

## HUMIC ACID-LIKE MATTER ISOLATED FROM GREEN URBAN WASTES. PART II: PERFORMANCE IN CHEMICAL AND ENVIRONMENTAL TECHNOLOGIES

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Novel uses of the organic fraction of municipal solid wastes for diversified technological applications are reported. A humic acid-like substance (cHAL2) isolated from green urban wastes was tested as a chemical auxiliary for fabric cleaning and dyeing, and as a catalyst for the photodegradation of dyes. The results illustrate the fact that biomass wastes can be an interesting source of products for the chemical market. Process and product development in this direction are likely to offer high economic and environmental benefits in a modern, more sustainable waste treatment strategy.

*Keywords:* Urban refuses; Compost; Biosurfactants; Detergents; Textile dyeing aids, Humic acids, Biomass; Biophotosensitizer; Photodegradation

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### INTRODUCTION

Very recently we have shown that compost is a rich source of humic-like substances with excellent surfactant properties, and suggested for these materials a range of potential applications in the chemical industry (Quagliotto et al. 2006). This work focused primarily on upgrading biomass wastes in chemical technology (Savarino et al. 2007). To this purpose we plan in the long range to isolate from biomass wastes and to establish structure-properties relationships for products to be recycled to the market as chemical auxiliaries. Such results seem achievable by building a data inventory, which at some point will make it possible to understand how the parameters characterizing the waste nature and the composting process influenced the structure and chemical properties of the isolated humic-like substances, and also to assess how much the source and the structural differences of these substances affected their performance in the proposed chemical technologies.

In this context, our previous papers (Quagliotto et al. 2006; Savarino et al. 2007) have reported the chemical structure, surfactant properties and performance in textile dyeing of a humic acid-like compound (cHAL) isolated from a mix of municipal solid and green wastes mix composted for 15 days. We wish now to report on a new humic acid-like compound (cHAL2), which was isolated from a different source and under different conditions: i.e., from green urban wastes and before composting. The isolated cHAL2 material, compared to cHAL, has shown some significant differences in chemical

structure and surfactant properties which have been reported in Part I of this work (Montoneri et al. 2008): i.e., relative to cHAL, cHAL2 has a higher content of aliphatic and of O-alkyl C atoms relative to aromatic, phenoxy and carboxy C atoms; also, the values for the critical micellar concentration ( $CMC = 0.97 \text{ g L}^{-1}$ ) and surface tension at the CMC ( $\gamma = 37.8 \text{ mN/m}$ ) of cHAL2 were higher than those for cHAL ( $CMC = 0.40 \text{ g L}^{-1}$  and  $\gamma = 36.1 \text{ mN/m}$ ). Also cHAL, compared to the two major synthetic commercial surfactants sodium dodecylsulfate (SDS) and sodium dodecylbenzenesulfonate (SDBS), was found to have quite remarkable surfactant properties (Quagliotto et al. 2006) and to perform as a chemical auxiliary for dyeing nylon 6 (Savarino et al. 2007) as well and more conveniently, we wish now to report on how the new cHAL2 biosurfactant compares with SDBS and SDS for its technological performance. For this purpose, three potential applications for these materials have been chosen as ground for comparison. The range of potential applications of surfactants, however, is very wide and multidisciplinary (Research and Markets 2007; Houston 2007). We are also aware that high tech specialized knowledge is required nowadays for the development of new products from laboratory to commercial scale. We wish therefore to stress that the case studies chosen in this work are not meant as problems to be solved, but rather as grounds for assessing the value of the cHAL2 biosurfactant relative to major commercially synthetic surfactants. Our specific aims in this work were two. Firstly, we wished to demonstrate that cHAL2 might perform as well as or better than the established commercial surfactants under the same experimental conditions. Secondly, we wished to stimulate specialists in diversified technological applications to joint our efforts for assessing which level the organic fraction of municipal solid wastes could be a real alternative to synthetic commercial chemical auxiliaries and for developing new processes and products from renewable sources.

## EXPERIMENTAL

The humic acid-like material (cHAL2) investigated in this work was isolated from ground urban green wastes, collected from the Amiat municipal plant in Torino, Italy. The wastes were treated 24 h at  $65 \text{ }^\circ\text{C}$  under  $\text{N}_2$  with aqueous  $0.1 \text{ mol}\cdot\text{L}^{-1}$  NaOH and  $0.1 \text{ mol}\cdot\text{L}^{-1}$   $\text{Na}_4\text{P}_2\text{O}_7$  at 1:50 w/v compost/solution ratio. The resulting suspension was cooled to room temperature and centrifuged at 6000 rpm for 20 minutes. The supernatant solution was separated. The solid residue was washed repeatedly with distilled water until the supernatant liquid phase was clear. All collected liquid fractions were mixed and acidified with 50 % sulfuric acid to  $\text{pH} < 1.5$ . The precipitated cHAL2 fraction was separated by centrifugation as above, washed with water until the final washing had neutral pH, vacuum dried at  $60 \text{ }^\circ\text{C}$ , and weighed. The extraction yield for the final product was 12 % of compost dry matter. This material was found to contain 7.47 % water, 91.60 % volatile solids, and 0.93 % ash by the weight losses measured after heating first at 105 and then at  $800 \text{ }^\circ\text{C}$ . Further characterization for cHAL2 was performed by elemental analysis, solid state  $^{13}\text{C}$  and solution  $^1\text{H}$  NMR spectroscopy, IR spectroscopy, molecular weight, and surface tension measurements. Analytical and instrumental details, as well as the results of these measurements, are reported in the

preceding Part I of this work (Montoneri et al. 2008). Textile dyeing (Savarino et al. 1999 and 2007), and fabric washing tests (EMPA 2006) were performed under the same experimental conditions reported in the cited references, unless otherwise indicated. For the dyeing tests the disperse dye, here called dye 1, was prepared as previously reported (Carpignano 1985). The dyeing bath had liquid to solid ratio (V/w) 5, pH 7 by 0.1 M tris buffer, and 1% dye related to the fiber weight. Dye dispersion was helped by bath sonication, using a Vibra-cell 120 W apparatus at 1.5-5 W for 10-15 min. Our indicators of dyeing efficiency were the color intensity ( $\Delta E$ ) and the color uniformity ( $\sigma\Delta E$ ), which were determined by tristimulus colorimetry, using a Minolta CR200 instrument (Savarino et al. 1999). The  $\Delta E$  parameter is the mean of five determinations of the color difference between the dyed and undyed fabric performed over five different sites comprised in a 2.5 cm<sup>2</sup> specimen area, while  $\sigma\Delta E$  is the standard deviation around the mean  $\Delta E$  value. Provided that each specimen had 10 x 10 cm<sup>2</sup> size, in most cases duplicate  $\Delta E$  and  $\sigma\Delta E$  values for the same specimen were obtained by repeating the set of five determinations on a different 2.5 cm<sup>2</sup> specimen area.

Similarly, the textile washing efficiency was evaluated according to published guidelines (EMPA 2006) on standard fabric EMPA 106 soiled with carbon black/mineral oil, which was purchased from Ausiliari Tessili Srl, Cornaredo, Mi. For our detergency tests, 10 x 10 cm (1.9-2.0 g) samples were cut and treated with 20 ml surfactant solution containing Na<sub>2</sub>CO<sub>3</sub> at 2 g/L concentration in a tumble container at 90 °C for 20 min. Afterwards, the sample was withdrawn from the bath containing the surfactant solution, immersed in 100 ml deionized water at 30 °C for 20 min, withdrawn, and allowed to dry at room temperature. The washing efficiency was determined by measuring the  $\Delta E$  parameter as above. In this case  $\Delta E$  is the mean of eight measurements of the color difference between the standard soiled sample and the washed sample, which were performed across both faces of the specimen.

Dye photodegradation tests were performed by irradiating for three hours 5 mL aqueous solution of a sulfonated azodye (ethylorange, 5 mg L<sup>-1</sup>) in a closed Pyrex<sup>®</sup> cell with a Xenon (1500W) lamp and a cut-off filter for wavelengths below 340 nm. The analysis of the ethylorange residue in solution after irradiation was done by HPLC, carried out according to a previously reported procedure (Bianco Prevot et al. 2004). Dye degradation kinetics was then studied in a cylindrical photochemical reactor (Helios-Italquartz, Milan), equipped with a 125 W medium pressure Hg lamp, under aerobic conditions by irradiating 500 mL of aqueous solutions containing 5-50 mgL<sup>-1</sup> of ethylorange and various amounts of cHAL2 in order to increase the cHAL2/EO ratio in the 0-200 w/w range. The system was kept under continuous stirring in order to avoid the formation of a concentration gradient, and air was bubbled to maintain the oxygen supply. Cold water circulating in the jacket surrounding the lamp kept the temperature within the reactor at 20°C; a Pyrex<sup>®</sup> glass jacket acting as a cut-off filter for wavelengths below 300 nm was employed, in order to avoid any possible contribution coming from direct dye photolysis.

## RESULTS AND DISCUSSION

Our previous work (Quagliotto et al. 2006; Savarino et al. 2007; Montoneri et al. 2007) has indicated that the potential of humic acid-like substances isolated from compost to be recycled to the chemical market is connected to their surfactant properties. To rate these substances for their potential economic impact on the waste management industry, one should consider the current surfactant market. Recent estimates (Houston 2007) report a relatively large market size for performance surfactants (over 360,000 metric tons, worth € 738 million in Europe). These types of chemicals remain the formulators' best tool to fine tune and achieve special performance to differentiate new products. As industrial competition and environmental concern increase, performance surfactants must satisfy a number of requirements, such as high technology performance, low environmental impact, and low cost. Surfactants have a wide range of functional applications in which they can be used, and therefore are consumed in a number of end-user markets (Research and Markets 2007). Most of the surfactants are used up to make up detergents (Showell 2006). SDBS is the work-horse of this industry, and this justifies our approach to use it as reference material to evaluate the performance of our cHAL2 biosurfactant. Textile dyeing is another important application for surfactants, whose yearly global consumption in this industry is over  $2 \times 10^9$  U.S. \$. The discovery that humic acid-like substances, in addition to their surfactants properties, could also catalyze the photodegradation of organic chemicals (Amine-Khodja 2006), prompted us to study also their effect on the photodegradation of dyes, as this seemed a very attracting perspective in connection with their application as chemical auxiliaries enhancing dyeing quality. We therefore chose the above three field of application for rating the technological potential of our cHAL2 compound, i.e., in fabric cleaning, fabric dyeing, and dye photodegradation.

### Performance in Textile Dyeing

Rayon acetate (RA) fiber and the water insoluble dye 1 represented in Fig. 1 are a typical dyeing system (Savarino et al. 1995; Wang and Zhu 2006).

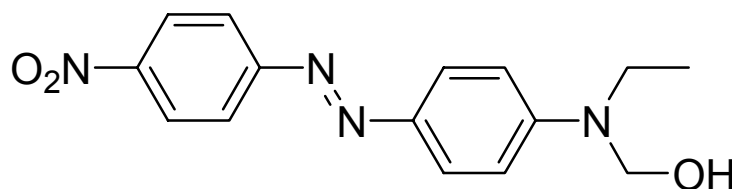


Fig. 1. Disperse dye 1.

Uptake of dyes having poor water solubility by the RA fiber may occur by hydrophobic and/or polar interaction between the fabric and the dye. However, the main problem is the dye solubility. Poor water solubility of the dye causes non-homogenous distribution of the dye throughout the fabric solid phase and the accumulation of the dye preferably on the fibre surfaces. Enhanced dye water solubility is achieved by addition of surfactants. These compounds are expected to perform based on the capacity of their

molecules (S) to aggregate and yield micelles in solution (Rosen 1989; Quagliotto et al. 2006):



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



The complexation equilibrium in reaction 2 would enhance the dye solubility in the dyeing bath, control the rate of release of the free dye concentration in solution, and, in turn, control the rate and yield of the dye uptake by the fiber.

**Table 1.** Color Intensity ( $\Delta E$ )<sup>a</sup> and Uniformity ( $\sigma\Delta E$ )<sup>a</sup> of Rayon Acetate Fiber Dyed by the Disperse Dye 1 in the Presence cHAL2 at Variable Concentration (C, g·L<sup>-1</sup>) under Bath Sonication at 4 W for 15 min.

| C <sup>a</sup> | $\Delta E_1$ | $\sigma\Delta E_1$ | $\Delta E_2$ | $\sigma\Delta E_2$ | $\sigma_{\text{pool}}$ <sup>b</sup> | d.f. <sup>c</sup> | $\Delta E_{\text{avg}}$ <sup>d</sup> |
|----------------|--------------|--------------------|--------------|--------------------|-------------------------------------|-------------------|--------------------------------------|
| 0.00           | 84.8         | 1.72               | 76.3         | 11.75              |                                     |                   |                                      |
| 0.28           | 81.8         | 6.85               | 81.7         | 6.93               | 6.89 c                              | 8                 | 81.7 a                               |
| 0.45           | 85.9         | 0.41               | 83.9         | 1.70               |                                     |                   |                                      |
| 0.60           | 85.4         | 0.40               | 79.8         | 10.82              |                                     |                   |                                      |
| 0.60           | 85.8         | 0.65               | 83.0         | 4.19               |                                     |                   |                                      |
| 0.75           | 85.6         | 0.21               | 83.4         | 2.33               |                                     |                   |                                      |
| 0.90           | 84.8         | 0.35               | 84.2         | 0.44               | 0.40 a                              | 8                 | 84.5 a                               |
| 1.20           | 85.3         | 0.30               | 83.0         | 2.58               |                                     |                   |                                      |
| 1.20           | 85.2         | 0.88               | 84.5         | 0.93               |                                     |                   |                                      |
| 1.50           | 84.3         | 2.56               | 83.0         | 2.53               | 2.54 b                              | 8                 | 83.7 a                               |
| 2.00           | 86.0         | 0.27               |              |                    | 0.33 a                              | 12                | 86.0 b                               |
| 2.00           | 86.1         | 0.37               | 86.1         | 0.35               |                                     |                   |                                      |

<sup>a</sup>Duplicate values reported in the same line pertain to the same specimen (see experimental); results reported for the same C value, but in different lines, pertain to different specimen dyed at different time under the same conditions.

<sup>b</sup>Pooled standard deviation calculated from individual  $\sigma\Delta E$  values for samples at the same C value, provided that the individual  $\sigma\Delta E$  values were not statistically different by F test at 95 % confidence level (Natrella 1966); letters next to figures indicate variance inequalities by F test at 95 % confidence level: i.e., a < b < c.

<sup>c</sup>Degrees of freedom of  $\sigma(\text{pool})$ .

<sup>d</sup>Average color intensity ( $\Delta E_{\text{avg}}$ ) calculated from individual  $\Delta E$  values for samples at the same C value whose  $\sigma\Delta E$  values were not significantly different by F test at 95 % confidence level; letters next to figures indicate  $\Delta E_{\text{avg}}$  inequalities at 95 % confidence level (Natrella 1966): i.e., a < b.

Surfactants can also perform in textile dyeing for their dispersing power, which helps to achieve uniform and better dye penetration into the fiber. Dispersants do not necessarily need to micellize to achieve the desired performance. Polymers comprising carboxyl groups are well known to assist in particle suspension. Our chemical character-

ization of cHAL2 reported in Part I of this work (Montoneri et al. 2007) has shown that this humic acid-like substance consists of both small molecules with 400-450 Da molecular weight that can micellize, as well as macromolecules with  $10^5$  Da molecular weight. The latter ones by virtue of the flexibility of the C chain length may fold and coil to yield pseudo-micelles (von Wandruszka 2000), which have hydrophobic cavities to host small molecules and thus enhance their solubility.

**Table 2.** Color Intensity ( $\Delta E$ )<sup>a</sup> and Uniformity ( $\sigma\Delta E$ )<sup>a</sup> of Rayon Acetate Fiber Dyed by the Disperse Dye 1 at 80 °C, 1 h Dyeing Time and 5 V/w Liquor/Solid Ratio in the Presence of cHAL2, SDS, and SDBS at 1-2 g L<sup>-1</sup> Surfactant Concentration (C) under Bath Sonication at 1.5 W for 10 min.

| Surfactant | C <sup>a</sup><br>(g L <sup>-1</sup> ) | $\Delta E_1$ | $\sigma\Delta E_1$ | $\Delta E_2$ | $\sigma\Delta E_2$ | $\sigma_{\text{pool}}$ <sup>b</sup> | d.f. <sup>c</sup> | $\Delta E_{\text{avg}}$ <sup>d</sup> |
|------------|----------------------------------------|--------------|--------------------|--------------|--------------------|-------------------------------------|-------------------|--------------------------------------|
| none       |                                        | 74.9         | 13.61              |              |                    |                                     |                   |                                      |
| none       |                                        | 81.8         | 1.63               |              |                    |                                     |                   |                                      |
| SDBS       | 1.0                                    | 85.6         | 0.30               | 84.7         | 0.47               | 0.39 a                              | 8                 | 85.1a                                |
| SDBS       | 2.0                                    | 86.1         | 0.30               | 85.6         | 0.36               | 0.39 a                              | 24                | 85.7c                                |
| SDBS       | 2.0                                    | 86.0         | 0.34               | 85.3         | 0.38               |                                     |                   |                                      |
| SDBS       | 2.0                                    | 86.1         | 0.43               | 85.4         | 0.52               |                                     |                   |                                      |
| SDS        | 1.0                                    | 84.4         | 1.28               | 84.1         | 1.50               | 1.39 b                              | 8                 | 84.3a                                |
| SDS        | 2.0                                    | 85.4         | 0.54               | 85.2         | 0.37               | 0.44 a                              | 16                | 85.4b                                |
| SDS        | 2.0                                    | 85.7         | 0.45               | 85.2         | 0.37               |                                     |                   |                                      |
| cHAL2      | 1.0                                    | 83.7         | 3.11               | 83.4         | 2.65               | 2.89 b                              | 8                 | 83.6 a                               |
| cHAL2      | 2.0                                    | 85.4         | 0.47               | 84.7         | 0.38               | 0.49 a                              | 12                | 85.1a,b                              |
| cHAL2      | 2.0                                    | 85.1         | 0.59               |              |                    |                                     |                   |                                      |

<sup>a</sup>Duplicate values reported in the same line pertain to the same specimen (see experimental); results for one surfactant reported at the same C value, but in different lines, pertain to different specimen dyed at different time under the same conditions.

<sup>b</sup>Pooled standard deviation calculated from individual  $\sigma\Delta E$  values for samples containing the same surfactant at the same C value, provided that the individual  $\sigma\Delta E$  values were not statistically different by F test at 95 % confidence level (Natrella 1966); letters next to figures indicate variance inequalities by F test at 95 % confidence level: i.e., a < b

<sup>c</sup>Degrees of freedom of  $\sigma(\text{pool})$ .

<sup>d</sup>Average color intensity. ( $\Delta E_{\text{avg}}$ ) calculated from individual  $\Delta E$  values for samples containing the same surfactant at the same C value whose  $\sigma\Delta E$  values were not significantly different by F test at 95 % confidence level; letters next to figures indicate  $\Delta E_{\text{avg}}$  inequalities at 95 % confidence level (Natrella 1966): i.e., a < b < c.

In order to rate the performance of cHAL2 as a chemical auxiliary in textile dyeing, we have used the same approach that was previously reported for cHAL (Quagliotto et al. 2006). We therefore ran dyeing tests under the same conditions in the absence of additives and in the presence of each one of the following three additives used separately: i.e, cHAL2 and the two widely used commercial synthetic surfactants SDS and SDBS. The dyeing efficiency was rated by the measured values of the fabric color indicators defined in the experimental section: i.e., the color intensity ( $\Delta E$ ) and the color uniformity ( $\sigma\Delta E$ ) parameters. As our previous work with cHAL, SDS, and SDBS (Quagliotto et al. 2006) in dyeing nylon 6 had indicated that for best performance the

additive concentration in the dyeing bath had to be above its CMC value, and that the order of surfactants performance seemed to follow the surfactant capability to micellize, we first wanted to confirm that this was true also for cHAL2. Thus, the dyeing efficiency against the cHAL2 concentration in the dyeing bath was first studied, and the data in Table 1 were collected. Afterwards, we obtained the data in Table 2, which compare cHAL2 and the other two synthetic surfactants at the concentration that was indicated best for cHAL2 by the results reported in Table 1.

Our data elaboration and interpretation was accomplished based on the following criteria. Provided that each specimen had  $10 \times 10 \text{ cm}^2$  size, and that each  $\Delta E$  value shown in Tables 1 and 2 is the average of five determinations taken across a randomly chosen  $2.5 \text{ cm}^2$  specimen area, we ranked dyeing quality first by the equality, established via T and F tests at 95 % confidence level, between  $\Delta E$  values, and between  $\sigma\Delta E$  values respectively resulting from measurements performed across one specimen and/or over more than one specimen dyed under the same conditions. Secondly, we compared by the same T and F tests samples dyed at different additive concentration that passed the above  $\Delta E$  and  $\sigma\Delta E$  equality test. Samples not passing the variance equality tests were ranked last. For the samples passing the variance equality test, the pooled standard deviation values ( $\sigma_{\text{pool}}$ ) were calculated, and the samples were ranked based on 95 % confidence level F test run over  $\sigma_{\text{pool}}$  values and on the average color intensity values ( $\Delta E_{\text{avg}}$ ) taken over measurements across one same specimen and/or different specimen dyed under the same conditions. The statistical ranking order of  $\sigma_{\text{pool}}$  and  $\Delta E_{\text{avg}}$  values is indicated in Table 1 by the letters next to each numerical value. Based on these criteria, the data in Table 1 show that in the absence of cHAL2 the product quality was rather bad: i.e., large differences of color homogeneity and intensity across the specimen. This situation somehow improved already in the presence of low concentration of cHAL2 ( $0.28 \text{ g L}^{-1}$ ), but the best product quality seemed achievable at cHAL2 concentration above  $1.5 \text{ g L}^{-1}$ . The comparison of  $\sigma_{\text{pool}}$  values shows that, although at  $0.9 \text{ g L}^{-1}$  cHAL2 concentration a satisfactory color homogeneity across one specimen may result, the best product quality was attained at  $2 \text{ g L}^{-1}$  cHAL2 concentration for the following reasons. The samples dyed in the presence of  $2 \text{ g L}^{-1}$  cHAL2, compared to all other samples, showed no differences in color homogeneity and intensity both across the single specimen and between different specimens dyed under the same conditions. As indicated from the statistical comparison and rating of the reported  $\sigma_{\text{pool}}$  and  $\Delta E_{\text{avg}}$  values, these specimens also exhibited the best values for the color indicators across the whole additive concentration range: i.e., lowest  $\sigma_{\text{pool}}$  value = 0.33 and highest average color intensity value ( $\Delta E_{\text{avg}}$ ) = 86.0. The results in Table 2 confirm the bad dyeing efficiency in the absence of surfactants by the wide color difference of both the dyeing indicators between the two specimens dyed with no added surfactant, and evidence also the better performance of cHAL2 at  $2 \text{ g L}^{-1}$  concentration than at  $1 \text{ g L}^{-1}$ . The former concentration value corresponds to nearly twice the surfactant CMC value and seems consistent with equilibrium 2 being shifted to the right upon increasing the number of the surfactant micelles in solution, and therefore with increasing the dye solubility in the dyeing bath. The statistical comparison of the  $\sigma_{\text{pool}}$  values for the three surfactants in Table 2 also suggests that at  $2 \text{ g L}^{-1}$  surfactant concentration no significant difference in color uniformity can be assessed between cHAL2 and the other two synthetic surfactants, although the color intensity at this surfactant concentration

seems slightly higher in the presence of SDBS ( $\Delta E_{\text{avg}} = 85.7$ ) than in the presence of cHAL2 and SDS ( $\Delta E_{\text{avg}} = 85.1-85.4$ ).

One last worthwhile comment on the performance of the above surfactants in textile dyeing pertains to the lowest additive concentration to achieve the best dyeing efficiency ( $C_{\text{min}}$ ). Table 3 reports  $C_{\text{min}}$  values obtained in this work and in previous work next to the values obtained for the surfactant's CMC and for the measured color indicators in dyeing with two different fabric/dye systems. These data show that while the color intensity depended on the nature of the fabric/dye system, the color homogeneity indicator ( $\sigma\Delta E$ ) was not significantly affected by the nature of the fabric and of the dye. For our scope, therefore, the results for  $C_{\text{min}}$  in Table 3 were defined as the lowest surfactant concentration that makes it possible to achieve the  $0.28 \leq \sigma\Delta E \leq 0.44$  range of values. One may then readily observe that, while for both cHAL2 and SDS,  $C_{\text{min}}$  was definitely above  $1 \text{ g L}^{-1}$ , for SDBS  $C_{\text{min}}$  was not higher than  $1 \text{ g L}^{-1}$ . The SDS and SDBS  $C_{\text{min}}$  values found in this work for dyeing rayon acetate with dye 1 were similar to those previously reported (Quagliotto et al. 2006) for dyeing nylon 6 with the water insoluble dye 2. In the latter system we used, however, a humic acid-like surfactant (cHAL) with a rather low CMC value, and this exhibited accordingly a very low  $C_{\text{min}}$  ( $0.4 \text{ g L}^{-1}$ ), which corresponded to the CMC value. All together the data in Table 3 confirm that in dyeing with the two water insoluble azo-dyes 1 and 2, the surfactant  $C_{\text{min}}$  value to be used must be equal to or above the surfactant CMC value. Thus, although some contribution from cHAL2 macromolecules to the additive performance in assisting the fiber dyeing may not be excluded, a large part of the positive effect on the dyed product quality is apparently to be ascribed to the capacity of the additive low molecular weight components to micellize.

**Table 3.** Surfactants CMC and Minimum Surfactant Concentration ( $C_{\text{min}}$ ) to Achieve Best Dyeing Efficiency (as measured by the  $\Delta E$  and  $\sigma\Delta E$  indicators defined in the experimental part) with Different Water Insoluble Dyes and Textile Fabrics at pH 7.

| Surfactant | CMC ( $\text{g L}^{-1}$ ) | $C_{\text{min}}$ ( $\text{g L}^{-1}$ ) | Textile Fabric/Dye         | $\sigma\Delta E$  | $\Delta E$        | d.f. <sup>b</sup> |
|------------|---------------------------|----------------------------------------|----------------------------|-------------------|-------------------|-------------------|
| cHAL       | 0.40                      | 0.40                                   | nylon 6/dye 2 <sup>a</sup> | 0.28              | 46.5              | 8                 |
| cHAL2      | 0.97                      | 2.00                                   | rayon acetate/dye 1        | 0.42 <sup>c</sup> | 85.6 <sup>d</sup> | 24                |
| SDBS       | 0.70-1.40                 | 1.00                                   | nylon 6/dye 2 <sup>a</sup> | 0.39              | 47.7              | 8                 |
| SDBS       | 0.70-1.40                 | 1.00                                   | rayon acetate/dye 1        | 0.39              | 85.1              | 8                 |
| SDS        | 2.33                      | 2.36                                   | nylon 6/dye 2 <sup>a</sup> | 0.32              | 49.0              | 8                 |
| SDS        | 2.33                      | 2.00                                   | rayon acetate/dye 1        | 0.44              | 85.4              | 16                |

<sup>a</sup>Data from previous work (Savarino et al. 2007); dye 2 as in Fig. 2.

<sup>b</sup>Degrees of freedom of  $\sigma\Delta E$  and  $\Delta E$ .

<sup>c</sup>Pooled standard deviation calculated from individual  $\sigma\Delta E$  values in Tables 1 and 2 for samples containing cHAL2 at  $2 \text{ g L}^{-1}$  concentration.

<sup>d</sup>Average value calculated from individual  $\Delta E$  values in Tables 1 and 2 for samples containing cHAL2 at  $2 \text{ g L}^{-1}$  concentration.



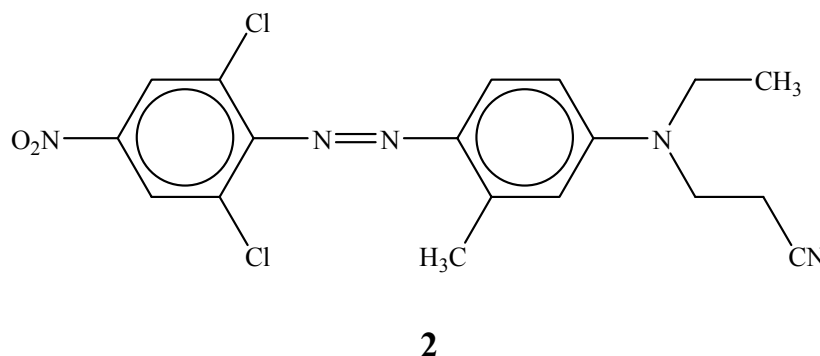
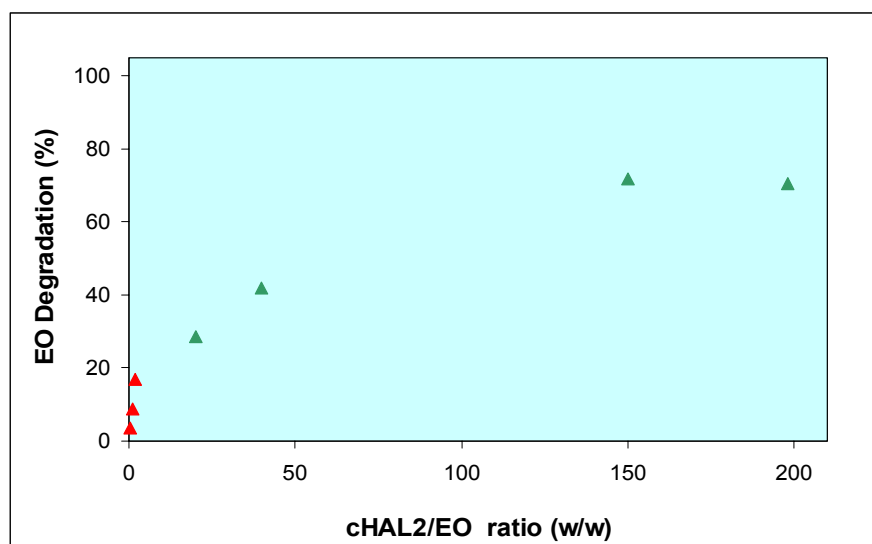


Fig. 2. Disperse dye 2.

### Performance as Photosensitizer Agent.

In the textile industry more than three thousand dyes are used, and it is estimated that about 15% of the world dyes production is lost in the environment during the dyeing process (Zollinger 1991; Robinson et al. 2001). The environmental impact of dyes is not only related to their color, but also to their reduction producing carcinogenic aromatic amines (Gottlieb 2003). For these reasons they have to be efficiently removed from either industrial wastes or polluted natural water streams. Classical treatments such as physico-chemical, oxidative or, most commonly, active sludge biochemical processes have as a main drawback the production of secondary pollution due to the introduction of chemicals and/or to the possible accumulation of other bio-resistant species in the environment. As a possible innovative approach the use of advanced oxidation techniques has been proposed (Palmisano 2000), among which heterogeneous photocatalysis in the presence of  $\text{TiO}_2$  suspensions has been shown to be convenient, since it works at ambient condition and uses a cheap and safe catalyst, atmospheric oxygen and solar (or simulated) light (Bahnemann 2004). Many papers have been published concerning the  $\text{TiO}_2$  mediated degradation of azodyes in aqueous solutions (Konstantinou 2004). In this process, photosensitization (Kamat 1993) of the dye occurs upon excitation by visible light followed by electron transfer from the excited dye to  $\text{TiO}_2$ , and reaction with water and dissolved oxygen to form highly reactive hydroxyl, superoxide, and perhydroxyl radicals. These species can then react with the cationic dye radical and lead to a complete mineralization of the organic substrate. It has been reported that also aquatic humic substances can undergo light excitation processes, which are able to produce reactive oxygenated species influencing the chemistry of dissolved organic compounds in natural waters (Hoigné et al. 1989; Canonica et al. 1995; Sakkas et al. 2002). Most recently, two papers have reported on the photosensitizing properties of humic-like substances (HLS) isolated from mixtures of yard trimmings, sewage sludge, and/or animal manure and grapes residues, which were collected after composting for 0-130 days. From the composted mixes, the humic-like substances were obtained either by simple water extraction (Amine-Khodja et al. 2006a) or by alkaline extraction followed by precipitation at acid pH (Amine-Khodja et al. 2006b). These substances have been found to enhance the photodegradation of organic pollutants in solar light, and their photodegrading activity has been found to increase between 0 and 70 days of composting and to remain quite constant between 70 and 130 days.

Provided that the ability of compost HLS to degrade organic pollutants under light excitation is of great importance from the environmental point of view, in connection to our research on compost isolated humic acid-like compounds, the above published results were particularly intriguing. Indeed, to qualify the potential of compost as source of chemicals for the industry, it was rather important to find out if cHAL2, in addition to enhancing the dyed product quality (as reported above), had potential for facilitating the disposal of the exhaust dye bath. We tested the performance of cHAL2 as a photosensitizer on ethylorange (EO) as the probe molecule. This azo-dye was chosen as a first model test dye because its high water solubility made it possible to use a relatively simple experimental procedure for our preliminary exploratory investigation. Figure 3 reports the dye percentage of degradation, calculated from the decrease of the starting EO concentration, as a function of the initial cHAL2/EO w/w ratio upon irradiation of each solution for three hours.



**Fig. 3.** Ethylorange (EO) degradation rate as a function of starting cHAL2/EO ratio in solution.

In these samples, the EO concentration was  $50 \text{ mg L}^{-1}$  for the cHAL2/EO w/w ratio below 10, and  $5 \text{ mg L}^{-1}$  for the cHAL2/EO w/w ratio  $\geq 20$ . A continuous increase of the degradation efficiency was observable up to a constant value of about 75 %, which was reached at ca. 150 cHAL2/EO w/w ratio where the cHAL2 concentration ( $0.75 \text{ g L}^{-1}$ ) approached its CMC value. These results offer scope for further investigation of humic acid-like substances isolated from different source wastes to use for the treatment of dye exhaust bath or dye-contaminated waters. Provided that the above high dye degradation rate allows easy removal of the color from the exhaust dye bath, we wished to find out if the dye degradation might result in the formation of uncolored toxic species. We chose to measure phytotoxicity to obtain a preliminary ready indication of the potential environmental impact of the above irradiated solutions. To this scope we measured the germination index of *Lepidium sativum* seeds according to a known procedure (Accotto

et al. 1998). Our tests showed no critical hindering of this plant germination rate either by the plain cHAL2 and by the cHAL2-EO solutions irradiated in the above experimental conditions. Work is currently in progress in order to assess the degradation mechanism and the ultimate fate of the dye and of the humic acid-like substance organic carbon. The photosensitizing effect of cHAL2 in the dye exhaust bath adds further potential credit to its use in dyeing technology, and should not be conflicting with the stability of the dyed fabric, provided that the additive was washed out of the dyed fabric upon completion of the dyeing process.

### Performance in Fabric Detergency

Laundry detergents are expected to remove oily soil from fabric. This requires that soil transferred from the fabric to the detergent solution and dissolved into the latter. Surfactants by their capacity to lower the water surface tension and host oily soil particles into their hydrophobic micellar core provide the basis and bulwark of the cleaning power. However, in detergents formulations they are accompanied by a variety of other products (Watson 2006). Among these, polymers with carboxylic functional groups, poly(acrylic acid) for example, are used due to their dispersing power for soil particles. In this regard, fabric detergency and fabric dyeing may be considered to occur by similar mechanisms, but involving opposite processes: i.e., transfer of the soil particle from the fabric to the detergent solution in the former case, and of the dye from its solution bath to the fabric in the latter case. As reported above, cHAL2 containing small molecules and macromolecules with acid carboxylic groups seemed to have both of the above active principle types, i.e., the surfactant and the dispersing polymer. This humic acid-like substance seemed therefore very appealing to be tested in fabric detergency.

The results of our washing tests performed with cHAL2 are reported in Table 4 and Fig. 4. Our experimental plan involved washing the standard soiled fabric (see experimental section) with a water solution containing 2 g/L of  $\text{Na}_2\text{CO}_3$  in the absence of any other additive, and in the presence of cHAL2 or of the synthetic commercial surfactants SDBS and SDS. To evaluate the data in Table 4 and Fig. 4, it should be understood that increasing values of the  $\Delta E$  parameter (see experimental section) indicate increasing whiteness of the sample relative to the standard soiled sample, and therefore higher washing efficiency by the solution. The data in Table 4 show that relative to washing with the plain  $\text{Na}_2\text{CO}_3$  solution, the degree of whiteness of the standard soiled fabric was significantly improved already at  $0.4 \text{ g L}^{-1}$  cHAL2, whereas the highest washing efficiency is reached with  $1.2 \text{ g L}^{-1}$  cHAL2, just above the additive CMC value, and at higher cHAL2 concentration no major or significant change of the washing efficiency ( $6.40 \leq \Delta E \leq 8.61$ ) was observed.

The graphic representation in Fig. 4 allows a ready appreciation of the difference in the trend of performance ( $\Delta E$ ) versus surfactant concentration (C) for the biosurfactant cHAL2 and the commercial synthetic SDBS surfactant. Whereas at low concentration SDBS seemed to perform better than cHAL2, the  $\Delta E$  difference between the two surfactants seemed to be attenuated at higher C values and certainly annulled at  $2 \text{ g L}^{-1}$  surfactant concentration. At this concentration, the second commercial surfactant (SDS) exhibited the lowest performance.

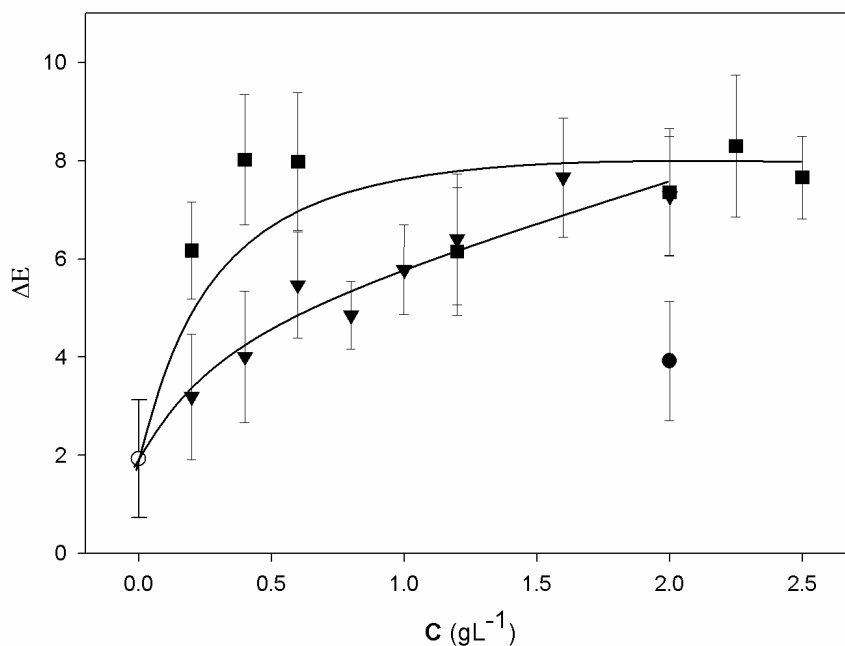
**Table 4.** Washing Efficiency ( $\Delta E$ )<sup>a</sup> of Standard Soiled Fabric by 2 g L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> Solutions, with and without Added Humic Acid-like Substance Isolated from Compost (cHAL2) and Synthetic Commercial Surfactants at Variable Additive Concentration (C).

| Surfactant | C <sup>b</sup> (g L <sup>-1</sup> ) | $\Delta E$ <sup>a</sup> | $\sigma\Delta E$ <sup>a</sup> |
|------------|-------------------------------------|-------------------------|-------------------------------|
|            | 0.00                                | 1.93 a                  | 1.20                          |
| SDBS       | 0.20                                | 6.17c,d                 | 0.98                          |
| SDBS       | 0.40                                | 8.02 d                  | 1.33                          |
| SDBS       | 0.60                                | 7.98 d                  | 1.40                          |
| SDBS       | 1.20                                | 6.15 c,d                | 1.29                          |
| SDBS       | 2.00                                | 7.75 d                  | 1.12                          |
| SDBS       | 2.00                                | 7.15 c,d                | 1.36                          |
| SDBS       | 2.00                                | 6.35 c,d                | 1.20                          |
| SDBS       | 2.00                                | 7.66 d                  | 1.05                          |
| SDBS       | 2.00                                | 6.55 c,d                | 1.59                          |
| SDBS       | 2.00                                | 8.70 d                  | 1.39                          |
| SDBS       | 2.25                                | 8.30 d                  | 1.45                          |
| SDBS       | 2.50                                | 7.66 d                  | 0.84                          |
| SDS        | 2.00                                | 1.99 a                  | 0.93                          |
| SDS        | 2.00                                | 4.06 b                  | 1.13                          |
| SDS        | 2.00                                | 5.72 c                  | 1.52                          |
| cHAL2      | 0.20                                | 3.19 a                  | 1.28                          |
| cHAL2      | 0.40                                | 4.01 b                  | 1.34                          |
| cHAL2      | 0.60                                | 5.47 b                  | 1.08                          |
| cHAL2      | 0.80                                | 4.85 b                  | 0.69                          |
| cHAL2      | 1.00                                | 5.78 c                  | 0.92                          |
| cHAL2      | 1.20                                | 6.40 c,d                | 1.33                          |
| cHAL2      | 1.60                                | 7.66 d                  | 1.21                          |
| cHAL2      | 2.00                                | 7.63 d                  | 1.17                          |
| cHAL2      | 2.00                                | 6.43 c,d                | 1.29                          |
| cHAL2      | 2.00                                | 6.47 c,d                | 1.29                          |
| cHAL2      | 2.00                                | 8.61 d                  | 1.08                          |

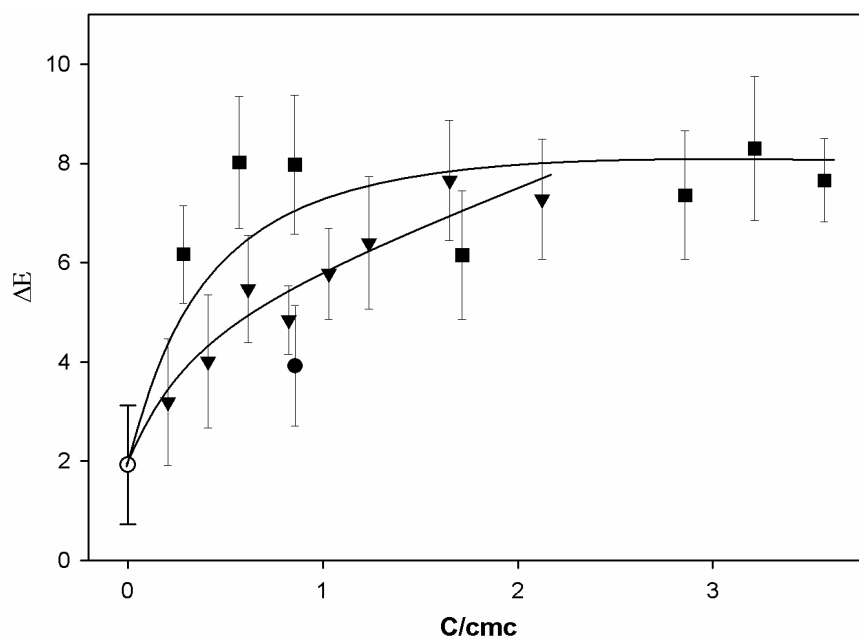
<sup>a</sup>As defined in experimental section; letters next to figures indicate  $\Delta E$  inequalities by T test at 95 % confidence level (Natrella 1966): i.e., a < b < c < d

<sup>b</sup>Results for one surfactant reported at the same C value, but in different lines, pertain to different specimen washed at different time.

It should however be pointed out that SDS at 2 g L<sup>-1</sup> is below its 2.33 g L<sup>-1</sup> CMC value (Savarino et al. 2007), whereas SDBS and cHAL2 are well above their CMC values. By comparison, the plot of  $\Delta E$  vs. the CMC multiple (C/CMC) reported in Fig. 5 shows that the performance differences between surfactants at the same C/CMC value appear smaller than those shown at the same C value (Fig. 4). Although this fact may point out the importance of micelles formation for best performance, in real practice the additives are purchased on a weight basis and therefore it is more important to compare performances at the same additive weight, rather than at the same CMC multiple. The comparison of individual surfactants may yield hints regarding their performance potential. However, in real practice, mixtures of surfactants are used, as these may exhibit synergic effects. Our data show that cHAL2 may be an interesting candidate for use in detergents formulation.



**Fig. 4.** Plot of  $\Delta E$  vs.  $C$  data which are reported in Table 4 for plain sodium carbonate solution ( $\circ$ ), SDBS ( $\blacksquare$ ), SDS ( $\bullet$ ) and cHAL2 ( $\blacktriangledown$ );  $\Delta E$  values for SDS, SDBS, and cHAL2 at  $2 \text{ g L}^{-1}$  are averages taken over the replicate specimen shown in Table 4 for each surfactant. Error bars for the average  $\Delta E$  values represent the pooled standard deviations calculated (Natrella 1966) from the single specimen standard values in Table 4.



**Fig. 5.** Plot of  $\Delta E$  vs. the CMC multiple ( $C/CMC$ ):  $\Delta E$  and  $C$  as in Fig. 4; CMC values (Savarino et al. 2007) =  $2.33 \text{ g L}^{-1}$  for SDS ( $\bullet$ ),  $0.97 \text{ g L}^{-1}$  for cHAL2 ( $\blacktriangledown$ ),  $0.7 \text{ g L}^{-1}$  for SDBS ( $\blacksquare$ ).

## CONCLUSIONS

1. We have shown that municipal solid wastes (MSW) contain valuable organic matter with surfactant properties, which can be recycled to the chemical market for several technological applications.
2. This fact, coupled with the expected friendly environmental impact of the above bio-surfactants, and with the large use of surfactants in modern life, allows us to expect promising economic returns on new biomass waste treatment processes that were specifically developed for recycling products to the chemical market. Indeed, assuming that the MSW isolated biosurfactants (MSWBS) were placed in the surfactant chemical market at the same price (Houston, 2007; Modler et al. 2007) as the commercial synthetic surfactants (CSS), the sales price of the former ones might run about 1-2 €/kg. Thus, using compost as source of bio-surfactants would raise the market value of this biomass waste from 15 €/ton (Newman 2006) to a few hundreds €/ton, deriving the value from bio-surfactant sales only. Such perspectives offer enough incentive to continue investigating the performance of wastes bio-surfactants in other applications, to assess product specifications and to optimize processes for their isolation. Particularly, as for materials of biological origin the source-product variability is mostly critical, further work on humic-like substances should be aimed to establish relationships between their source, structure, properties, and technological performance.
3. The advantages of demonstrating the potential for real commercialization of organics isolated from biomass residues would not be limited to the likely economic return of new waste management processes, but would also involve savings of oil consumption for manufacturing synthetic chemicals with similar properties and decrease of the related CO<sub>2</sub> emission to the atmosphere. To get a rough appreciation of the extent to which biosurfactants isolation and recycling may impact the current waste management practice, it should be considered that the oil world consumption for the manufacture of linear alkylated sulfonates, the major commercial synthetic anionic surfactants, is about 1 million tons/year (Modler et al. 2007) while the total biomass waste flow in the European Union alone is estimated to be a few billion tons/year (Piccinini 2005).
4. As the amount of available biomass wastes far exceeds the amount necessary to obtain enough biosurfactants to virtually replace all synthetic surfactants in the chemical market, the recovery of biosurfactants from biomass wastes cannot be used as the only means for an environmentally and economically efficient management of the wastes. However it may represent one good process to be integrated in biorefineries (Wang et al. 2004). Promotion of biorefineries producing multiple products, including higher-value chemicals as well as fuels and power, is indeed the most modern research trend on biomass treatment and is a priority topic in the current European Union (EU) calls for proposals (FP7 Energy 2007). Integration of the soluble organics extraction process with other biomass treatment technologies, such as those for biogas, bioethanol, or biodiesel production, is likely to affect the final plant products yield and quality and to increase the overall process economic return.

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