Photochemical UVC/H_2O_2 Oxidation System as an Effective Method for the Decolourisation of Bio-Treated Textile Wastewaters: Towards Onsite Water Reuse

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Abstract

A photochemical UVC/H_2O_2 oxidation system was applied for the decolourisation of two real textile wastewaters, textile wastewater A – TWA and textile wastewater B - TWB - collected after biological oxidation from two different textile wastewater treatment plants. The photochemical oxidation assays were performed in a lab-scale photo-reactor, where a borosilicate tube is associated to an internal concentric quartz tube filled with a UVC lamp (6W). Photochemical reaction rates were determined under different operational conditions: H_2O_2 dosage (0-40 mM), pH (3, 5 and 9) and temperature (15, 23 and 35°C). For both TWA and TWB, it was observed a positive influence on the UVC/H_2O_2 efficiency at higher hydrogen peroxide dosages and wastewater temperature. However, the pH conditions differently affected each wastewater. Although the dissolved organic content remained almost similar during the UVC/H_2O_2 reaction period, the biodegradable organic fraction increased for values higher than 40%. To achieve the colour discharge limits imposed by the Brazilian regulations, it was necessary 180/75 min of UVC irradiation (8.3/3.4 kJ_{UVC} L^{-1}) using an H_2O_2 dose of 25.0 mM, natural pH of 8.1/7.7 and T = 23 °C, respectively for the TWA/TWB. The photochemical-treated textile wastewater – PTWB was used as bathwater during bleaching and dyeing of cotton fibres in order to assess its onsite reuse in the textile manufacturing process. Compared with the same bleaching process made with distilled water, all quality indicators monitored showed small differences, which demonstrate the possible reuse of PTWB in this process. Finally, reuse of PTWB mixed with 50% distilled water as bathwater in the dyeing process with Direct Blue 71 resulted in similar samples (ΔE* = 0.76) when compared with standard dyeing process.

Keywords: Real Textile Dyeing Wastewater; UVC/H_2O_2 Oxidation System; Decolourisation; Polishing Step; Water Reuse.

1. Introduction

The textile industry is one of the most chemically intensive industries on earth, and associated with the high water consumption (Wang et al., 2004), leads to generation of high amounts of polluted wastewaters. Although the textile industry wastewaters can vary largely on the composition, they are generically characterized by a moderate organic content, low biodegradability, variable pH values, usually in the alkaline range and intense colour (Correia et al., 1994). The recalcitrant organic matter is mainly associated with dyes, synthetic resins, surfactants, solvents, oxidizing agents, reducing agents, and many other chemical auxiliaries that are employed in different stages of the manufacturing (Delée et al., 1998).

Although biological oxidation processes show good results for the mineralisation of the biodegradable organic fraction of textile wastewater (Doumic et al., 2015; Oller et al., 2007), these conventional processes do not provide satisfactory results on the wastewater decolourisation. Besides, if the wastewater contains a high concentration of synthetic organic chemicals with biological persistence, the biological oxidation cannot provide an efficient mineralization (Arslan Alaton et al., 2006; Arslan-Alaton and Alaton, 2007). As result, the combination of biological and polishing processes, aiming to reduce costs and optimize the treatment, is currently the most common approach applied to textile wastewater treatment. Physical and chemical technologies such as membrane filtration (Bes-Piá et al., 2002; Cheng et al., 2012; Petrinić et al., 2015), coagulation (Freitas et al., 2015; Han et al., 2016; Verma et al., 2012) and adsorption (Cengiz et al., 2012; Hassani et al., 2015; Mehta et al., 2015) have proven to be able to remove the dyes in bio-treated textile wastewaters, even if with some disadvantages such as expensive investments, membrane fouling and sludge generation (Oller et al., 2011; Rafatullah et al., 2010; Verma et al., 2012; Zahrim and Hilal, 2013).

In the last years, advanced oxidation processes (AOPs) have been tested for the treatment of wastewaters contaminated with organic components presenting high chemical stability and/or low biodegradability, e.g. textile wastewaters (Buthiyappan et al.; Gernjak et al., 2006; Kalra et al., 2011; Malato Rodríguez et al., 2004; Malato et al., 2007; Malato et al., 2003; Malato et al., 2009). More recently, many other studies dealing with the combination of biological and chemical oxidation processes for industrial wastewater decontamination have been reported (Cassano et al., 2011; Oller et al., 2011; Oller et al., 2007). AOPs based on Fenton's reaction chemistry like Fenton, electro-Fenton, photo-Fenton and photoelectro-Fenton have been showing interesting results on wastewater decolourisation (Moreira et al., 2013), but the needs for acidification/neutralization and iron removal steps, constitutes a barrier to its implementation. In this sense, among many advanced oxidation processes, the UVC/H_2O_2 system is one of the most commonly applied AOP (Karci et al., 2013; Liu et al., 2012), where hydroxyl radicals are generated through the photolysis of hydrogen peroxide under UVC radiation. Although the application of photochemical UVC/H_2O_2 oxidation systems for drinking water disinfection started in the 1990's, studies on the degradation of different organic pollutants in wastewaters have been only extensively investigated in the last years. These studies include the degradation of pesticides (Antoniou and Andersen, 2015), antibiotics (Jung et al., 2012) and dyes solutions on lab scale prototypes (Alaton et al., 2002; Basturk and Karatas, 2015; Shu et al., 2005).

The high water consumption in the textile industry, up to 150 L of water is required to produce a kilogram of textile product (Allègre et al., 2006; Chidambaram et al., 2015), and the scarcity in certain regions has caused the increase of water costs. In addition, the new environmental policies are focused on water recycling and reuse. Wastewater reuse involves both environmental and economic benefits. Despite the evident reuse potentials within the textile industry, state of the art indicates that implementation of water reuse is still an uncommon practice (Vajnhandl and Valh, 2014). The reuse of wastewater for irrigation is practised in some countries of the world (Bhuiyan et al., 2016). However, new perspectives about onsite reuse of the textile wastewater, after adequate treatment, in the different textile processing steps have been emerged (Bhuiyan et al., 2016; Buscio et al., 2015; Zou, 2015). The literature shows different technologies to treat and reuse textile effluents (Blanco et al., 2012), most of them including the use of membranes, often combined with other treatments (Sahinkaya et al., 2008; Zuriaga-Agusti et al., 2010). Indeed, the combination of different processes is usually required to obtain an effluent with the required final quality for reuse purposes.

This study aims to assess the decolourisation of two bio-treated real textile wastewaters, from cotton and synthetic fibres dyeing, using a photochemical UVC/H_2O_2 oxidation system as a polishing step, towards onsite water reuse. The efficiency of hydrogen peroxide photolysis under UVC radiation on the decolourisation of the wastewaters was evaluated at different H_2O_2 dosages, temperature and pH values. The biodegradability of the textile wastewaters was evaluated through a Zahn-Wellens test at different photochemical oxidation times. In addition, the reuse of photochemical-treated textile wastewater in cotton bleaching and dyeing processes was also evaluated.

2. Experimental methodology

2.1. Bio-treated real textile wastewaters

Bio-treated real textile wastewater samples were collected in two different textile wastewater treatment plants (WWTP) located in southern Brazil. Both WWTP comprise the following treatment units: equalization tank; neutralization tank; activated sludge biological reactor; sedimentation tank; and coagulation/flocculation system. Both bio-treated real textile wastewater samples were collected at the outlet of the sedimentation tank. Table 1 shows their main physicochemical characteristics.

Insert Table 1

2.2. Chemicals

Hydrogen peroxide was purchased from Merck (30% (w/v), concentrated sulphuric acid and sodium hydroxide, both of analytical grade and used for pH adjustment, were supplied by LAFAN Química Fina Ltda. Ultrapure water and distilled water were produced in a Millipore® (model Direct-Q) and a Biopar distiller (model BD5L), respectively.

The following chemicals were used in the fabrics bleaching process: sodium silicate and magnesium sulphate heptahydrate were purchased from VETEC Química Fina LTDA and hydrogen peroxide 130 vol. from LAFAN Química Fina Ltda. Two direct dyes (Direct Red 80 and Direct Blue 71) and sodium sulphate (Quimibrás S.A.) were used in the cotton dyeing process. A non-ionic humectant (Manchester Chemical S.A.) was used in the bleaching process and in the cotton dyeing process. Before the dyeing process, catalase 0.1 g L^{-1} (Sigma Aldrich, 2500 U mg^{-1} bovine liver) was employed for H_2O_2 elimination.

2.3. Analytical determinations

Prior to the analyses, all samples, with the exception of those for the determination of chemical oxygen demand (COD), total suspended solids (TSS) and volatile suspended solids (VSS), were centrifuged in a JOUAN SA B 4i centrifuge at 4000 rpm for 5 minutes. That procedure was necessary since, for these wastewaters, the filtration procedure retained uneven amounts of dyes, which could compromise the results.

The following parameters were monitored: H_2O_2 (vanadate method) (Nogueira et al., 2005), alkalinity (titration with H_2SO_4 at pH 4.5 - Method 2320 D) (Rice et al., 2012), pH, temperature and conductivity were measured using a pH meter AZ ®, model 86505, biochemical oxygen demand (BOD_5) (OXITOP# system - Method 5210 B) (Rice et al., 2012). Sulphate, chloride, nitrate and phosphate were measured according to the method 4110 B (Rice et al., 2012). Nitrite, total nitrogen and total dissolved phosphorous were measured according to the methods 4500 NO_2B, method 4500 N C and 4500 P E, respectively (Rice et al., 2012). Ammonium was measured according to the ISO 14911:1998 (ISO, 1998). The dissolved organic carbon (DOC) was measured using a Shimadzu - TOC-V_{CPH} (Method 5220 D) (Rice et al., 2012).

A 28 days biodegradability test (Zahn–Wellens test) was performed according to the EC protocol, Directive 88/ 303/EEC (OECD, 1992). Activated sludge from a municipal WWTP of Porto, Portugal, previously centrifuged, and mineral nutrients (KH_2PO_4, K_2HPO_4, Na_2HPO_4, NH_4Cl, $CaCl_2$, $MgSO_4$ and $FeCl_3$) were added to the samples. The control and blank experiments were prepared using glucose and distilled water, respectively. The percentage of biodegradation (D_t) was determined by equation (EPA, 1996):

$$D_t = \left[1 - \frac{C_t - C_B}{C_A - C_{BA}}\right] \times 100 \tag{1}$$

where C_A and C_{BA} are the DOC (mg L^{-1}) in the sample and in the blank, measured 3 hours after the beginning of the experiment, C_t and C_B are the DOC (mg L^{-1}) in the sample and in the blank, measured at the sampling time *t*.

Two different methods were used for the colour measurement: i) the absorbance at three wavelengths, 436, 525, and 620 nm according to the standard DIN EN ISO 7887:2012 (Standardization, 2012) and; ii) the platinum-cobalt (Pt-Co) method, at a wavelength of 400 nm (Rice et al., 2012). The spectrophotometric measurements to obtain the textile wastewaters' UV absorption spectra and to determine the concentration of H_2O_2 were carried out with a UV-Vis model V-1200 spectrophotometer. All analytical procedures are reported elsewhere (Soares et al., 2016).

A spectrophotometer (CM 3600A; Konica Minolta Co. Ltd.) was used to measure the colour of the samples in the L*a*b* colour space. The instrument was calibrated with a white and black balance according to the Konica Minolta calibration procedure. The L*a*b* colour space is a colour system that contains complementary colour pairs to calculate colour differences (ΔE*) (Eq. 2) (American Association of Textile Chemists and Colorists, 2010), and is based on:

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{2}$$

According to American Association of Textile Chemists and Colorists (2010, the colour difference (ΔE*) is described by a three-dimensional coordinate system. The parameter a* extends from green (–a*) to red (+a*) and value b* from blue (–b*) to yellow (+b*). Both a* and b* vary between (-120) to (+120). Parameter L* stands for the colour brightness. A value of lightness L* = 0 indicates black, and value L* = 100 stands for white.

The whiteness index of different bleached cotton fabric samples was measured according to AATCC test method 110-1995 (American Association of Textile Chemists and Colorists, 2010), which was also performed by colour measurement at the Konica Minolta spectrophotometer (model CM 3600A).

2.4. Experimental set-up

All photochemical oxidation reactions were performed in a lab-scale tubular photo-reactor (Fig. 1), which was already shown by Soares et al. (2016 and comprised: i) a photo-reactor in which a borosilicate tube is associated with an internal concentric quartz tube containing a UVC lamp, the former being positioned in the focus of two stainless steel reflectors; ii) a glass vessel (1.5 L capacity) with a cooling jacket coupled to a refrigerated thermostatic bath; iii) a gear pump (Ismatec, model BVP-Z, with a flow rate of 1.6 L min^{-1}) to recirculate the water between the photo-reactor and the glass vessel; and iv) a pH and temperature meter (pH meter AZ®, model 86505). The incident light flux, determined by the hydrogen peroxide (Nicole et al., 1990) actinometry method, was 0.88 J_{UV} s^{-1} (6W lamp power). The amount of UV energy ($Q_{UV,n}$, in kJ L^{-1}) accumulated inside the reactor within a time interval Δt per unit of volume of solution was calculated by Eq. (3):

$$Q_{UV,n} = pf \frac{t_n}{V_S \times 1000} \tag{3}$$

where *pf* is the photonic flux reaching the system (in J_{UV} s^{-1}), t_n is the time corresponding to the *n* sample (in s), V_s is the solution volume (in L) and 1000 is a conversion factor (in J kJ^{-1}).

The photo-reactor is inside a stainless steel box for security reasons, since it blocks the UVC radiation, even knowing that the borosilicate tube transmissibility for UVC radiation is almost negligible.

Insert Figure 1

2.5. Experimental procedure

During the photochemical treatment, for each trial, 1.2 L of the textile wastewater was added to the glass vessel and homogenized by recirculation in the dark. The set-point of the refrigerated thermostatic bath was controlled to give the intended temperature (15, 23 and 35ºC). The wastewaters pHs were adjusted using sulphuric acid or sodium hydroxide (3.0, 5.0, 9.0). The UVC radiation source was turned on (0.88 J_{UV} s^{-1}) and hydrogen peroxide was added (3.8, 9.0, 12.5, 25.0 and 39.0 mM H_2O_2). Samples were taken at pre-defined time intervals to evaluate the decolourisation process.

For reuse tests, the bleaching and dyeing procedures are shown in Fig. 2. The cotton bleaching process was carried out in a bleaching machine (Mathis WJ – touch 35, Werner Mathis AG) and it was done using a ratio between the amount of fibre to be bleached and the bathwater of 1:6 (kg:L). The cotton dyeing process was carried out in a dyeing machine for small samples (Mathis ALT-B, Werner Mathis AG), using a ratio between the amount of fibre to be dyed and the water used in the bath of 1:10 (kg:L). It is important to note that photochemical treated textile wastewater – PTWB shows a considerable sulphate concentration (459 mg SO_4^{2-} L^{-1}) (Table 1), which was considered during the bleaching and dyeing processes when the PTWB was used as bathwater. In the same way, the residual concentration of H_2O_2 found in PTWB after UVC/H_2O_2 was also considered during the bleaching process and removed before the dyeing process, through the addition of catalase (0.1 g L^{-1}).

Insert Figure 2

3. Results and discussion

3.1. Characteristics of the bio-treated real textile wastewaters

The textile wastewater TWA shows an intense greenish colour, equivalent to 420 mg Pt-Co L^{-1} and 32.5 m^{-1} (DFZ_{436nm}), 27.8 m^{-1} (DFZ_{525nm}) and 31.6 m^{-1} (DFZ_{620nm}), which indicates high values of absorbance throughout the spectrum. The textile wastewater TWB also shows an intense colourisation but in this case the predominant colour is purple, resulting from the mixture of different dyes and showing colour indicators equivalent to 140 mg Pt-Co L^{-1} and 13.2 m^{-1} (DFZ_{436nm}), 10.7 m^{-1} (DFZ_{525nm}) and 6.3 m^{-1} (DFZ_{620nm}) (Table 1). The high values of colour indicators show a low decolourisation efficiency of the biological treatment, which is in agreement with the results reported in other studies (Araña et al., 2013; Barragán et al., 2007; Kandelbauer and Guebitz, 2005).

Both TWA and TWB show low values of organic load, 79 mg C L^{-1} and 83 mg C L^{-1}, and low biodegradability, 18% and 15% (Zahn-Wellens test), respectively. The biodegradability given by the Zahn-Wellens test was in agreement with the BOD_5/COD ratio (0.16 for TWA and 0.20 for TWB).

Both wastewaters show a near neutral pH value and high conductivity mainly related to the high amounts of chlorides and sulphates salts widely used on the cotton dyeing (Bisschops and Spanjers, 2003). While the TWB has a high concentration of nitrogen and a considerable presence of phosphorus, the TWA shows low values of both. The first one is associated with the intensive use of textile auxiliaries as surfactants, lubricants and crease inhibitors, and the second is present in various textile auxiliaries used as dispersing, sequestering and wetting agents.

The bio-treated real textile wastewaters were found to be in accordance with the Brazilian regulations (CONAMA, 2005; CONAMA, 2011) for discharge into water bodies with the exception for the colour limits. Although the Brazilian legislation does not set numerical limits for wastewater colour, determines that the release of wastewater may not modify the original feature of the water receiving bodies, and in this case, the colour limit for watercourses is 75 mg Pt-Co L^{-1} (CONAMA, 2005). Additionally, the German textile wastewater discharge standard (Germany, 2009) was also used during this study, which establishes 7 m^{-1} (DFZ_{436nm}), 5 m^{-1} (DFZ_{525nm}) and 3 m^{-1} (DFZ_{620nm}) as maximum values for textile wastewater colour. This legislation was also considered for two main reasons: i) a simple and efficient technique for colour measurement based on DIN EN ISO:7887 (Standardization, 2012); and ii) instead of Brazilian legislation, which consists in a generalist law, the German law has a specific legislation for textile wastewaters with specific limits for colour parameter. So, also considering the colour discharge limits imposed by German law, both bio-treated textile wastewaters cannot be discharged in water receiving bodies before additional treatment targeting colour removal.

3.2. Photochemical oxidation

A photochemical oxidation process (UVC/H_2O_2) was applied to the bio-treated textile wastewaters as a polishing step, targeting colour removal (Fig. 3 and Table 2). All reactions were carried out with a 6 W UVC lamp, at 23°C of temperature, natural wastewaters pH (TWA = 8.1 and TWB = 7.7) and using 25.0 mM of H_2O_2 as initial dosage. Further reactions with UVC (6 W UVC lamp) or H_2O_2 (25.0 mM H_2O_2) alone were also performed.

Insert Figure 3

UVC or H_2O_2 alone were not efficient in the decolourisation of the TWA, which suggests that this wastewater is photolytically stable under UVC radiation and the oxidizing potential of H_2O_2 is not sufficient to decolourise the wastewater. For the TWB, a small colour abatement was observed with H_2O_2 in the initial phase of the reaction, achieving 12.3% (Pt-Co method), 17.0% (DFZ_{436nm}), 17.1% (DFZ_{525nm}) and 25.9% (DFZ_{620nm}) of decolourisation. Also, the UVC photolysis of the TWB resulted in a small increase in the Pt-Co indicator and a decrease in the DFZ_{525nm} and DFZ_{620nm} indicators. This can be associated with the hypsochromic shift of the dyes molecules under irradiation, resulting in the displacement of the absorption to shorter wavelength (Irie, 2000; Oliveira et al., 2002; Queiroz et al., 2000; Tehrani Bagha et al., 2007).

Unlike the reactions with UVC and H_2O_2 alone, the photolysis of hydrogen peroxide using UVC radiation showed high potential for the decolourisation of both wastewaters. As expected, there is a strong contribution of $^{\bullet}OH$ generated from H_2O_2 cleavage under UVC radiation (Eq. 4).

$$H_2O_2 \xrightarrow{h\nu} 2^{\bullet}OH \quad (4)$$

For the TWA, the UVC/H_2O_2 system showed colour reduction of 81% (Pt-Co method), 83% (DFZ_{436nm}), 88% (DFZ_{525nm}) and 86% (DFZ_{620nm}) with 25.0 mM H_2O_2 (consuming only 7.1 mM) after 8.3 $kJ_{UVC}\,L^{-1}$ (180 min). On the other hand, the observed decolourisation for TWB was 68% (Pt-Co method), 72% (DFZ_{436nm}), 76% (DFZ_{525nm}) and 69% (DFZ_{620nm}) with 25.0 mM H_2O_2 (consuming only 4.4 mM) after 5.5 $kJ_{UVC}\,L^{-1}$ (120 min). Further UVC/H_2O_2 reactions were performed, for both wastewaters, in order to evaluate the effect of different reaction variables, such as H_2O_2 dosage, wastewater pH and temperature.

Insert Table 2

3.2.1. Effect of H_2O_2 dosage

The H_2O_2 concentration plays an important role in the efficiency of the UVC/H_2O_2 system, since it can greatly affect the colour removal due to low availability of hydroxyl radicals produced at a low H_2O_2 concentration; while a too high H_2O_2 concentration could also inhibit the decolourisation rate because H_2O_2 could compete for $HO^{\bullet}$ inhibiting the oxidation of the target organic compounds, as shown in Eq. (5) (Shah et al., 2013; Soares et al., 2016; Zalazar et al., 2007; Zhou et al., 2012).

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \quad (5)$$

Besides, according to the lamp power and reactor pathlength, there is an optimal H_2O_2 concentration that is able to maximize the absorption of the UVC photons. Therefore, the influence of H_2O_2 dosage on the photochemical treatment of the bio-treated textile wastewaters was assessed in the range 3.8-39.0 mM (Fig. 4). For both TWA and TWB, the decolourisation rates increase significantly with the availability of hydrogen peroxide, being twelve times higher for the H_2O_2 dose of 39.0 mM when compared with 3.8 mM for TWB decolourisation and, six times higher for TWA decolourisation in the same dosage range.

Insert Figure 4

As can be seen in Fig. 4, considering the TWA decolourisation reactions, the possible inhibiting effect of a high H_2O_2 concentration - cited above - was not observed, probably because the H_2O_2 concentration did not reach such a high level. For the TWB decolourisation assays it was observed that for H_2O_2 dosages higher than 25.0 mM the reaction rates remain almost unchanged, indicating that an equilibrium between the $^{\bullet}OH$ radicals and H_2O_2 concentrations was achieved, and an increase in the hydrogen peroxide concentration cannot enhance the free radical concentration. However, even not resulting in an improvement in the reaction rate, higher dose of H_2O_2 (39.0 mM) showed a considerable increase in the hydrogen peroxide consumption, resulting in a consumption rate two times higher when compared with the reaction at 25.0 mM H_2O_2. The evaluation of the decolourisation by platinum-cobalt method – Pt-Co (Fig. 4) and DFZ indicators showed good agreement with each other and with the visual observations, as can be seen in Fig. 5. The exception was the DFZ_{620nm} profiles during the photochemical treatment of the TWB, which showed inconsistent data probably because of the extremely low values observed for this indicator.

It is important to highlight that high residual H_2O_2 concentrations are obtained at the end of the assays, especially when high H_2O_2 dosages were used. So, the complete decomposition of the H_2O_2 present in the wastewater, before its discharge to the aquatic environment, is a pressing need. However, considering the reuse of the wastewater in the fabrics bleaching process, the presence of H_2O_2 can be beneficial.

Insert Figure 5

3.2.2. Effect of pH

The UVC/H_2O_2 reaction was tested at different initial pH values (3.0; 5.0; natural wastewaters pH (TWA = 8.1; TWB = 7.7) and 9.0), considering a T = 23ºC; 6W UVC lamp; [H_2O_2] = 25.0 mM. As shown in Fig. 6, the preliminary action of raising the reaction pH (Q_{UVC} < 0 kJ L^{-1}) virtually does not change the colour indicators for both wastewaters. On the other hand, for the TWA, the preliminary acidification step resulted in a small increase of the absorption in shorter wavelengths, observed by Pt-Co and DFZ_{436nm} colour indicator and, an considerable absorbance decrease in higher wavelengths, reaching almost 20% of reduction for both DFZ_{525nm} and DFZ_{620nm} colour indicators. This effect can be related to the dissociation of some dyes present in the wastewater, which leads to different absorption properties as a pH function (Ebead, 2010; Gomes et al., 2012; Pérez-Urquiza and Beltrán, 2001). The results for TWB were opposite to that observed for TWA during the acidification step, where all colour indicators suffered a reduction.

Insert Figure 6

After the radiation was turned on, the influence of solution pH in the decolourisation process was different for the TWA and TWB wastewaters. While the TWA decolourisation under natural wastewater pH (pH = 8.1) shows better colour removal when compared with reactions under alkaline or acidic conditions, the decolourisation of TWB was most efficient at acidic and alkaline pH values, which resulted in a decolourisation rate up to three times higher than the reaction at neutral pH (Table 2).

The observed difference in the decolourisation assays at equivalent conditions can be a consequence of differences in structural features of the dyes present in the wastewaters. For example, although the mechanism of radical •OH reactions with dyes is still not clear, theoretical methods using quantum mechanical calculations and proposed reaction mechanisms based on product analysis have revealed that the addition of radical •OH to the azo bond is more favorable than addition to the C–N bond (Ince and Tezcanli-Güyer, 2004; Özen et al., 2003).

In addition, some studies describe that the UVC/H_2O_2 system conducted in acidic medium is more efficient in the colour removal (Arslan-Alaton et al., 2008; Muruganandham and Swaminathan, 2004; Saharan et al., 2011). Galindo and Kalt (1999) attributed this fact to changes in the dye structure as a function of solution pH, whereas for Basturk and Karatas (2015) and for Arslan-Alaton et al. (2008) the probably reason is the fast decomposition of hydroxyl radicals and hydrogen peroxide at high pH and fast reaction of radicals with the organic dyes molecules at low pH value.

For both TWA and TWB, when the solution pH was alkaline (pH 9.0), it was observed a substantially increment on the hydrogen peroxide consumption (Fig. 7), which was not reflected in an increase of the decolourisation rates. In alkaline medium, the H_2O_2 becomes highly unstable and self-decomposition occurs, which is strongly pH dependent (Chan et al., 2004). The self-decomposition will rapidly break down the H_2O_2 molecules into water and oxygen and they lose their characteristics as an oxidant, and most importantly as source of hydroxyl radicals (Eq. 6).

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{6}$$

Insert Figure 7

3.2.3. Effect of temperature

It has been reported that, in general, the increment on temperature favours the UVC/H_2O_2 reaction rate, suggesting that the generation of $^{\bullet}OH$ radicals through H_2O_2 photolysis is enhanced (Alnaizy and Akgerman, 2000; Sanz et al., 2013; Stapleton et al., 2009). However, it is worth to mention that the influence of temperature can also be conditioned by the nature of contaminant, as already observed by Camarero et al. (2003 for an indigo carmine dye (5,5-indigo sulfonate disodium (5,5-IDS). Fig. 8 shows the effect of temperature on the decolourisation of the bio-treated wastewaters using the UVC/H_2O_2 system.

Insert Figure 8

Considering all colour indicators monitored during TWA photochemical treatment, it was observed that the decolourisation rates were always favoured at higher temperatures, in agreement with the Arrhenius' Law, resulting in activation energy of 50 ± 2 kJ mol^{-1} (considering the kinetic constants for Pt-Co profiles). Unfortunately, the thermal decomposition of peroxide, and the consequent formation of H_2O and O_2 (inactive species) (Eq. 6), is also favoured with temperature, which resulted in a substantial increase of H_2O_2 consumption, especially when the temperature was increased from 23ºC to 35ºC (Figure 9).

Even though the increment on temperature resulted in higher decolourisation rates for both wastewaters, it is possible to observe that the effect on TWB is not in agreement with the Arrhenius' Law, since the activation energy observed when the temperature rises from 15 to 23ºC was 8 kJ mol^{-1} and from 23 to 35ºC was 73 kJ mol^{-1}, which indicates that temperature has produced different effects for each tested temperature range.

Insert Figure 9

3.2.4. Biodegradability evaluation

In order to observe how the UVC/H_2O_2 reaction affects the wastewaters biodegradability, samples were taken at different time intervals during the photochemical oxidation and a Zahn-Wellens test was conducted (Fig. 10). The raw TWA and TWB wastewaters show low biodegradability, 18% and 15%, respectively.

The photochemical oxidation improved the TWA biodegradability in more than 60%, from 18% to 80% after 9.7 kJ_{UVC} L^{-1}. As observed with TWA, the TWB biodegradability also increased during the photochemical oxidation, achieving 53% of biodegradable organic carbon after an accumulated UV energy of 5.4 kJ_{UVC} per litre of solution. Therefore, despite the organic matter content has remained constant throughout the photochemical oxidation (final DOC values of 76 and 79 mg C L^{-1} for TWA and TWB, respectively), the biodegradable organic fraction increased significantly for both wastewaters. This means that the UVC/H_2O_2 system was able to break the original recalcitrant molecules into more simple and biodegradable ones.

Insert Figure 10

3.3. Recycling of the PTWB in the processing of cotton fabric

The textile dyeing process consumes more than 150 litres of water per kilogram of fibre processed (Vajnhandl and Valh, 2014). Textile wastewater recycling can represent a cost saving for the textile industry as also a big contribution for sustainable water resources management and ecosystem protection (Bhuiyan et al., 2016; Buscio et al., 2015; Vajnhandl and Valh, 2014; Zheng et al., 2015). Therefore, in this work, the recycling of the photochemical-treated real textile wastewater (PTWB) was also tested as bathwater during the cotton bleaching and dyeing processes.

3.3.1. Bleaching process

The bleaching process destroys the natural pigments present in cotton to impart permanent whiteness. The bleaching process was carried out according to the process described in Fig. 2 using two bathwaters: the photochemical-treated wastewater and distilled water.

The efficiency of bleaching can be measured by determining the weight loss. Commercially 4–8% weight loss is acceptable for cotton fibre (Karmakar, 1999). The weight loss observed in both bleaching processes was inside the range cited above; 4.5% of weight loss when the distilled water was used as bathwater and 4.1% of weight loss when the PTWB was used as bathwater. The bleaching performance was also analysed through the whiteness index of the fabric samples. In general, bleached samples having whiteness index between 75 and 85 are commercially acceptable (Bhuiyan et al., 2016). However, the whiteness level targeted in the bleaching process depends on the end use of the fabrics and consequently, when higher whiteness is required it is necessary to perform a repeated oxidizing treatment, i.e. short time pre-bleaching with hypochlorite, followed by peroxide bleaching (Tzanov et al., 2003). In this case, a single bleaching step with H_2O_2 (12 g L^{-1}) was carried out, and the whiteness index (WI) obtained using PTWB as bathwater was very similar to the WI obtained for the sample bleached with distilled water as bathwater (58.3 for bleaching process with PTWB and 59.8 for bleaching with distilled water).

Another bleaching performance indicator used was the colour deviation (ΔE^*), which shows the colour differences between samples (American Association of Textile Chemists and Colorists, 2010). The colour deviation observed for the bleaching processes comparison was 1.58, which indicates that the difference between samples was small (Standardization, 2012), with a slight tendency to a less white fabric when the PTWB was used as bathwater (Supplementary Material, Figures S1 and S2).

It is important to highlight that, in addition to water reuse, the bleaching process with PTWB can enable the reduction of costs with consumables, since the presence of hydrogen peroxide and sulphate in PTWB reduced the amount of these compounds to be added in 6.3% and 11.5%, respectively.

3.3.2. Dyeing process

Dyeing is the process of colouring textile materials by immersing into an aqueous solution containing dye (Bhuiyan et al., 2016). The dyeing of cotton knit fabric is usually carried out following scouring and bleaching. The dyeing processes were carried out according to the scheme showed in Fig. 2, wherein two different dyes were tested, Direct Red 80 (C.I.35780) and Direct Blue 71 (C.I.34140). The bio-treated wastewater (TWB), the photochemical-treated wastewater (PTWB), a mix of 50% of the PTWB with distilled water were used as bathwater in dyeing of cotton. The dyeing performance was evaluated in terms of colour differences with that of the standard (dyeing process with distilled water).

First of all, the bio-treated wastewater (TWB) was used as dyeing bathwater in order to know its reuse potential before photochemical treatment. As can see in Table 3, for both used dyes, the dyeing process with TWB showed extremely high colour differences (ΔE^*) when compared with the standard dyeing process (dyeing process with distilled water), demonstrating the inability to reuse the bio-treated textile wastewater in the dyeing processes tested (Supplementary Material, Figures S3-S9).

The reuse of PTWB as bathwater in the dyeing process was tested using only photochemical-treated textile wastewater and in a mix with distilled water (50% PTWB - 50% distilled water). While all samples dyed with Direct Red 80 showed elevated values of colour differences when compared with standard dyeing process, the dyeing processes with Direct Blue 71 dye using a mix of PTWB and distilled water as bathwater resulted in similar samples ($\Delta E^* = 0.76$). However, the dyeing process with PTWB as bathwater, showed high value of colour differences, $\Delta E^* = 3.78$.

It is normal that the created colour does not completely match the given standard and can have a variation (Bhuiyan et al., 2016). According to DIN EN ISO 11664 (Standardization, 2012), colour difference (ΔE^*) values above 1.5 correspond to distinguishable differences, generally not accepted for the production of fabrics for the international market ($\Delta E^* < 1.0$).

Insert Table 3

As observed with bleaching process, in addition to water reuse, the dyeing process with PTWB can enable the reduction cost with consumables, since the presence of sulphate in PTWB reduced the addition necessity of this compound substantially.

4. Conclusions

The photochemical UVC/H_2O_2 oxidation system was able to achieve the decolourisation of two bio-treated textile wastewaters, as polishing step. UVC and H_2O_2 alone showed negligible colour removal, indicating that the hydroxyl radicals generated from hydrogen peroxide photolysis under

UVC radiation is the principal reaction mechanism. For both TWA and TWB, the decolourisation rates using the UVC/H_2O_2 system were favoured using higher hydrogen peroxide dosages and wastewater temperature. The wastewater composition plays an important role in the effect of wastewater pH on the photochemical UVC/H_2O_2 system, showing higher decolourisation rates at near neutral pH (8.1) for the TWA wastewater and at acidic or alkaline conditions for the TWB (3.0, 5.0 and 9.0) wastewater. Although the UVC/H_2O_2 system was not able to promote an efficient mineralization during the reaction period, the oxidation improved significantly the biodegradability of both wastewaters. Colour indicators of the oxidized wastewater were in agreement with the Brazilian and German discharge limits. Finally, the PTWB was used as bathwater during cotton bleaching and dyeing processes and, in both processes, the obtained samples showed good quality indicators when compared with the standard processes. In this sense, further studies should be done to establish the maximum percentage of photochemical-treated textile wastewater that can be reused and fulfil the more restrictive acceptance criteria.

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Legends

Figure 1. Views of the lab-scale lamp photoreactor.

Figure 2. Scheme of cotton fibres bleaching and dyeing processes.

Figure 3. Bio-treated real textile wastewaters decolourisation. Operation conditions: T = 23ºC; 6W UVC lamp; [H_2O_2] = 25.0 mM; pH_{TWA} = 8.1 and pH_{TWB} = 7.7. (■) - UVC; (●) – H_2O_2; (▲) – UVC/ H_2O_2.

Figure 4. Decolourisation of the bio-treated real textile wastewaters using the UVC/H_2O_2 system at different H_2O_2 dosages. Operation conditions: T = 23ºC; 6W UVC lamp; pH_{TWA} = 8.1 and pH_{TWB} = 7.7. Solid symbols – colour (mg Pt-Co L^{-1}); open symbols – H_2O_2 consumed. (●) - Pseudo-first-order kinetic constants (L kJ^{-1}); (○) - H_2O_2 consumption rates (mM kJ^{-1}); (▼,▽) - [H_2O_2] = 3.8 mM; (◆,◇) - [H_2O_2] = 9.0 mM; (⬟,⬠) - [H_2O_2] = 12.5 mM; (,) – [H_2O_2] = 19.0 mM; (▲,△) - [H_2O_2] = 25.0 mM; (▶,▷) - [H_2O_2] = 39.0 mM.

Figure 5. Evolution of the DFZ colour indicators during photochemical treatment of the bio-treated real textile wastewaters at different H_2O_2 dosages. Operation conditions: T = 23ºC; 6W UVC lamp; pH_{TWA} = 8.1 and pH_{TWB} = 7.7. (●) - Pseudo-first-order kinetic constants (L kJ^{-1}); (▼) - [H_2O_2] = 3.8 mM; (◆) - [H_2O_2] = 9.0 mM; (⬟) - [H_2O_2] = 12.5 mM; ( ) – [H_2O_2] = 19.0 mM; (▲) - [H_2O_2] = 25.0 mM; (▶) - [H_2O_2] = 39.0 mM.

Figure 6. Decolourisation of the bio-treated real textile wastewaters using the UVC/H_2O_2 system at different pH values. Operation conditions: T = 23ºC; 6W UVC lamp; [H_2O_2] = 25.0 mM. (●) - Pseudo-first-order kinetic constants (L kJ^{-1}); (■) – pH 3.0; (●) – pH 5.0; (▲) – natural wastewater pH (pH_{TWA} = 8.1 and pH_{TWB} = 7.7); (▼) – pH 9.0.

Figure 7. Consumption of H_2O_2 during photochemical treatment of the bio-treated real textile wastewaters at different pH values. Operation conditions: T = 23ºC; 6W UVC lamp;

$[H_2O_2]$ = 25.0 mM. (○) - H_2O_2 consumption rate (mM kJ^{-1}); (■) – pH 3.0; (●) – pH 5.0; (▲) – natural wastewater pH (pH_{TWA} = 8.1 and pH_{TWB} = 7.7); (▼) – pH 9.0.

Figure 8. Decolourisation of the bio-treated real textile wastewaters using the UVC/H_2O_2 system at different temperatures. Operation conditions: 6W UVC lamp; $[H_2O_2]$ = 25.0 mM; pH_{TWA} = 8.1 and pH_{TWB} = 7.7. (●) - Pseudo-first-order kinetic constants (L kJ^{-1}); (■) – T = 15ºC; (●) – T = 23ºC; (▲) – T = 35ºC.

Figure 9. Consumption of H_2O_2 during photochemical treatment of the bio-treated real textile wastewaters at different temperatures. Operation conditions: 6W UVC lamp; $[H_2O_2]$ = 25.0 mM; pH_{TWA} = 8.1 and pH_{TWB} = 7.7. (○) - H_2O_2 consumption rate (mM kJ^{-1}); (■) – T = 15ºC; (●) – T = 23ºC; (▲) – T = 35ºC.

Figure 10. Zahn–Wellens test for selected samples during the UVC/H_2O_2 treatment. Operation conditions: T = 23ºC; 6W UVC lamp; $[H_2O_2]$ = 25.0 mM; pH_{TWA} = 8.1 and pH_{TWB} = 7.7. (■) – Reference; (●) – 0 min (0 kJ_{UVC} L^{-1}); (▲) – 30 min (1.4 kJ_{UVC} L^{-1}); (▼) – 90 min (4.1 kJ_{UVC} L^{-1}); (◀) – 120 min (5.5 kJ_{UVC} L^{-1}); (▶) – 180 min (8.3 kJ_{UVC} L^{-1}); (   ) – 210 min (9.7 kJ_{UVC} L^{-1}).

Table 1. Characteristics of the bio-treated real textile wastewaters.

Parameters		Units	TWA	TWB
pH		Sorënsen scale	8.1	7.7
Conductivity		mS cm^{-1}	10.4	6.4
Alkalinity		mg $CaCO_3$ L^{-1}	814	589
COD – Chemical oxygen demand		mg O_2 L^{-1}	217	240
BOD_5 – Biochemical oxygen demand		mg O_2 L^{-1}	35	48
BOD_5/COD ratio		-	0.16	0.20
DOC - Dissolved organic carbon		mg C L^{-1}	79	83
Biodegradability - Zahn-Wellens test		%	18.3	15.5
Colour	DFZ_{436nm}	m^{-1}	32.5	13.2
	DFZ_{525nm}	m^{-1}	27.8	10.7
	DFZ_{620nm}	m^{-1}	31.6	6.3
	Pt-Co Scale	mg L^{-1}	420	150
Chloride		mg Cl^- L^{-1}	2122	1416
Sulphate		mg SO_4^{2-} L^{-1}	123	459
Total Dissolved Nitrogen		mg N L^{-1}	6.5	120.0
Nitrate		mg $N\text{-}NO_3^-$ L^{-1}	0.17	19.1
Nitrite		mg $N\text{-}NO_2^-$ L^{-1}	<0.02	0.20
Ammonia		mg $N\text{-}NH_4^+$ L^{-1}	2.0	0.8
Phosphate		mg $P\text{-}PO_4^{3-}$ L^{-1}	0.4	6.0
Total Dissolved Phosphorus		mg P L^{-1}	2.6	10.6
Total suspended solids		mg TSS L^{-1}	0.02	0.05
Volatile suspended solids		mg VSS L^{-1}	0.01	0.04

Table 2. Operational conditions and kinetic constants for UVC/H_2O_2 reactions.

$[H_2O_2]^a$	T^b	pH	Kinetic parameters							
			TWA				TWB			
			Decolourisation		H_2O_2 consumption		Decolourisation		H_2O_2 consumption	
			k^c	R^2	$k_H{}^d$	R^2	k^c	R^2	$k_H{}^d$	R^2
3.8	23	natural pH[e]	0.045±0.003	0.852	0.12±0.01	0.982	0.017±0.004	0.772	0.11±0.01	0.904
9.0			0.073±0.004	0.972	0.24±0.01	0.989	0.076±0.007	0.925	0.33±0.02	0.890
12.5			0.126±0.006	0.985	0.34±0.02	0.932	-	-	-	-
19.0			0.14±0.01	0.966	0.55±0.01	0.998	0.139±0.008	0.966	0.50±0.02	0.975
25.0			0.16±0.01	0.965	0.69±0.01	0.984	0.218±0.005	0.991	0.57±0.01	0.979
39.0			0.245±0.006	0.998	1.01±0.03	0.988	0.23±0.02	0.953	1.30±0.01	0.924
25.0	23	3.0	0.105±0.004	0.987	0.42±0.01	0.994	0.39±0.03	0.975	0.64±0.02	0.988
		5.0	0.112±0.003	0.993	0.44±0.02	0.978	0.58±0.05	0.962	0.69±0.01	0.994
		natural pH[e]	0.16±0.01	0.964	0.69±0.01	0.992	0.218±0.005	0.991	0.57±0.01	0.979
		9.0	0.141±0.004	0.993	0.85±0.03	0.974	0.46±0.03	0.976	1.01±0.06	0.973
25.0	15	natural pH[e]	0.087±0.003	0.989	0.29±0.01	0.985	0.200±0.006	0.993	0.40±0.02	0.940
	23		0.16±0.01	0.964	0.69±0.01	0.992	0.218±0.005	0.991	0.57±0.01	0.979
	35		0.34±0.02	0.990	1.9±0.1	0.945	0.69±0.07	0.960	1.54±0.05	0.983

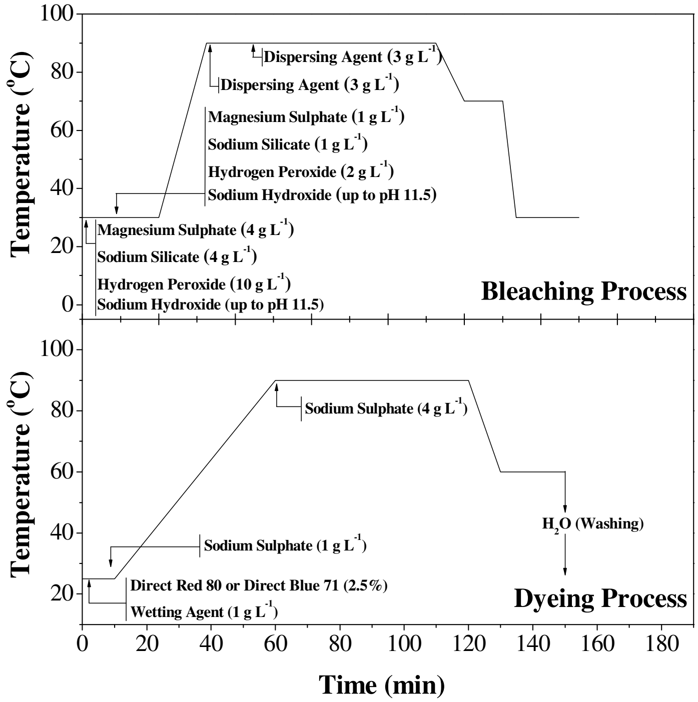
[a]H_2O_2 initial concentration (mM); [b]Temperature (ºC); [c](Pt-Co indicator) Pseudo-first-order kinetic constant (L kJ^{-1}); [d]H_2O_2 consumption rate (mmol kJ^{-1}); [e]pH_{TWA} = 8.1 and pH_{TWB} = 7.7.

Table 3. Colour difference values (ΔE) for dyeing using different direct dyes with different types of bath water.

Dyeing process	ΔL*	Δa*	Δb*	ΔE*
Direct Blue 71				
100% of distilled water				
50% of distilled and 50% of PTWB	-0.68	0.15	-0.32	0.76
100% of PTWB	-3.48	0.40	-1.42	3.78
100% of TWB	-5.05	0.64	-1.10	5.21
Direct Red 80				
100% of distilled water				
50% of distilled and 50% of PTWB	-3.10	5.18	1.43	6.20
100% of PTWB	-4.79	5.17	1.40	7.19
100% of TWB	-5.08	7.17	2.26	9.08

Figure 1.

Figure 2.



Temperature (°C)
Dispersing Agent (3 g L-1)
Dispersing Agent (3 g L-1)
Magnesium Sulphate (1 g L-1)
Sodium Silicate (1 g L-1)
Hydrogen Peroxide (2 g L-1)
Sodium Hydroxide (up to pH 11.5)
Magnesium Sulphate (4 g L-1)
Sodium Silicate (4 g L-1)
Hydrogen Peroxide (10 g L-1)
Sodium Hydroxide (up to pH 11.5)
Bleaching Process
Sodium Sulphate (4 g L-1)
H2O (Washing)
Sodium Sulphate (1 g L-1)
Direct Red 80 or Direct Blue 71 (2.5%)
Wetting Agent (1 g L-1)
Dyeing Process
Time (min)

Figure 3.

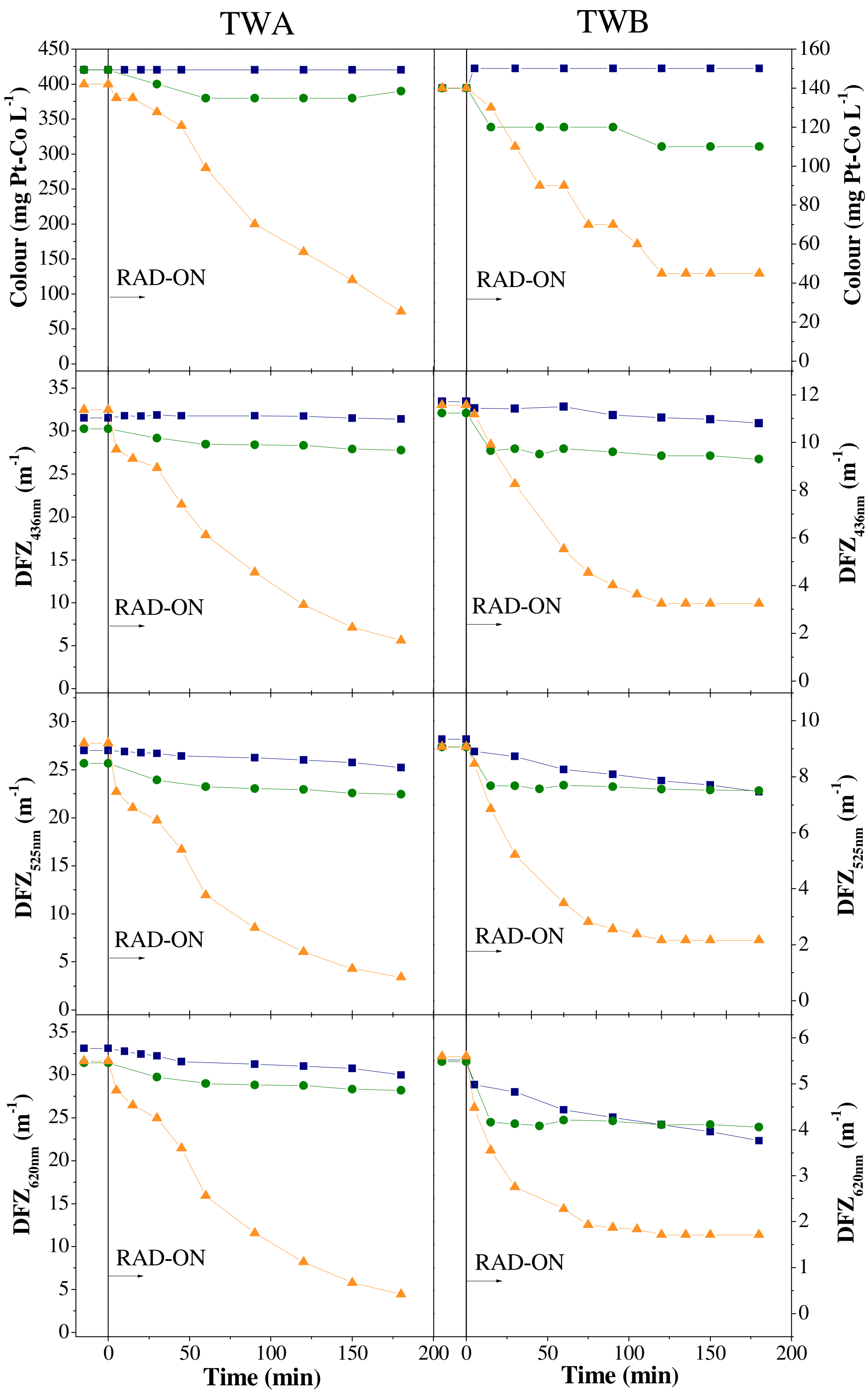

TWA
TWB
Colour (mg Pt-Co L^{-1})
DFZ$_{436nm}$ (m^{-1})
DFZ$_{525nm}$ (m^{-1})
DFZ$_{620nm}$ (m^{-1})
RAD-ON
Time (min)

Figure 4.

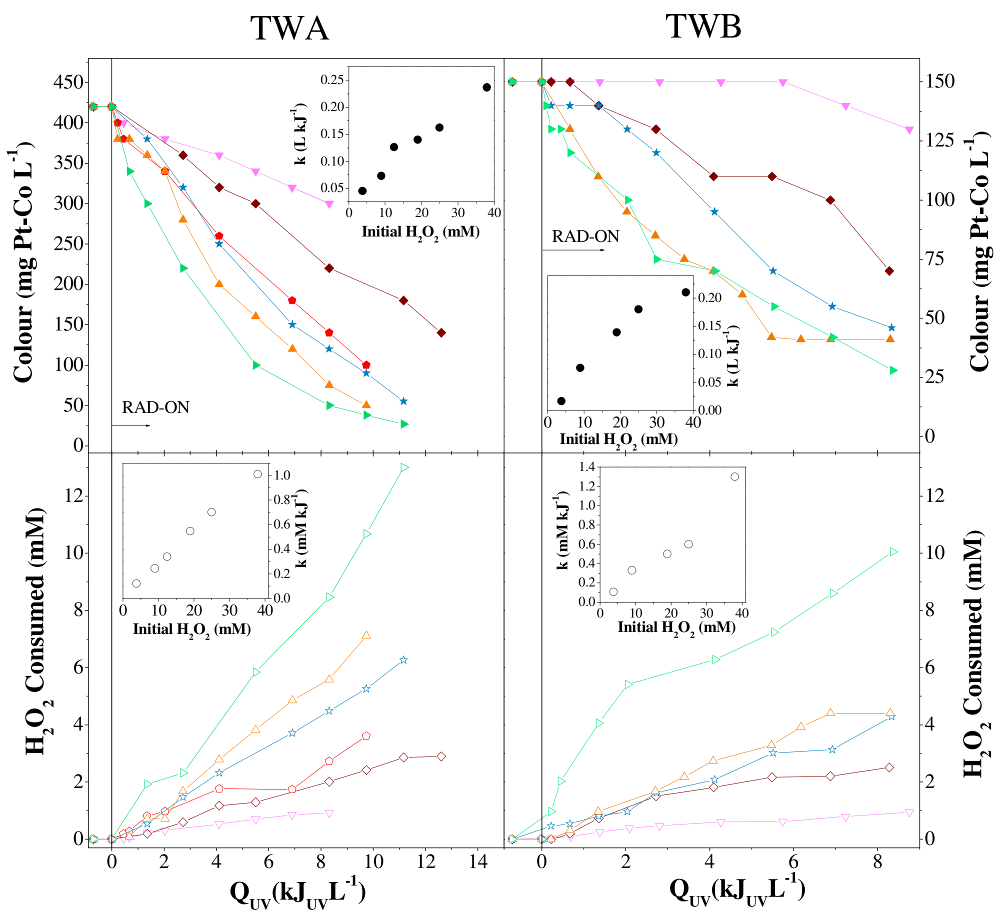

TWA
TWB
Colour (mg Pt-Co L^{-1})
k (L kJ^{-1})
Initial H_2O_2 (mM)
RAD-ON
H_2O_2 Consumed (mM)
k (mM kJ^{-1})
Q_{UV} ($kJ_{UV}L^{-1}$)

Figure 5.

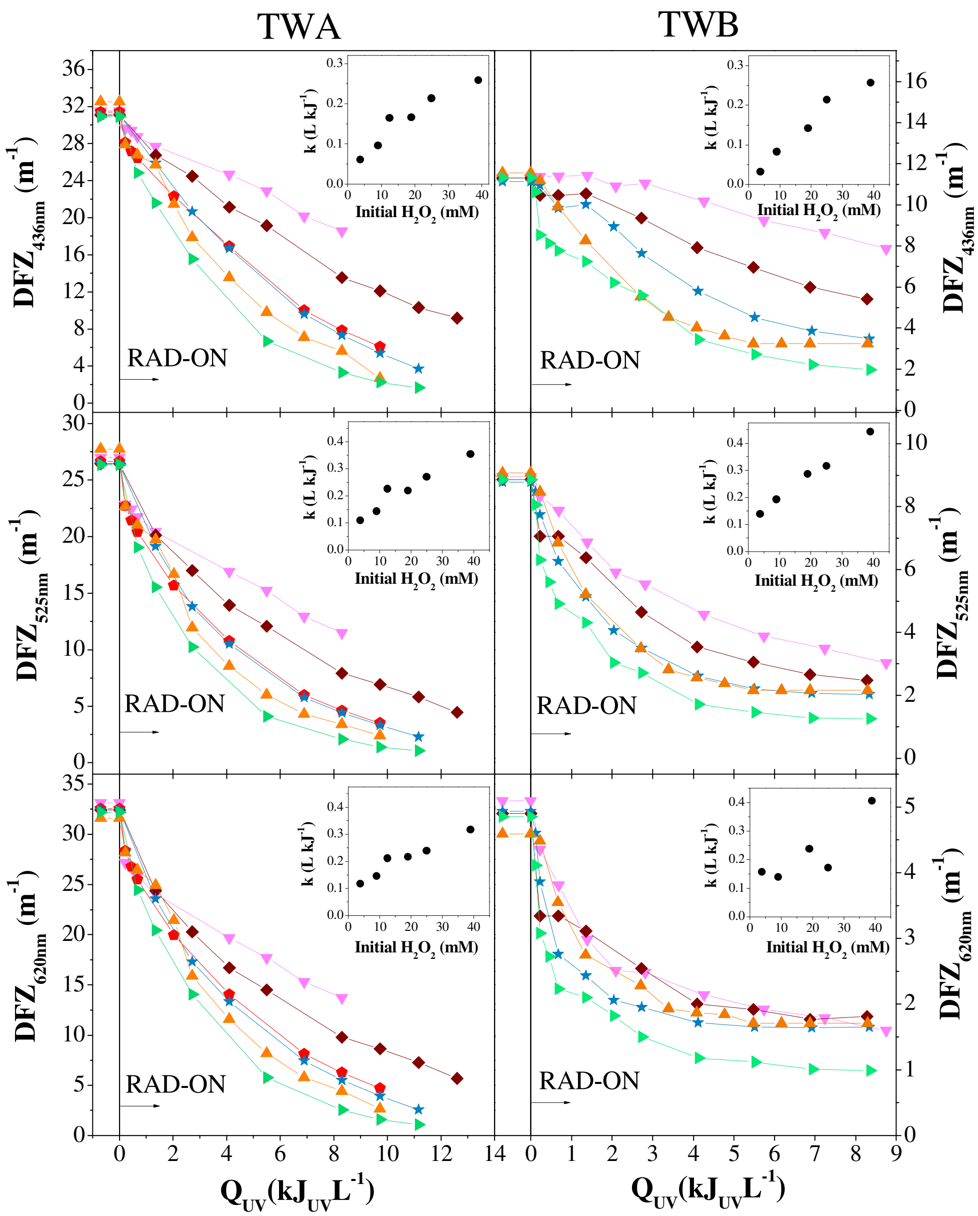

TWA
TWB
DFZ436nm (m-1)
DFZ525nm (m-1)
DFZ620nm (m-1)
RAD-ON
k (L kJ-1)
Initial H2O2 (mM)
QUV(kJUVL-1)

Figure 6.

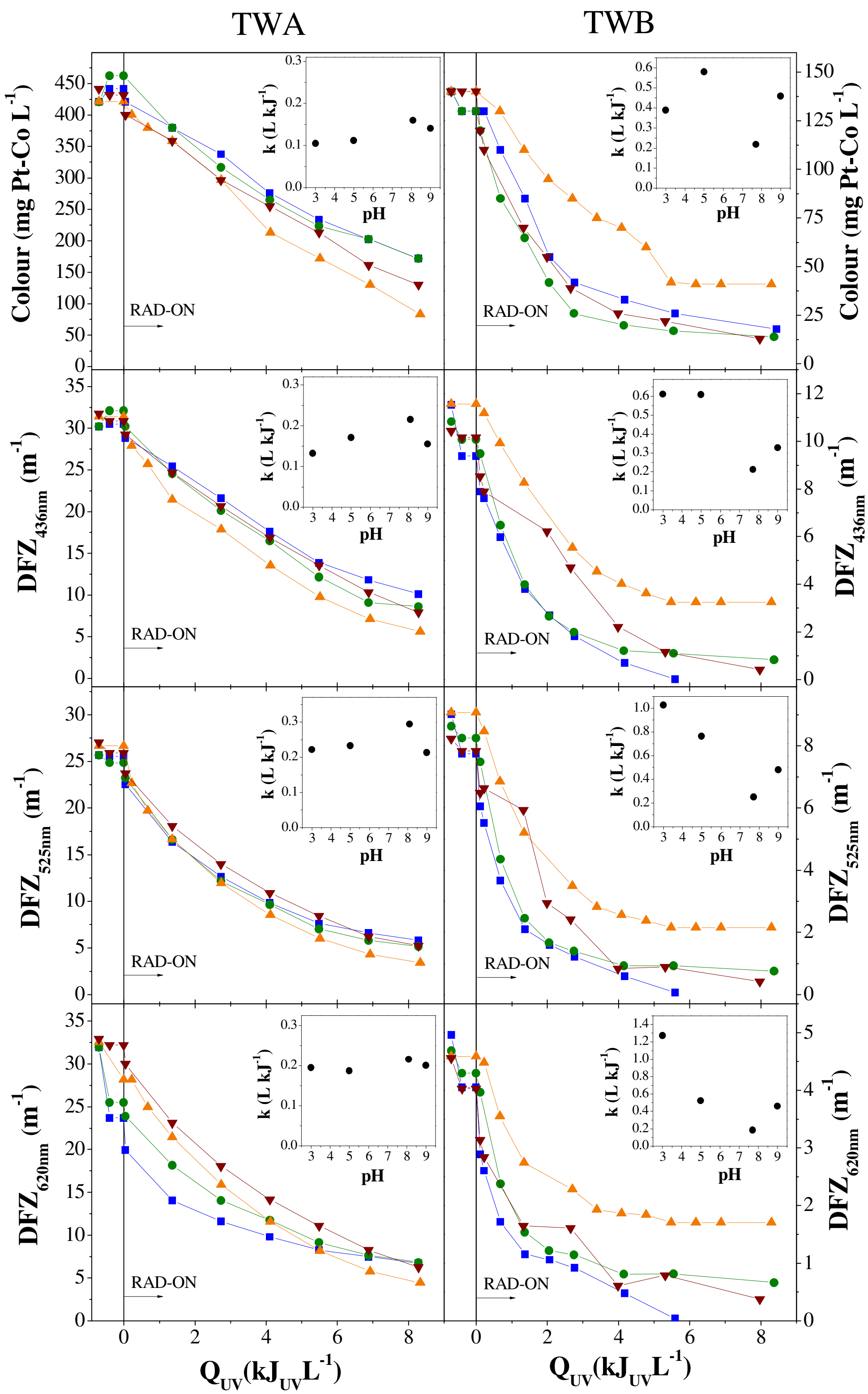

TWA
TWB
Colour (mg Pt-Co L^{-1})
DFZ$_{436nm}$ (m^{-1})
DFZ$_{525nm}$ (m^{-1})
DFZ$_{620nm}$ (m^{-1})
k (L kJ^{-1})
pH
RAD-ON
Q$_{UV}$(kJ$_{UV}$L^{-1})

Figure 7.

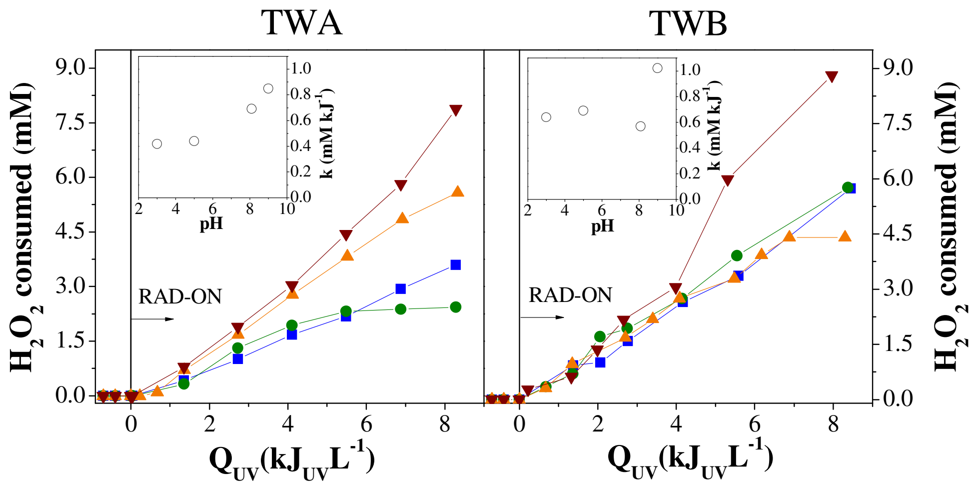
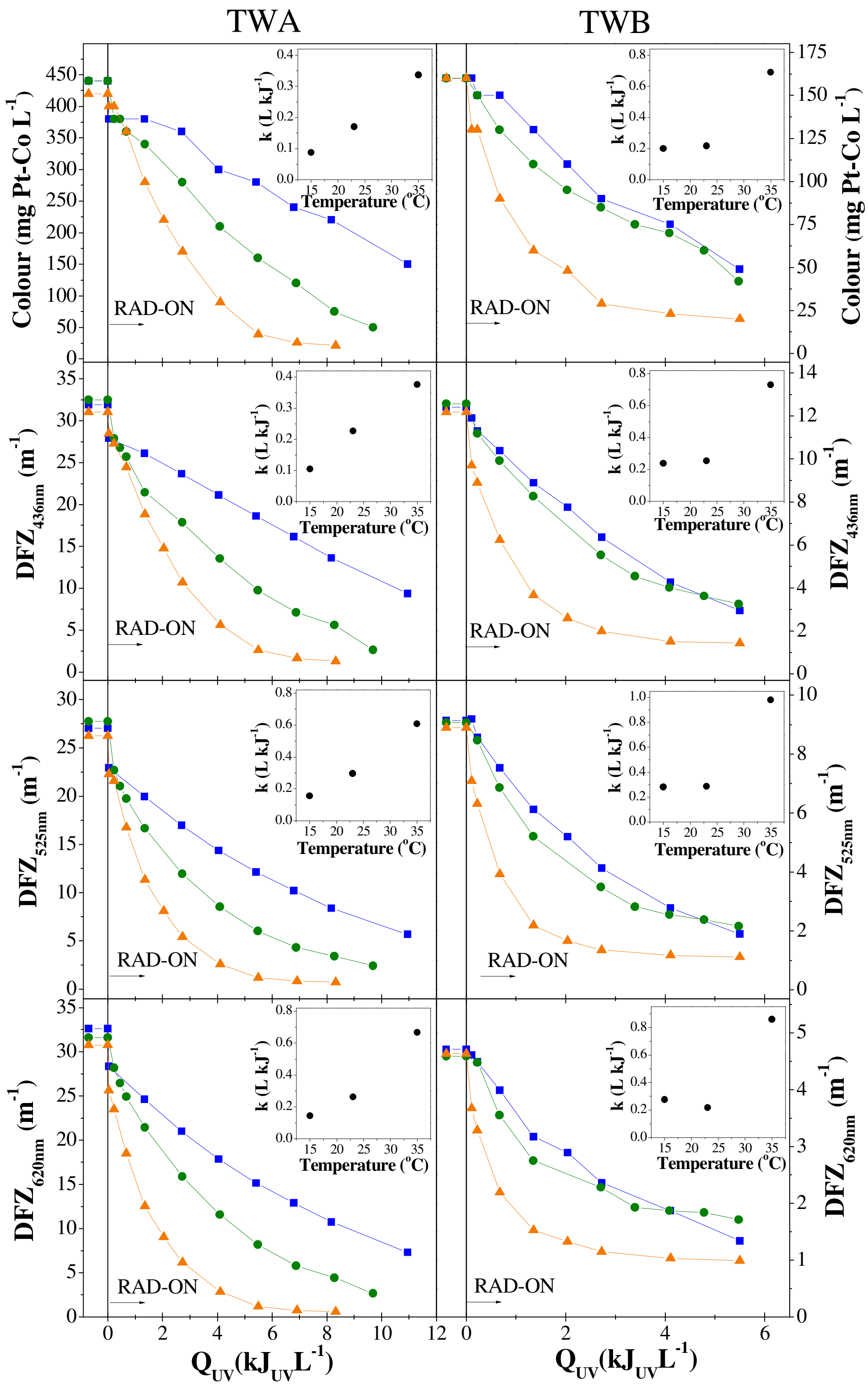

TWA
TWB
RAD-ON
RAD-ON
H_2O_2 consumed (mM)
H_2O_2 consumed (mM)
$Q_{UV}(kJ_{UV}L^{-1})$
$Q_{UV}(kJ_{UV}L^{-1})$
pH
pH
k (mM kJ^{-1})
k (mM kJ^{-1})
0.0
1.5
3.0
4.5
6.0
7.5
9.0
0
2
4
6
8

Figure 8.



TWA
TWB
Colour (mg Pt-Co L-1)
DFZ436nm (m-1)
DFZ525nm (m-1)
DFZ620nm (m-1)
k (L kJ-1)
Temperature (oC)
RAD-ON
QUV(kJUVL-1)

Figure 9.

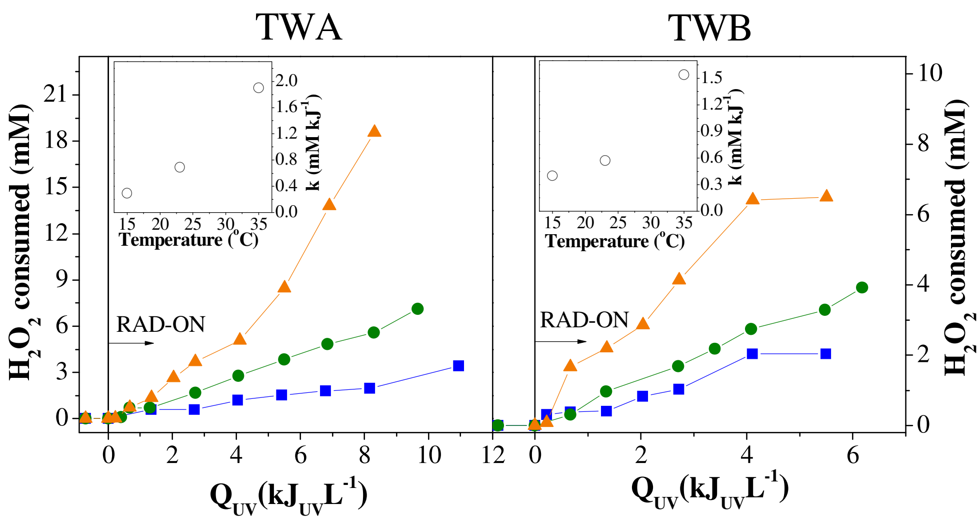
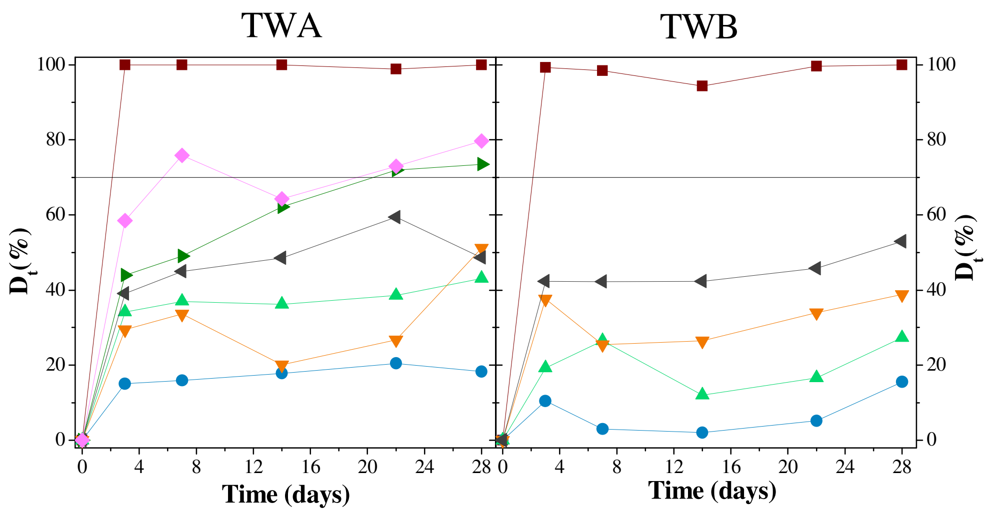
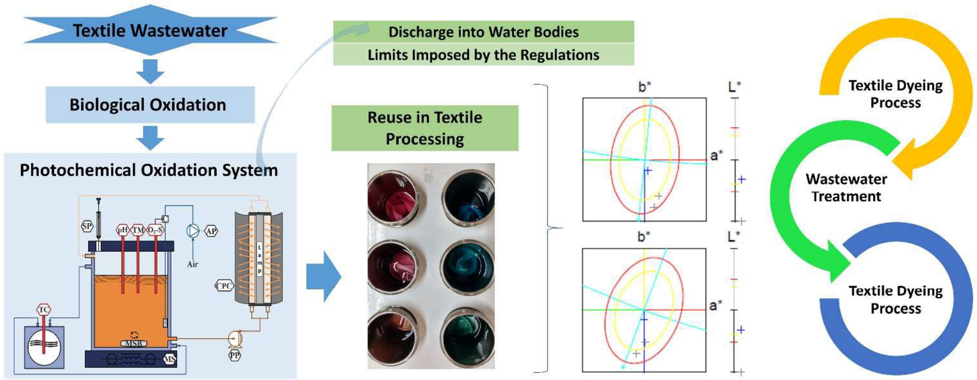

TWA
TWB
RAD-ON
RAD-ON
Temperature (°C)
Temperature (°C)
k (mM kJ-1)
k (mM kJ-1)
H2O2 consumed (mM)
H2O2 consumed (mM)
QUV(kJUVL-1)
QUV(kJUVL-1)

Figure 10.





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