-1}, pH 5.4, LGR 10) > cHAL (0.8 g L^{-1}, pH 5.4, LGR 5) = SDS (5 g L^{-1}, pH 4–5.4, LGR 5–10) > SDBS (1 g L^{-1}, pH 5.4, LGR 10) = SDBS (1 g L^{-1}, pH 4, LGR 10). It may readily be observed that among the range of experimental conditions yielding relatively good colour uniformity ($\sigma \Delta E \leq 0.92$), cHAL offers the most attractive experimental conditions, being able to yield high colour intensity ($\Delta E = 79.26$) coupled

with very good colour uniformity ($\sigma \Delta E = 0.33$) at low additive concentration (0.8 g L^{-1}) and at the lower LGR value (5). Similar performance is attained with the other two surfactants, but either at higher LGR value (10, SDBS) or at higher additive concentration (2.46 g L^{-1}, SDS). These experimental results provide interesting indications (from the industrial point of view) of the reduction in costs consequent to savings in water, energy for the heating baths and volumes of effluent to be treated.[19] Thus, although cHAL yields product quality equal to that of the two synthetic surfactants, operation with cHAL is more favourable, both from process cost and environmental impact points of view. Operation with the synthetic surfactants under conditions indicated by the experimental data to obtain optimum product quality would pose serious problems. These are related not only to the high volume of exhausted effluent to be treated and/or to the high amount of surfactant to be used, but also to the low biodegradation rate of the synthetic surfactants.[28]

Performance of the surfactants when microfiber dyeing with water insoluble dye

To determine the suitability of cHAL as an additive in dyeing nylon 6 microfiber with the water insoluble dye **2,** in comparison with SDS and SDBS, dyeing tests were performed in the absence and in the presence of the additives at the same experimental temperature (80 °C), dyeing time (1 h) and LGR (20), but at two pH levels (5.4 and 7) and two different bath mixing conditions, i.e. with sonication and with mechanical dispersion. The purpose of introducing different bath mixing conditions was to find which one gave the best dye solubility rate in the presence of each surfactant. The concentrations (g L^{-1}) of the additives were chosen to include the above reported cmc values of each surfactant. The indicators of dyeing efficiency were the same as for the dyeing tests with the soluble dye, i.e. ΔE and $\sigma \Delta E$. The results for each additive and parameter set are reported in Table 2 and Figs 5 and 6. With the water insoluble dye, the surfactants significantly affected both the ΔE and $\sigma \Delta E$ indicators. Of the three dyeing bath parameters investigated for each additive, i.e. the surfactant concentration (C), pH and the bath mixing conditions, the concentration of the additive showed the most definite and significant effects on product quality. Generally, the colour uniformity improved upon increasing the additive concentration (Fig. 6), except in the cases of SDBS at pH 5.4 and 7 with bath sonication, and cHAL at pH 5.4 with bath sonication. In these cases, when increasing C above the minimum experimental value either no effect or a random effect was obtained. The effect of C on colour intensity (Fig. 6) presented interesting features. This varied depending on the additive. For SDS the colour intensity increased only for $C \geq 2.36$, whereas at lower C no effect was observed relative to dyeing in the absence of additive. For the other two additives, the
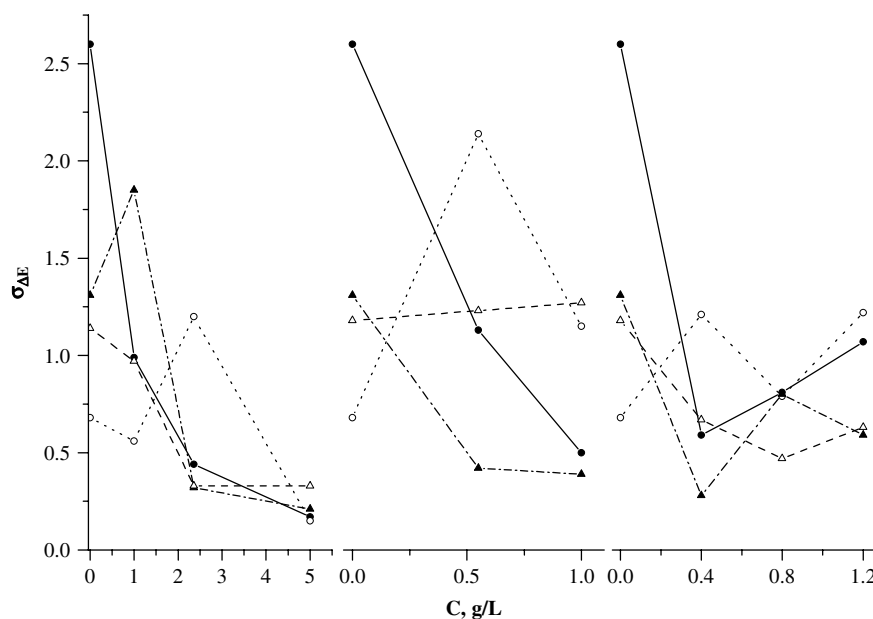
Figure 5. Colour homogeneity ($\sigma \Delta E$) versus concentration (C, g L^{-1}) of SDS ($0 \leq C \leq 5$), SDBS ($0 \leq C \leq 1$) and cHAL ($0 \leq C \leq 1.2$) for nylon 6 microfiber dyed by dye **2** under the following conditions: ● pH 5.4, mechanical dispersion; ○ pH 5.4, sonication; ▲ pH 7, mechanical dispersion; △ pH 7, sonication.

Figure 6. Colour intensity (ΔE) versus concentration (C, g L^{-1}) of SDS ($0 \leq C \leq 5$), SDBS ($0 \leq C \leq 1$) and cHAL ($0 \leq C \leq 1.2$) for nylon 6 microfiber dyed by dye **2** under the following conditions: ● pH 5.4, mechanical dispersion; ○ pH 5.4, sonication; ▲ pH 7, mechanical dispersion; △ pH 7, sonication.
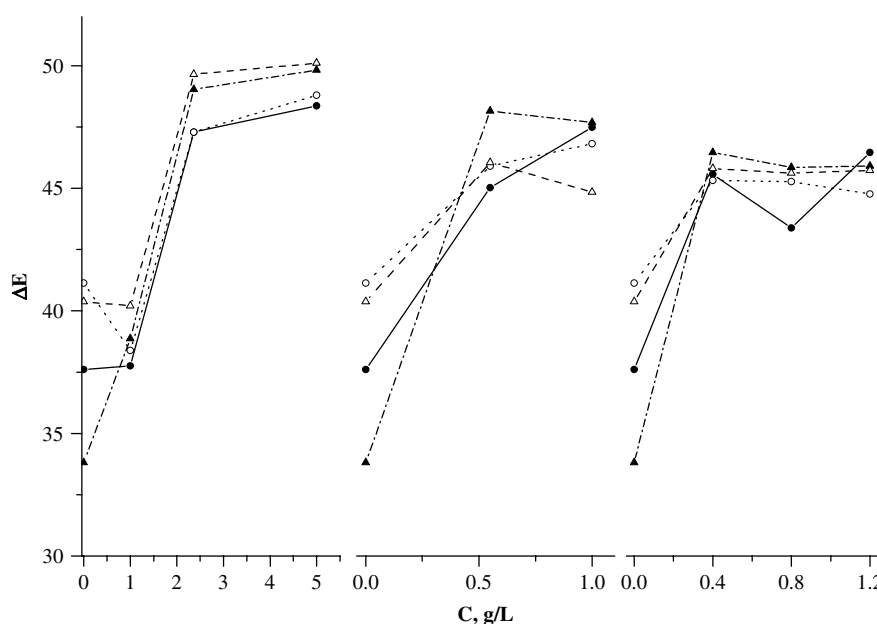
improvement of colour intensity was readily evident even at the lowest investigated C value, i.e. $0.55\,\mathrm{g\,L}^{-1}$ for SDBS and $0.4\,\mathrm{g\,L}^{-1}$ for cHAL. For these additives, the experimental concentration range starts at the cmc value and ends at 2 or 3× cmc values, while for SDS the experimental concentration range starts below the cmc value. Thus, it appears that with each additive a concentration value corresponding to the cmc value or greater is necessary to obtain improvement in the product colour intensity. This appears consistent with enhancement of the dye water solubility above the additive cmc value. The water solubility of the dye

in the presence of SDBS and cHAL at additive concentration below or equal to $1\,\mathrm{g\,L}^{-1}$ may result in better performance than in the presence of SDS at the same concentration either because of the lower cmc value of the former two additives and/or because of the presence of aromatic rings both in SDBS and in cHAL.

No definite pH effect could be assessed in the experimental range investigated. The best colour uniformity attained was $0.15 \leq \sigma \Delta E \leq 0.31$. Based on an F-test at 95% confidence level, $\sigma \Delta E$ values in this range are not statistically different from each other.

Table 2. Colour intensity (ΔE) and uniformity ($\sigma \Delta E$) of nylon 6 microfiber dyed by the disperse dye **2** at 80 °C, 1 h dyeing time and 20 V/w liquor/good ratio in the presence of cHAL, SDS and SDBS at variable additive concentration (C, g L^{-1}), pH and bath mixing (BM) conditions

Additive, pH, BM[a]	C	ΔE	$\sigma \Delta E$[b]
SDS, pH 5.4, MD	0.00	37.61	2.60 d,e
	1.00	37.75	0.99 c,d
	2.36	47.29	0.44 b,c
	5.00	48.36	0.17 a,b
SDS, pH 5.4, SN	0.00	41.13	0.68 c
	1.00	40.19	0.56 b,c
	2.36	47.29	1.20 c,d
	5.00	48.80	0.15 a
SDS, pH 7, MD	0.00	33.81	1.31 c,d
	1.00	35.87	1.85 d,e
	2.36	49.03	0.32 b
	5.00	49.82	0.21 a,b
SDS, pH 7, SN	0.00	40.38	1.18 c,d
	1.00	40.23	1.00 c,d
	2.36	49.65	0.33 b,c
	5.00	50.11	0.36 b,c
SDBS, pH 5.4, MD	0.00	37.61	2.60 d,e
	0.55	47.50	1.13 e
	1.00	45.02	0.50 b,c
SDBS, pH 5.4, SN	0.00	41.13	0.68 c
	0.55	45.90	2.14 d,e
	1.00	46.82	1.15 c,d
SDBS, pH 7, MD	0.00	33.81	1.31 c,d
	0.55	48.16	0.42 b,c
	1.00	47.68	0.39 b,c
SDBS, pH 7, SN	0.00	40.38	1.18 c,d
	0.55	46.05	1.23 c,d
	1.00	44.84	1.27 c,d
cHAL, pH 5.4, MD	0.00	37.61	2.60 d,e
	0.40	45.57	0.59 b,c
	0.80	43.48	0.81 c,d
	1.20	46.46	1.07 c,d
cHAL, pH 5.4, SN	0.00	41.13	0.68 c
	0.40	45.32	1.21 c,d
	0.80	45.27	0.79 c,d
	1.20	44.76	1.22 c,d
cHAL, pH 7, MD	0.00	33.81	1.31 c,d
	0.40	46.46	0.28 a,b
	0.80	45.85	0.80 c,d
	1.20	45.90	0.59 b,c
cHAL, pH 7, SN	0.00	40.38	1.18 c,d
	0.40	45.80	0.67 b,c
	0.80	45.62	0.47 b,c
	1.20	45.73	0.63 b,c

[a] Sonication (SN), mechanical dispersion (MD).
[b] Letters next to figures indicate variance inequalities by F test at 95% confidence level:[29] i.e., a < b < c < d < e < f < g.

These values were obtained in the presence of SDS at 5 g L^{-1} and pH 5.4, with either bath sonication or mechanical dispersion, and at pH 7 with mechanical dispersion, and also in the presence of cHAL at 0.4 g L^{-1} at pH 7 with mechanical dispersion. Under these conditions, the colour intensity in the presence of SDS was 48.36–49.82, whereas in the presence of cHAL it was slightly lower (ΔE 46.46).

CONCLUSIONS

It has been shown that a new bio-surfactant (cHAL) isolated from urban and green waste compost performs as well and more conveniently than two major commercial synthetic surfactants (SDS and SDBS) when dyeing a challenging textile specimen (microfiber nylon 6) with either soluble or insoluble dye. It is hypothesized that the colour homogeneity and intensity in the two fabric–dye systems depends on the free dye concentration in solution, and that all three surfactants allow control of the free dye concentration, although by different interactions. In principle, in the hypothesized reactions 1–8, all reactions are likely to be influenced by pH. This parameter, however, has been found to influence the performance of cHAL only in the case of soluble dye. With water-soluble dye **1** in the 4–5.4 pH experimental range, the reactions 2–4 with SDS and SBDS appear not to be influenced by pH change, whereas the reactions 5 and 6 involving the weakly acidic cHAL are strongly influenced by the pH change. The results with cHAL suggest that in the presence of this additive there is an optimum free dye concentration in solution for best fabric colour uniformity and intensity: this was found to be 0.8 g L^{-1}L cHAL concentration and at pH 5.4. At other experimental pH levels and additive concentrations, the free dye solution concentration in the presence of cHAL is likely to be too low because of the higher number of micelles in solution, which causes the equilibria in reactions 5 and 6 to shift to the right. Although over a narrower experimental range than for the other two synthetic surfactants, cHAL yields very good colour uniformity coupled with high colour intensity at more convenient operating conditions than with the synthetic surfactants.

In dyeing trials of nylon 6 microfiber with the water insoluble dye **2**, surfactant concentration has been shown to be the main parameter correlating with the product quality. The data suggest that enhanced dye solubility occurs by diffusion of the dye into the surfactant's micellar core. Thus, the order of surfactant performance follows the surfactant capability to micellize. The cHAL bio-surfactant at 0.4 g L^{-1} has been shown to yield good colour intensity and the same colour uniformity as SDS at 5 g L^{-1}. From process cost and environmental impact points of view, cHAL has the advantages that this additive operates at much lower additive concentration and should be available at significantly lower cost than the synthetic SDS surfactant.

As to the main issue addressed by this work, i.e. compost matter being a potential source of chemicals, it is pointed out that the cHAL used was isolated from a mixture of food residues and public parks green waste that had previously been composted for 15 days.[1] Composting, however, yields a wide range of different products depending on the compost waste mix and the composting time. It is quite likely that by tuning the compost process, one could obtain other humic-like surfactant matter showing further

improvement of dyeing quality and process features. The idea to upgrade compost as a source of surfactants has, in principle, high economic value. As already pointed out, compost is currently proposed as a fertilizer, so that its current market value is not above 15 €/ton,[30] against a processing tipping fee of about 70 €/ton. Therefore, composting urban and vegetable residues has a net cost of about 55 €/ton. On the other hand, the current value of surfactants in the chemical market is around 1000–2000 €/ton.[31,32] In previous work[1] it was shown that cHAL may be extracted from compost with 12% w/w yield using currently available procedures. Assuming that cHAL could be placed in the surfactant chemical market at the same price as SDBS,[31] its sale price might be 1 €/kg. Thus, using compost as a source of bio-surfactants would raise the market value of this biomass waste to 120 €/ton, deriving from bio-surfactant sales only. More generally, it should be considered that urban and vegetable residues are only part of the total annual biomass waste flow. This includes several biomass categories such as field residues, animal manures, forestry residues, food packing/processing, municipal solid wastes, slaughter-house wastes, and sewage sludge. This wide variety of biomass waste is expected to contain a greater variety of bio-surfactants than is commercially available nowadays by chemical synthesis. These facts, coupled with the expected friendly environmental impact of bio-surfactants, and with the large use of surfactants in modern life, lead to the expectation of highly promising economic returns on new biomass waste treatment processes specifically developed to recycle products to the chemical market. Such proposals, encouraged by the results of this and previous work,[16] offer a worthwhile and intriguing scope for continued investigation of the performance of waste bio-surfactants in other applications, the assessment of product specifications and the optimization of processes for their isolation. The advantages of such new technology would not be limited to the likely economic return of new waste management processes, but would also involve savings in oil consumption for manufacturing synthetic surfactants.

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