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Treatment and reuse of textile wastewaters by mild solar photo-Fenton in the presence of humic-like substances

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Abstract

In this paper the possibility of reusing textile effluents for new dyeing baths has been investigated. For this purpose, different trichromies using Direct Red 80, Direct Blue 106 and Direct Yellow 98 on cotton have been used. Effluents have been treated by means of a photo-Fenton process at pH 5. Addition of humic-like substances isolated form urban wastes is necessary in order to prevent iron deactivation because of the formation of non-active iron hydroxides. Laboratory scale experiments carried out with synthetic effluents shows that comparable results were obtained when using as solvent water treated by photo-Fenton with SBO and fresh deionized water. Experiments were scaled up to pilot plant illuminated under sunlight, using in this case a real textile effluent. Decolouration of the effluent could be achieved after moderate irradiation and cotton dyed with this water presented similar characteristics as when deionized water was used.

Keywords

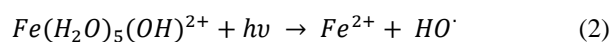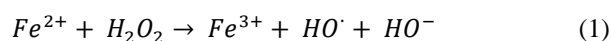Reuse; textile wastewaters; mild solar photo-Fenton; humic-like substances

Introduction

In recent years, textile industry has devoted important effort to minimize wastewater produced during preparation, dyeing and finishing processes. These effluents show, in general, high amounts of organic matter, conductivity and colour (Sharma et al. 2007; Ali et al. 2009). Dyes and pigments with complex aromatic structures, surfactants, dispersants, chlorinated organic compounds, heavy metals or inorganic acids, bases and salts are commonly present in those effluents (Ghaly et al. 2014), with both direct and indirect toxic effects on humans and life aquatics (Wang et al. 2002; Bakshi et al. 2003, Yoo et al. 2013; Khandare et al. 2015). However, significant differences can be observed in their composition, as the nature of the textile and the dyeing processes used are variable, as well as the materials and reagents employed. Furthermore, textile is an extensive water consuming industry and research is focused on developing technologies to enable water reuse (Ergas et al. 2006); however, to reach this goal, the effluent has to be treated to make their properties compatible with their future use.

Several conventional technologies have been used for the treatment of textile effluents, among them physical (Mrinmoy 2016), chemical (Malpass et al. 2007) and biological processes (dos Santos et al. 2007; Sarayu et al. 2012, Cheng et al. 2015). Although the physical-chemical treatments are in most cases able to remove the colour of the textile effluents, bioprocesses have been demonstrated as less efficient, due to non-biodegradable and/or toxic nature of the effluents.

Among the chemical methods, the application of advanced oxidation processes (AOPs) seems a meaningful alternative for the treatment and reuse of textile effluents (Ince et al., 1999). AOPs include a group a treatments that are based on the generation of highly oxidizing species as HO•, and that are able to remove recalcitrant pollutants (Pignatello et al. 2006; Malato et al. 2009; Maezono et al. 2011; Baba et al. 2015). In recent years, numerous studies have applied AOPs on these effluents (Rodriguez et al. 2002; Anjaneyulu et al. 2005; Duran et al. 2008; Arslan-Araton et al. 2009; Rosa et al. 2015), and in some cases, they have been combined with other physical and chemical pre-treatments (Azbar et al. 2004; Oller et al. 2011; Prato-García et al. 2011; Blanco et al. 2014).

In particular, photo-Fenton is an AOP that is based on the ability of iron salts to decompose hydrogen peroxide into reactive species, mainly hydroxyl radical (Pignatello et al, 2006). Although the mechanism is complex, it can be summarized by equations 1-2. Equation 2 is greatly accelerated upon irradiation, and sunlight can be employed for this purpose (Malato et al. 2002; Neamtu et al. 2003).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + HO^{-} \qquad (1)$$

$$Fe(H_2O)_5(OH)^{2+} + h\upsilon \rightarrow Fe^{2+} + HO^{\cdot} \qquad (2)$$

However, photo-Fenton process is not free of disadvantages, being the highly acidic pH required (ca. 3) its major drawback. This problem is even worse in the case of the treatment of dyeing effluents because they commonly show neutral or basic pH; furthermore, colour and turbidity may prevent optimal absorption of solar light (Amorim et al. 2013; Manenti et al. 2015). To overcome this problem, complexing agents are being used to extend the applicability of photo-Fenton towards milder pH. Among the substances that re employed can be found polycarboxylic acids as oxalate, malonate or citrate or aminopolycarboxylic acids as nitrilotriacetic acid (NTA) or ethylenediamine-N,N'-disuccinic acid (EDDS) (Huang et al. 2013).

Alternative complexing agents are humic-like substances (HLS). They are macromolecules that show high affinity for some metals, among them iron (Sutton et al. 2005). They were named as soluble bio-based organic substances (SBO) and results reached with pharmaceuticals, showed that they were efficient to drive photo-Fenton at pH = 5 (Gomis et al. 2013 and 2015)., most probably due to their ability to form photochemiclly active complexes with iron until this pH, as recently demonstrated (Garcia-Ballesteros et al., 2017). Also, surfactant properties have been reported for different SBOs, which depended on their different chemical structures (Montoneri et al. 2008 a,b and 2009). Hence, it is interesting to check the applicability of these substances in textile procedures, as they could be used as surfactants and as auxiliaries for photo-Fenton, having as a final goal, reuse of the effluents for further dyeing.

With this background the aim of this paper is to explore the applicability of HLS to allow reutilization of textile effluents. For this purpose, fabrics will be dyed at laboratory scale using a trichromy composed by three commercial dyes, namely Direct Red 80, Direct Blue 106 and Direct Yellow 98 were employed. Baths will be treated by mild photo-Fenton and reused. Finally, real textile effluents will also be decolourized using a pilot plant for wastewater treatment, also to be reused.

Material and methods

Reagents

Heptahydrated ferrous sulphate ($FeSO_4 \cdot 7H_2O$), hydrogen peroxide (33% w/v), sodium sulphate (Na_2SO_4) and sulphuric acid (98% w/v) were purchased from Panreac; All of them were analytical-grade and were used without further purification. Catalase from bovine liver was provided by Sigma. The SBO employed, isolated from urban biowastes, was kindly supplied by University of Torino (Prof. A. Bianco-Prevot and E. Montoneri) They were isolated in the ACEA Pinerolese waste treatment plant (Pinerolo, Italy). It contained about 72% (w/w) of volatile solids and 38.3% the carbon content (see Gomis et al. 2013, for further details of the isolation procedure and physical-chemical characteristics).

Three commercial synthetic azo dyes, namely Direct Red 80 (C.I. 35780), Direct Blue 106 (C.I. 51300) and Direct Yellow 98 (Amarillo solar 3LG, CAS 12222-58-1) were supplied by Clariant, with a purity higher than 90% (see Fig. 1 for structures). Aqueous solutions (1 g/L of each) were obtained with deionized water produced in a reverse osmosis system, which had a conductivity about 2.19 µS/cm. The fabric used was a 100% cotton twill 210 g/m^2, which has been chemically blanched with peroxide in an industrial process.

Dyeing procedures and samples

Dyeing processes were performed on cotton tissues described above. For this purpose different trichromatic samples at 1.25 % w/f (weight/fiber) were prepared, using the three azo dye. Different samples were obtained by tuning the amount of each dyestuff. (see Table 1). Dyeing was performed in a Tin Control from Reginal composed by eight containers (Quimiboro 564/4), each one with 400 mL capacity used. Water (400 mL), 10 g of cotton fabric and the required amount of dyes were introduced into the Tin Control and preheated to a temperature of ca. 40-50^{0}C . The temperature raised to 110^{0}C until the solution began to boil. Then, Na_2SO_4 (10 g·L^{-1}) was added and left for an hour. The exhaustion bath kept and the tissue was washed twice; then, all three aqueous samples were combined and stored to be treated either is solar simulator or pilot plant (Fig. 2).

When dealing with real effluents, the dyeing final effluents (DFE) were collected in a textile industry located in Alcoy, Spain, that uses wet textile processes such as washing, bleaching, dyeing, printing and finishing,. Individual effluents are discharged in a homogenization tank previous to biological treatment of effluents. Samples were collected at the outlet of the homogenizing tank. They were characterized before 24 hours (see Table 2) and stored at 4ºC until further use.

Analytical determinations

To determine iron concentration a spectrophotometric method based on ISO 6332:1998 was used. Hydrogen peroxide was determined according to the vanadate spectrophotometric method. The pH, conductivity and TSS (Total Suspended Solids) were analyzed according to the Standard Methods for the Examination of Water and Wastewater (22end Edition 2012). The DOC (Dissolved Organic Carbon) and TDN (Total Dissolved Nitrogen) were analyzed by a Shimadzu TOC-VCSH. Residual peroxide was removed with catalase. Except of the determination of COD (Chemical Oxygen Demand) by Merck Spectroquant kits, before the analysis, the DFEs were passed through nylon filters (0.45 μm) purchased from VWR. When required, (e.g. COD or DOC analyses) the excess of H_2O_2 was removed using catalase.

Absorbance at 254 nm was analyzed with a Spectrophotomer UH5300 Hitachi; this value was associated with the aromaticity of the organics present in the DFE. Colour measurement in azo dyes aqueous solutions and the DFEs was evaluated according to the absorbance at three wavelengths (436, 525 and 620 nm). Then, the measured absorbance values were converted to *Indexes of transparency* (DFZ, DurchsichtsFarbZahl) values according to method DIN EN ISO:7887:2011 determined by equation 3, where Abs_λ is the absorbance at the considered wavelength and d, the pathlength, measured in cm:

$$DFZ_\lambda = 100 \times (^{Abs_\lambda}/_d) \qquad (3)$$

The colour of dyed tissues was determined according to the standardized procedure. Values were evaluated in terms of CIELAB values (L*, a*, b*, c*, h) and colour strength (K/S) using illuminant D_{65} (large area of observation on the sample, specularity excluded, d/8, $D_{65}/10°$) was recorded with a Minolta CM-3600d UV-visible spectrophotometer. CIE L*a*b* equations for surface colour measurements were stablished according to International Organization for Standardization (ISO) 105J01:2009.

Colour differences were assessed in accordance with ISO 105J03:2009. The total colour difference ΔE* is a single value that takes into account the differences between the L*, a*, and b* of the sample and compared with a previously stated standard (equation 4). If the ΔE* value is below 1 the colour difference is acceptable.

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \qquad (4)$$

The relative colour strength (in terms of K/S value) of different dyed cotton fabrics were measured at the maximum absorption using the Kubelka–Munk equation (equation 5) (Gupta et al. 2004; Han et al. 2005; Sarkar 2004; Ghoreishian et al. 2013), where K is the coefficient of absorption, S is the coefficient of scattering and R is the reflectance.

$$K/_S = \frac{(1-R) \times 2}{2R} \qquad (5)$$

Colour fastness to washing tests were carried out according to ISO 105-C06:2010. The dyed fibers were washed with standard soap solution at 40ºC for 30 min, keeping a liqueur to material ratio as 50:1. Dry and wet rubbing fastness were determined according to ISO 105-X12:2001 using a standardized Crockmeter.

Photo-Fenton processes

Photo-Fenton process was applied to dyeing effluents of trichromatic samples in a laboratory-scale solar simulator (Sun 2000, ABET Technologies) equipped with a 550W Xenon Short Arc Lamp. Irradiations were performed in 250 mL open cylindrical Pyrex vessels (55 mm internal diameter), they were loaded with 200 mL of the reaction mixture, consisting of the dyeing effluents and 5 mg/L of iron;. The pH was adjusted to the required value (2.8, 3.9 and 5) by dropwise addition of H_2SO_4. Then the stoichiometric amount of hydrogen peroxide required to mineralize the organic matter present in the effluent was added; it was calculated from the COD of the initial sample (Gomis etn al., 2015). When needed, SBO was added to sample (20 mg/L), which accounts for an extra DOC of ca. 8 mg/L. These experimental conditions have been optimized in a previous paper dealing with photo-Fenton treatment of pharmaceuticals in the presence of SBO (Gomis et al., 2015); three different pH were tested as 2.8 is the accepted optimum value for photo-Fenton, 5 is the limit pH found for efficient photo-Fenton in the presence of SBO and 3.9 is an intermediate value. Temperature was kept in the range 30–35°C throughout the reaction. Samples were periodically taken from the solution, filtered through nylon 0.45 μm and diluted 1:1 with methanol.

Controls performed with the same experimental set-up showed that decolouration of the effluents were negligible in the absence of iron and/or H_2O_2. Also experiments carried out only with SBO in the dark and under irradiation underwent no significant decolouration.

Dyeing final effluents (DFEs) were treated in a pilot plant (Solardetox Acadus-2001, Ecosystem) based on compound calendric parabolic collectors (CPCs). The plant had a total surface of 2.57 m^2, and the total irradiated volume was 15.1 L. It was equipped with a radiometer (Acadus 85), which measured the received solar irradiation (UV, $\lambda < 400$ nm); the accumulated energy could be obtained for any irradiation period by means of a PLC (programmable logic controller). The accumulated UV energy per unit of volume (Q_{UV}, in kJ·L^{-1}) needed for decolouration of DFEs is related to the average solar UV radiation, in W·m^{-2}, the irradiated surface (A, in m^{-2}) and V_T, the total volume of the water loaded in the pilot plant (5 L). More details on the pilot plant can be found in (Amat et al. 2004).

Results and discussion

Photo-Fenton treatment at laboratory- scale of trichromatic samples

Photo-Fenton process at laboratory scale was applied to six trichromatic samples (see Table 1), with 5 mg/L of Fe (II) ion at pH = 5 and the stoichiometric concentration of hydrogen peroxide required to mineralize all the organics present in the effluent. Experiments were performed without or with SBO (20 mg/L). Figure 3 shows the absorbance of the sample at three wavelengths vs time. It can be observed that decolouration was scarce in the experiments performed without SBO (in most cases in the range 30-35% in the studied wavelengths) leading to very high final absorbances ca. 0.1 AU and even higher in some cases). In sharp contrast, in the effluents that have been treated with SBO at pH = 5, the percentage of

decolouration reaches values close to 90 % in most cases (Figure 3) and the final absorbance was systematically below 0.05 AU, for all three monitored wavelengths, showing the efficiency of photo-Fenton in the presence of SBO. This has been attributed to the ability of humic-like substances to form photo-active complex, which prevent the generation of inefficient iron oxides or hydroxides (Gomis et al., 2013). It is also interesting to remark that different proportions among the three dyes did not have a significant effect on the efficiency of the process, as absorbance after 50 min of irradiation in reactions performed with SBO were very similar.

Reuse of treated water by photo-Fenton of trichromatic samples in dyebaths

As stated in the introduction, the final goal of the treatment is to treat the effluent to make it compatible for further use in dyebaths, aiming to decrease water consumption. To check this point, samples treated in the previous section with SBO were used as solvent in a dyeing procedure of cotton twill with the trichromy, and results were compared with controls with were treated following the same procedure, but using fresh deionized water instead. The colour differences of cotton dyed samples were calculated by CIE $L^*a^*b^*$ (see Table 3). The parameter L* represents lightness value, being the maximum value 100 (complete reflection of light), and the minimum is zero (which represents black). The parameters a* and b* represent the tone of the colour; positive values of a* and b* represent reddish and yellowish tones while negative values show greenish and bluish tones. C* represents chroma or purity of colour and h represent hue of colour. As shown in the ΔE*cmc results of the table 4, only the values of the samples dyed with treated water using SBO were within tolerance. It is noticeable that when water treated without SBO was employed, obtained samples were systematically out of tolerance; this is in agreement with a better performance of photo-Fenton driven with SBO a pH = 5. On the other hand, Table 4 shows the relative colour strength in terms of K/S value at 420, 550 and 650 nm (maximum absorption) of all dyed samples. When results are compared it can be observed that K/S value from the dyed sample with deionized water is lower than the corresponding K/S values obtained from dyed sample using treated water with or without SBO.

Photo-Fenton treatment in Pilot Plant of real dyeing final effluents (DFE) and reuse in new dyebaths

Results shown in previous section indicate that promising results have been achieved when SBO is employed. Hence, it is interesting to check if those results could be scaled up to pilot plant with solar irradiation and using real industrial effluents. The real dyeing final effluents (DFEs, characterized in Table 2) supplied by a textile industry were employed for this purpose. They were submitted to photo-Fenton using 20 mg/L of SBO, 5 mg/L of Fe(II), the stoichiometric concentration of hydrogen peroxide required to mineralize all the organics (according to COD) at pH =5. All of treated DFEs were filtered before treatment. Total effluent volume of 5 L was used and the UV energy per unit of volume, Q_{UV} in kJ/L required to reach decolouration of DFEs was calculated. Main parameters at the end of the treatment can also be observed in Table 2: there was a very significant removal of organic matter (more than 80% DOC removal) and COD decrease was also intense, although some amount of organics still remained in the treated effluent. The colour was nearly completely eliminated and absorbance at 254 nm was decreased in ca. 90%. Regarding to colour, Figure 4 shows the decolouration of three different samples

of DFEs vs. Q_{UV}. In all cases, an accumulated UV energy per volume of 1-1.5 kJ·L^{-1} was enough to ensure decolouration of dyeing effluents.

The treated water was used in new dyebaths according to the same experimental procedure described with the treated effluents in laboratory scale. In parallel, dyebaths using deionized water were also performed. The Colour differences and the relative Colour strength can be seen in Table 5. The results show that the differences of Colour (ΔE^*cmc) between the fabrics dyed with deionized water and with treated water in pilot plant are acceptable, since this value is below 1. The relative colour strength in terms of K/S value at 550 nm (maximum absorption of the dyeing final effluents) obtained for the samples dyed with treated water, was slightly higher than that obtained with deionized water. Finally, Table 6, shows the results of the rubbing test (dry and wet). As can be seen, all samples show very good to excellent Colour fastness (being the maximum level of 5, all test reaches that value or very close).

Conclusions

The photo-Fenton treatment at pH 5 using soluble SBO has been proven to be an effective method to decolourize the textile wastewaters, as it allows that treated effluents to be reused in new dyebaths. This is a very interesting result as developing a photo-Fenton at milder pH, instead of the optimum value of 2.8, results in decrease (or even suppression) of the amount of acid required for pH adjustment, with the related economic and ecologic advantages that it involves. This result cannot be achieved in the absence of SBO, a material that is obtained in a process that involves a waste revalorization, thus enhancing the sustainability of the process. Furthermore, the quality of the treated effluent is compatible with its reuse in other baths, producing cotton tissues with similar coloration. Hence, this process might be of interest and deserves further research at it addresses several key points of green chemistry, namely a decrease in the consumption of resources and waste production, the use of a by-product obtained from a waste, and to use o treatment process that can be implemented under solar irradiation.

Refergences

Ali, N., A. Hameed, et al. (2009). Physicochemical characterization and Bioremediation perspective of textile effluent, dyes and metals by indigenous Bacteria. Journal of Hazardous Materials 164(1): 322-328

Amat, Ana M., Antonio Arques, Miguel A. Miranda, Sergio Seguí (2004). Photo-Fenton reaction for the abatement of commercial surfactants in a solar pilot plant. Solar Energy 77, 559–566

Amorim C.C, Leão MMD, Moreira RFPM, Fabris JD, Henriques AB (2013). Performance of blast furnace waste for azo dye degradation through photo-Fenton-like processes. Chemical Engineering Journal, 224, 59–66

Anjaneyulu, Y., N. Sreedhara Chary, et al. (2005). Decolorization of industrial effluents: available methods and emerging technologies. Environmental Science and Biotechnology 4(4): 245-273

Arslan-Alaton, I.; Tureli, G.; Olmez-Hanci, T. (2009). Treatment of azo dye production wastewaters using Photo-Fenton-like advanced oxidation processes: Optimization by response surface methodology. Journal of Photochemistry and Photobiology A: Chemistry, 202, 142-153

Azbar N., T. Yonar, K. Kestioglu (2004). Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent. Chemosphere, 55, pp. 35–43

Baba Yusuke, Tomonori Yatagai, Takuma Harada, Yoshinori Kawase (2015). Hydroxyl radical generation in the photo-Fenton process: Effects of carboxylic acids on iron redox cycling. Chemical Engineering Journal, Volume 277, 1, Pages 229-241

Bakshi, D.K., P. Sharma (2003). Genotoxicity of textile dyes evaluated with ames test and rec-assay J. Environ. Pathol. Toxicol. Oncol., 22, p. 10

Blanco Jose, Francesc Torrades, Moises Morón, Marolda Brouta-Agnesá, Julia García-Montaño (2014). Photo-Fenton and sequencing batch reactor coupled to photo-Fenton processes for textile wastewater reclamation: Feasibility of reuse in dyeing processes. Chemical Engineering Journal 240, 469-475.

Chen Qing, Ying Yang, Mengsi Zhou, Meihong Liu, Sanchuan Yu, Congjie Gao (2015). Comparative study on the treatment of raw and biologically treated textile effluents through submerged nanofiltration. Original Research Article. Journal of Hazardous Materials, Volume 284, 2, Pages 121-129

dos Santos, A.B., F.J. Cervantes, J. van Lier (2007). Review paper on current technologies for decolorisation of textile wastewater: perspectives for anaerobic biotechnology. Bioresour. Technol. 37, 315-377.

Durán, A., J. M. Monteagudo, E. Amores (2008). Solar photo-Fenton degradation of Reactive Blue 4 in a CPC reactor. Applied Catalysis B: Environmental 80,(1-2): 42-50.

Ergas S., B. Therriault, D. Reckhow (2006). Evaluation of water reuse technologies for the textile industry. J. Environ. Eng. 132, 315-323

García Ballesteros, S., Costante, R. Vicente, R. Mora, M., Amat, A.M., Arques, A., Carlos, L, and García Einschlag, F. S. (2017) Humic-like substances from urban waste as auxiliaries for photo-Fenton treatment:ma fluorescence EEM-PARAFAC study, Ptotochem. Photobiol. Sci. in press, DOI: 10.1039/c6pp00236f

Ghaly, A. E., R. Ananthashankar, M. Alhattab, V.V. Ramakrishnan (2014). Production, characterization and treatment of textile effluents: a critical review. J. Chem. Eng. Process Technol., 05, pp. 1–18

Ghoreishian SM, Maleknia L, Mirzapour H, Norouzi M (2013) Antibacterial properties and color fastness of silk fabric dyed with turmeric extract. Fiber Polym 14(2):201-207. doi: 10.1007/s12221-013-0201-9

Gomis J., R.F. Vercher, A.M. Amat, D.O. Mártire, M.C. González, A. Bianco Prevot, E. Montoneri, A. Arques, L. Carlos (2013). Application of soluble bio-organic substances (SBO) as photocatalysts for wastewater treatment: Sensitizing effect and photo-Fenton-like process. Catalysis Today 209, 176-180

Gomis J., L. Carlos, A. Bianco Prevot, A.C.S.C. Teixeira, M. Mora, A.M. Amat, R. Vicente, A. Arques (2015). Bio-based substances from urban waste as auxiliaries for solar photo-Fenton treatment under mild conditions: Optimization of operational variables. Catalysis Today 240, 39-45

Gupta D, Khare SK, Laha A (2004) Antimicrobial properties of natural dyes against Gram negative bacteria. Color Technol 120(4):167-171. doi: 10.1111/j.1478-4408.2004.tb00224.x

Han S, Yang Y (2005) Antimicrobial activity of wool fabric treated with curcumin. Dyes Pigments 64(2):157-161. doi:10.1016/j.dyepig.2004.05.008

Huang Wenyu, Marcello Brigante, Feng Wu, Christine Mousty, Khalil Hanna, and Gilles Mailhot (2013). Assessment of the Fe (III)–EDDS Complex in Fenton-Like Processes: From the Radical Formation to the Degradation of Bisphenol A. Environ. Sci. Technol.,47 (4), pp 1952–1959

Ince N.H., G. Tezcanh (1999). Treatability of textile dye-bath effluents by advanced oxidation: Preparation for reuse. Water Science and Technology. Volume 40, Issue 1, 1999, Pages 183-190.

ISO 6332:1988. Water quality: Determination of iron, Spectrometric method using 1,10-phenanthroline

ISO 105-X12:2001. Textiles- Test for color fastness- Part X12: Color fastness to rubbing.

ISO 105-J01:2009. Textiles. Ensayos de solidez del color. Parte J01: Principios generales para la medición del color de superficies.

ISO 105-J03:2009. Textiles. Tests for colour fastness. Part J03: Calculation of colour differences

ISO 105-C06:2010. Textiles-Tests for color fastness-Part C06: Color fastness to domestic and commercial laundering.

ISO 7887:2011. Water quality: Examination and determination of colour. Method B.

Khandare Rahul V., Sanjay P. Govindwar (2015). Phytoremediation of textile dyes and effluents: Current scenario and future prospects. Review Article Biotechnology Advances, Volume 33, Issue 8, Pages 1697-1714

Maezono Takuya, Masahiro Tokumura, Makoto Sekine, Yoshinori Kawase (2011). Hydroxyl radical concentration profile in photo-Fenton oxidation process: Generation and consumption of hydroxyl radicals during the discoloration of azo-dye Orange II. Chemosphere, Volume 82, Issue 10, Pages 1422-1430

Malato S., J. Blanco, J. Cáceres, A.R. Fernández-Alba, A. Agüera, A. Rodríguez (2002). Photocatalytic treatment of water-soluble pesticides by photo-Fenton and TiO_2 using solar energy. Catalysis Today 76, 2002 (2-4): 209-220.

Malato S., P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Gernjak (2009). Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. Catalysis Today, Volume 147, Issue 1, Pages 1-59

Malpass G.R.P., D.W. Miwa, D.A. Mortari, S.A.S. Machado, A.J. Motheo (2007). Decolorisation of real textile waste using electrochemical techniques: effect of the chloride concentration. Water Res., 41, pp. 2969–2977

Manenti D, Soares P, Silva TCV, Módenes A, Espinoza-Quiñones F, Bergamasco R, Boaventura RR, Vilar VP (2015). Performance evaluation of different solar advanced oxidation processes applied to the treatment of a real textile dyeing wastewater. Environ Sci Pollut Res 22:833–845

Montoneri, E., Boffa, V., Quagliotto, P., Mendichi, R., Chierotti, M. R., Gobetto, R., and Medana, C. (2008 a). "Humic acid-like matter isolated from green urban wastes. Part 1. Structure and surfactant properties," BioRes. 3(1), 123-141.

Montoneri, E., Savarino, P., Bottigliengo, S., Musso, G., Boffa, V., Prevot, A. B., Fabri, D., and Pramauro, E. (2008 b). "Humic acid-like matter isolated from green urban wastes. Part II: Performance in chemical and environmental technologies," BioRes. 3(1), 217-233.

Montoneri E., Vittorio Boffa, Piero Savarino, Fulvia Tambone, Fabrizio Adani, Luca Micheletti, Carlo Gianotti, Roberto Chiono (2009). Use of biosurfactants from urban wastes compost in textile dyeing and soil remediation. Waste Management 29, 383–389

Mrinmoy Mondal, Sirshendu De (2016). Treatment of textile plant effluent by hollow fiber nanofiltration membrane and multi-component steady state modeling. Chemical Engineering Journal 285, 304-318

Neamtu M., A. Yediler, I. Siminiceanu, A. Kettrup (2003). Oxidation of commercial reactive azo dye aqueous solutions by the photo-Fenton and Fenton-like processes. J. Photochem. Photobiol. A, 161, pp. 87–93

Oller I., S. Malato, J.A. Sánchez-Pérez (2011). Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination—A review. Science of The Total Environment, Volume 409, Issue 20, 15 September, Pages 4141-4166

Pignatello J., E. Oliveros, A. MacKay (2006). Advanced oxidation processes for organic contaminant destruction based on the fenton reaction and related chemistry. Environmental Science and Technology 36, 1-84

Prato-Garcia Doria, Germán Buitrón (2011). Degradation of azo dye mixtures through sequential hybrid systems: Evaluation of three advanced oxidation processes for the pre-treatment stage. Journal of Photochemistry and Photobiology A: Chemistry 223, 103– 110

Rodriguez, M.; Sarria, V.; Esplugas, S.; Pulgarin, C. Photo-Fenton (2002). Treatment of a biorecalcitrant wastewater generated in textile activities: biodegradability of the photo-Treated solution. Journal of Photochemistry and Photobiology A: Chemistry, 151, 129-135

Rosa, Jorge M., Ana M.F. Fileti, Elias B. Tambourgi, Jose C.C. Santana (2015). Dyeing of cotton with reactive dyestuffs: the continuous reuse of textile wastewater effluent treated by Ultraviolet/Hydrogen peroxide homogeneous photocatalysis. Journal of Cleaner Production 90, 60-65

Sarayu K., S. Sandhya (2012). Current Technologies for Biological Treatment of Textile Wastewater-a review. Appl. Biochem. Biotech. 147(3) 645-661

Sarkar AK (2004) An evaluation of UV protection imparted by cotton fabrics dyed with natural colorants. BMC dermatology 4(1):15. doi: 10.1186/1471-5945-4-15

Sharma, K. P., S. Sharma, et al. (2007). "A comparative study on characterization of textile wastewaters (untreated and treated) toxicity by chemical and biological tests." Chemosphere 69(1): 48-54.

Standard Methods for the Examination of Water and Wastewater (2012). Part 2000: Physical & Aggregate properties. 22end Edition APHA, AWWA and WEF

Sutton R., G. Sposito (2005). Molecular structure in soil humic substances: the new view, Environ. Sci. Technol. 39, 9009-9015.

Wang Chunxia, Ayfer Yediler, Doris Lienert, Zijian Wang, Antonius Kettrup (2002). Toxicity evaluation of reactive dyestuffs, auxiliaries and selected effluents in textile finishing industry to luminescent bacteria *Vibrio fischeri*. Chemosphere, Volume 46, Issue 2, Pages 339-344

Yoo Jisu, Byeongyong Ahn, Jeong-Ju Oh, Taejun Han, Woo-Keun Kim, Sanghoon Kim, Jinho Jung. (2013) Identification of toxicity variations in a stream affected by industrial effluents using Daphnia magna and Ulva Pertusa. Original Research Article. Journal of Hazardous Materials, Volume 260, 15 September, Pages 1042-1049

Table 1. Trichromatic samples prepared with three dyes (total concentration 1.25% w/f). The percentage of each dye is given.

Azo Dyes	Trichr. 1	Trichr. 2	Trichr. 3	Trichr. 4	Trichr. 5	Trichr. 6
Direct Yellow 98	0.75	0.5	0.5	0.25	025	0.25
Direct Red 80	0.25	0.50	0.25	0.25	0.75	0.50
Direct Blue 106	0.25	0.25	0.50	0.75	0.25	0.50

Table 2. Main parameters of the dyeing final effluents (DFE) employed in this work. Data before and after the treatment are provided

Parameters	DFE1		DFE2		DFE3	
	Initial	Final	Initial	Final	Initial	Final
pH	6.9	4.8	7.14	4.9	7.23	4.8
Conductivity (mS/cm)	3.21	3.40	3.15	3.53	2.98	3.27
DOC[a] (mgC/L)	394	84.3	364	85.4	382	96.7
COD[b] (mgO$_2$/L)	1478	241	1390	218	1440	230
Colour						
$\quad$ DFZ$_{436}$ m^{-1}	13.4	0.8	12.8	0.6	14.1	0.9
$\quad$ DFZ$_{525}$ m^{-1}	11.8	0.7	10.4	0.6	10.1	0.8
$\quad$ DFZ$_{620}$ m^{-1}	3.2	0.2	2.1	0.1	2.8	0.2
Absorbance at 254 nm (UA)	3.14	0.38	2.87	0.29	3.02	0.41
Total dissolved nitrogen (TDN)	9.4	8.9	7.8	7.9	9.1	8.7
TSS[c] (mg/L)	279	-	261	-	294	-

(a) Dissolved Organic Carbon (DOC)
(b) Chemical Oxygen Demand (COD)
(c) Total suspended solids (TSD)

Table 3. Colour characterization of cotton samples dyed with reused water without SBO (Upper table) and with SBO (lower table).

Dyeing	L	a	b	ΔE*cmc
Deionized water	45.1213	19.6583	3.8478	
Tri 1	45.1680	19.9247	5.3582	1.5344
Tri 2	44.6919	20.3883	5.1247	1.5322
Tri 3	45.1489	19.8745	5.1872	1.3570
Tri 4	45.6325	19.9342	4.8871	1.1906
Tri 5	45.9889	20.5189	4.9974	1.6778
Tri 6	44.7852	20.4553	4.8245	1.3047

Dyeing trichromatic samples with treated water without SBO

Dyeing	L	a	b	ΔE*cmc
Deionized water	45.1213	19.6583	3.8478	
Tri 1	44.8089	19.5045	4.5432	0.7777
Tri 2	45.2278	19.2345	4.4171	0.7177
Tri 3	45.1890	19.3014	4.7847	1.0049
Tri 4	44.6919	19.9045	4.6298	0.9255
Tri 5	45.5578	19.8874	4.5863	0.8879
Tri 6	45.3662	19.4551	4.6180	0.8334

Dyeing trichromatic samples with treated water with SBO

Table 4. Colour coordinates of cotton dyed cotton fabrics and K/S value at peak wavelengths.

K/S	420 nm	550 nm	650 nm
Deionized water	3.2787	4.4137	1.2773
Treated water without SBO	3.4929	4.5580	1.3088
Treated water with SBO	3.5560	4.4575	1.2581

Table 5. Colour differences and relative Colour strength of samples dyed with reused water of pilot plant

Dyeing	L	a	b	ΔE*cmc	K/S (λ max)
Deionized water	45.3486	19.3479	3.9847		4.4171
Treated water DFE1	45.6947	19.9588	4.5112	0.8776	4.8012
Treated water DFE2	45.6003	19.7449	4.6411	0.8074	4.4996
Treated water DEF3	45.4265	19.8782	4.6209	0.8319	4.6006

λmax = 550 nm

Table 6. Wash and rub fastness of samples dyed with reused water of pilot plant

Dyeing	Rub fastness				Wash fastness		
	Dry		Wet		CC	CS	
	CC	CS	CC	CS		Co	Wo
Deionized water	5	5	4-5	4-5	4-5	4-5	4
Treated water DFE1	5	5	4-5	4-5	4-5	4-5	4
Treated water DFE2	5	5	4-5	4-5	4-5	4-5	4
Treated water DEF3	5	5	4-5	4-5	4-5	4-5	4

CC: Colour change; CS: Colour staining; Co: cotton; Wo: wool

Fig. 1
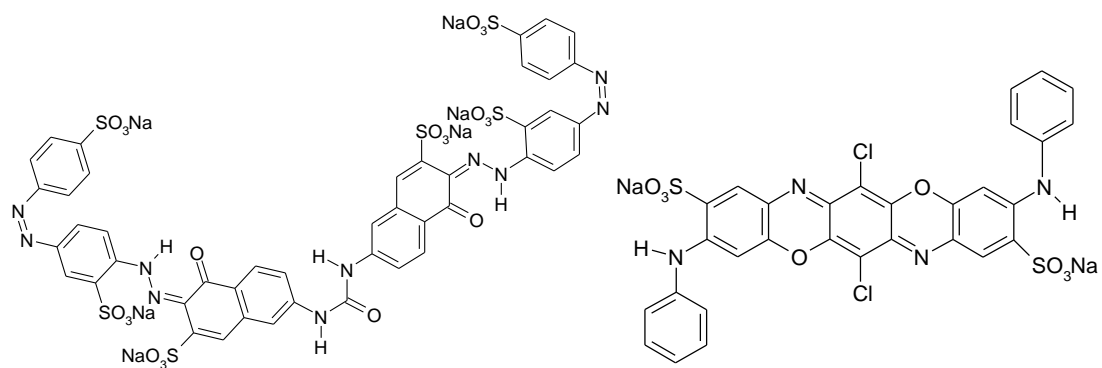
Fig. 1: Chemical structures of Direct Red 80 (left) and Direct Blue 106 (right). Structure of Direct Yellow 98 cannot be given because it is registered unknown molecule.
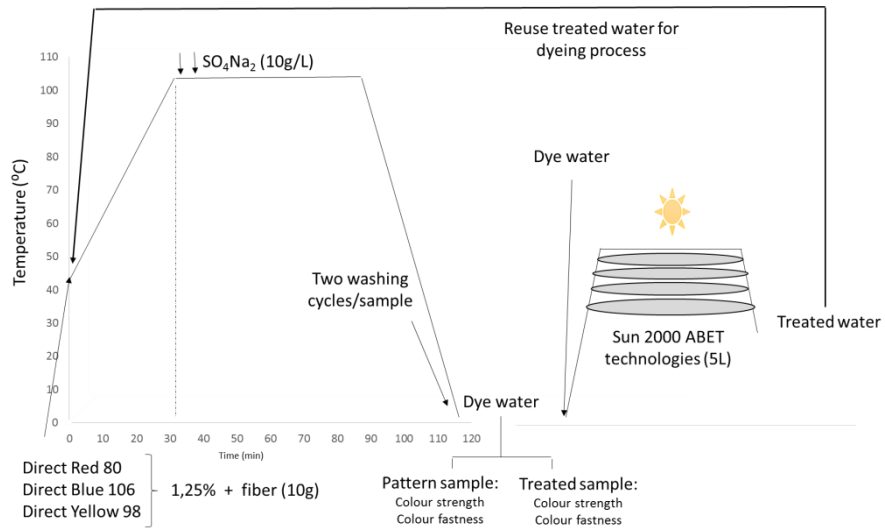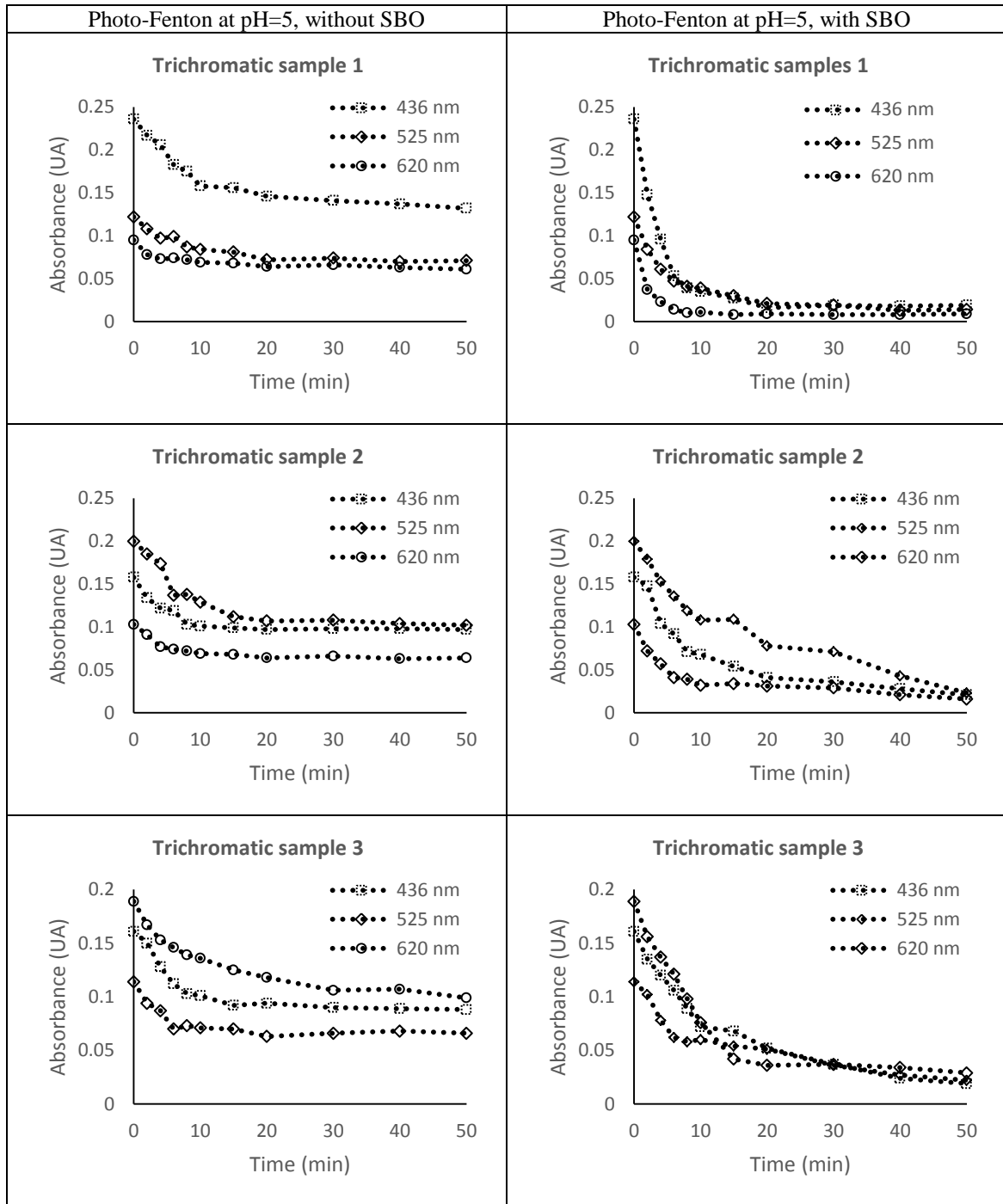
Fig. 2

Fig. 2: Schematic dyeing process experimental and solar pilot plant treatment
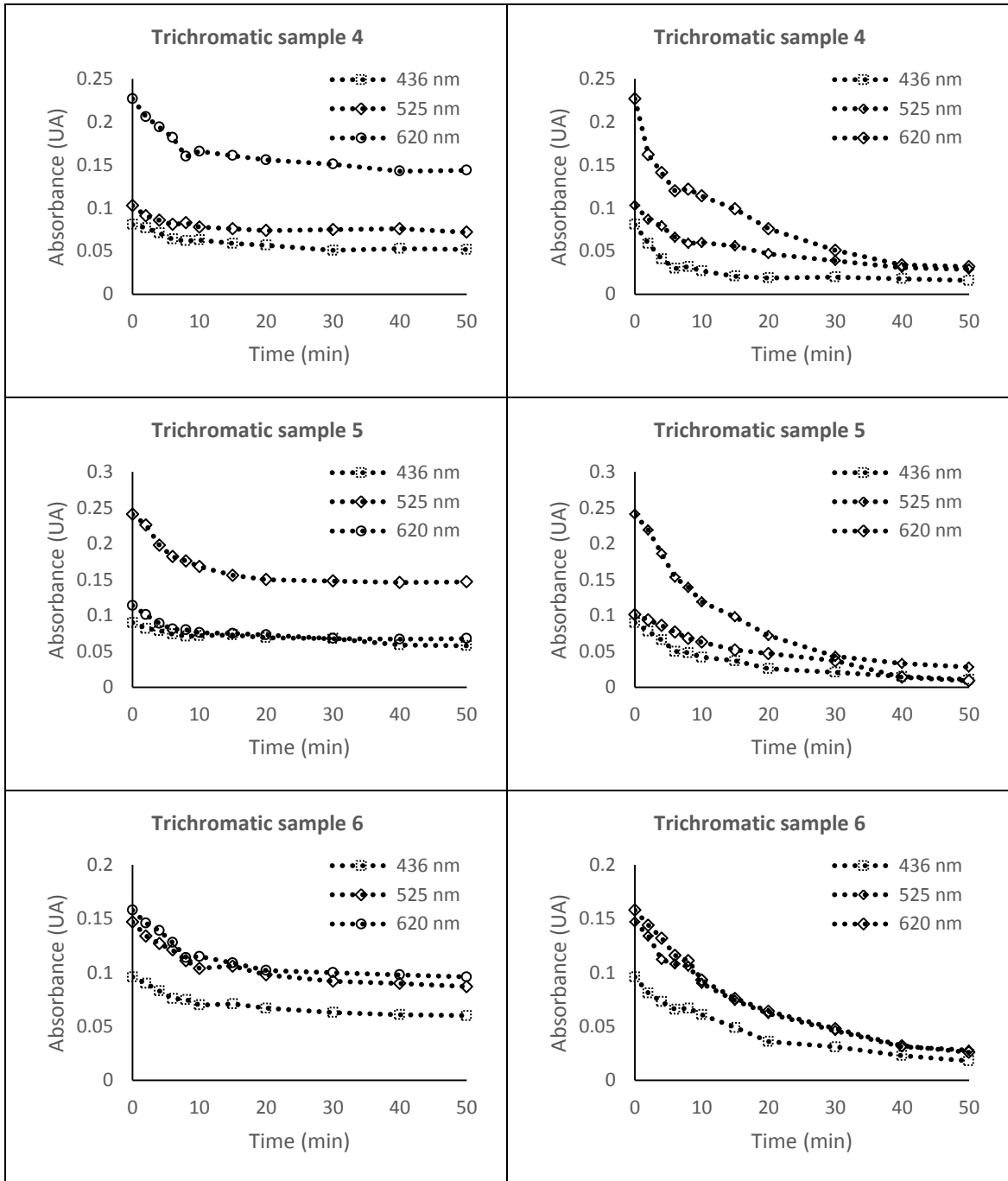
Fig. 3

Fig.3. Decolouration of trichromatic samples in function the absorbance of the sample at three wavelengths vs time

Fig. 4

Treatment of DFE 1 in Pilot Plant

Treatment of DFE 2 in Pilot Plant
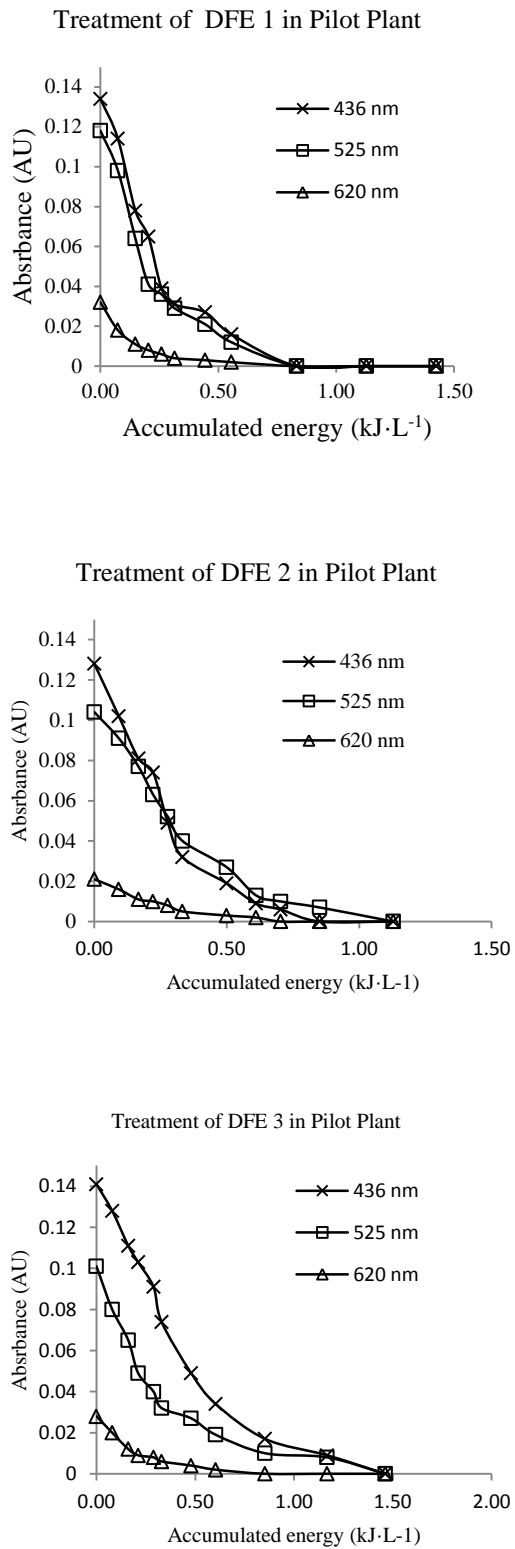

Treatment of DFE 3 in Pilot Plant

Fig. 4: Decolouration of three samples of DFE using photo-Fenton process at pH=5 with SBO in solar pilot plant