

OPTIMIZATION OF SUSPENDED PHOTOCATALYTIC TREATMENT OF TWO BIOLOGICALLY TREATED TEXTILE EFFLUENTS USING TiO₂ AND ZnO CATALYSTS

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ABSTRACT

In this study, the photocatalytic degradation of two biologically treated textile finishing wastewater was investigated using powdered TiO₂ and ZnO catalysts with UV-A lamp irradiation. Photodegradation and photodecolorization of the samples real textile industrial wastewater is observed directly proportional to pH and catalyst concentrations. Optimum catalyst concentration was found as 2 g l⁻¹ in both catalysts. COD removal in TiO₂ assisted system was obtained two fold higher than ZnO assisted system depending characteristics of the wastewater samples. Optimum pH values were determined to be 5 and 9 for TiO₂ and ZnO assisted systems respectively. A COD removal of 45% and 23% were obtained using and ZnO catalysts respectively during 3 h irradiation. The effluents of photocatalytic treated samples using both catalysts displayed no acute toxicity at the end of 3 h irradiation time at optimum experimental conditions. Results, in conclusion, revealed that both TiO₂ and ZnO catalysts were found to be very effective in color removal and provided safe and proper effluents to meet discharge limits, even reuse guideline values.

Keywords: biological treated textile wastewater, TiO₂, ZnO, photocatalysis, AOPs, *Daphnia magna*

1. Introduction

Textile industry wastewater treatment effluents generally contain large volume of colored effluents and contain various textile chemicals which are assessed to be toxic, carcinogenic poisoning harmful effect to aquatic environment (Villegas-Navarro *et al.*, 2001; Meriç *et al.*, 2005a; Sharma *et al.*, 2007; Khan and Malik, 2014). Biological treatment is also insufficient for decolorization due to the large degree of aromatics present in dye molecules and the bio-recalcitrant of dyes (Correia *et al.*, 1994). Moreover, soluble or particulate COD in the effluent of the biologically treated effluents generally cause a need to search advanced treatment technologies to comply with the strict discharge limits (Dulekgurgen *et al.*, 2007; Selçuk *et al.*, 2006; Eremektar *et al.*, 2007). Advanced Oxidation Processes (AOPs) have been studied as innovative and emerging alternatives for removal of recalcitrants (Arslan Alaton *et al.*, 2002). AOPs provide a high or complete removal of color, COD and toxicity in the effluents (Meriç *et al.*, 2005b). Heterogeneous photocatalysis is one of the effective AOPs for oxidation of dyes and textile wastewater (De Moraes *et al.*, 2000; Mahmoodi *et al.*, 2006; Pekakis *et al.*, 2006; Martins *et al.*, 2006; Alinsafi *et al.*, 2007, Gümüş and Akbal, 2011; Lima *et al.*, 2015). In this process, it is generated free radicals such as hydroxyl with electron-hole pairs in the catalyst system and this can be provided to convert a wide range of harmful dyes into non-toxic products, CO₂ and water (Fernandez-Ibanez *et al.*, 2003; Pelaez *et al.*, 2012). There have been many advances in catalysts (Das and Kumar Basu, 2015), while ZnO and TiO₂ have been the most common used photocatalyst in heterogeneous photocatalysis due to good stability, non-toxicity and insolubility (Alinsafi *et al.*, 2007; Pelaez *et al.*, 2012). Although the most common used catalyst is TiO₂,

both catalysts have similar photocatalytic mechanism and ZnO can often better performance than TiO₂ for the degradation (Frontistis *et al.*, 2012). Both catalysts have similar band gap energy (3.2 eV and 3.02 eV of TiO₂ and ZnO respectively) and photocatalytic activity levels (Abdollahi *et al.*, 2014; Pekakis *et al.*, 2006). However, ZnO has a higher conductivity and less stable than TiO₂ (Hoye *et al.*, 2013). Less stable characteristics of ZnO cause to enhance photocorrosion of ZnO and this could be decreased the photocatalytic activity (Hariharan, 2006). Furthermore, optimum pH value of each catalyst is different due to the different zero point of charge values (pH_{ZPC}) (Rizzo *et al.*, 2013; Abdollahi *et al.*, 2014). The most important advantages of ZnO are absorbing more bigger fraction of the solar spectrum and also more active in sunlight than TiO₂ (Sakhivel *et al.*, 2003; Chandraboss *et al.*, 2013). However, as all other AOPs, these processes also need toxicity based optimization to obtain safe effluent for the environment (Rizzo *et al.*, 2014). *Daphnia magna* is often used for the evaluation of acute/chronic toxicity in textile wastewater due to relatively simple test procedure and reproducibility of the results (Villegas-Navarro *et al.*, 2001; Meriç *et al.*, 2005a; b; Selçuk *et al.*, 2006; Sharma *et al.*, 2007) as well as of photocatalytic treated textile effluents (De Moraes *et al.*, 2000). Moreover, it has been well tested on photocatalytic treated municipal wastewater for reuse (Rizzo *et al.*, 2014) and water (Selçuk *et al.*, 2011) where emerging organic pollutants occurred. On the other hand, textile industry wastewater contains some metals including TiO₂ (Windler *et al.*, 2012) which can cause toxicity in the receiving waters (Aruoja *et al.*, 2009) when they become photocatalytically sensitized nanoparticles (Hund-Rinke and Simon, 2006). Thus, photocatalysis process needs to be followed by bioassays to test any hazard from phototransformation by-products and residual nanoparticles involved in the process for obtaining safe effluent.

The present study aimed to optimize suspended photocatalytic process using TiO₂ and ZnO catalysts in two biologically treated textile effluents which were characterized in a wide range of organic and color content, to ensure discharge limits and to evaluate reuse possibility. The catalyst loading and pH were optimized by means of COD, TOC, color and aromaticity removal in parallel to acute toxicity evolution to *Daphnia magna* for safeguard of treated effluents.

2. Materials and methods

2.1. Sampling

Two biologically treated textile wastewater effluents (WW1 and WW2) were collected from a dyeing and finishing textile industry located in Corlu, Tekirdag, Turkey. Grab samples were taken in November and December 2014.

2.2. Chemicals

Titanium dioxide (TiO₂) was purchased from Sigma Aldrich (CAS Number 13463-67-7) with specific surface areas of 35-65 m² g⁻¹ (BET) and mean particle size of 21 nm. Zinc oxide (ZnO) was provided from Merck (CAS Number 1314-13-2; Catalog No: 8849) with a specific surface area of 47 m² g⁻¹ (BET) and mean particle size of 230 nm (Hikmat *et al.*, 2010; Alizadeh *et al.*, 2007).

2.3. Experimental procedures

The photocatalytic experiments were carried out at UV Photoreactor equipped with sixteen UV-A light lamps (Philips, 8W) in 350 nm wavelength at a constant room temperature (25 °C) (4x2 lamps were positioned at left and right sides and 6 lamps were positioned on the top of reactor). Photo flux was measured by Universal Photometer (MRC Model YK-37UVSD) as 5.62 mW cm⁻². The lamps were switched off for 15 min as the pre-adsorption process before starting the photocatalytic experiments since adsorption-desorption capacities did not vary significantly (<5%) during 2 h of mixing in dark conditions. The photocatalytic experiments were carried out in 200 mL treated textile wastewater samples and pH was adjusted to the desired values by dosing 1 M NaOH and 1 M H₂SO₄. Experiments were run for 3 h of oxidation in accordance with the scientific literature (Mahmoodi *et al.*, 2006; Pekakis *et al.*, 2006; Martins *et al.*, 2006; Gümüş and Akbal, 2011). While a range of 0.5-2.5 g l⁻¹ TiO₂ loading was investigated in the WW1 sample, ZnO catalyst dose varied from 0.5 to 4.0 g l⁻¹ in the WW2 sample considering the literature

studies on textile wastewaters and dyes removal (De Moraes *et al.*, 2000; Mahmoodi *et al.*, 2006; Pekakis *et al.*, 2006; Martins *et al.*, 2006; Gümüş and Akbal, 2011; Lima *et al.*, 2015; Fernandez-Ibanez *et al.*, 2003; Pelaez *et al.*, 2012; Das and Kumar, 2015).

During optimization experiments, 8 mL of sample were collected at different time intervals and filtered through 0.45 µm cellulose acetate membranes (HA, Millipore) to measure soluble COD, TOC (as DOC) and UV absorbance parameters. Experiments were repeated at the optimized conditions in order to obtain reproducibility of the results and to collect samples for post toxicity measurements.

2.4. Ecotoxicity

Acute toxicity of raw and photocatalytic treated samples was assessed on freshwater crustaceans *Daphnia magna* (new born daphnids <24 h) according to ISO 6341 Method (1996). Toxicity tests were performed quadruplicate using five daphnids in each test beaker with 50 ml effective volume. A negative control test was run in parallel to control the quality of test organisms (<5% of immobilization). Daphnids were grown in the laboratory at 16 h day light - 8 h dark periods supplying a 3000 lux illumination at 20°C room temperature and were fed with *Selenastrum capricornutum* (300,000 cell ml⁻¹) and baker's yeast (*Schizosaccharomyces cerevisiae*, 200,000 cells ml⁻¹). Samples were diluted by 50% and set at pH 8. Results were expressed as a percentage of immobilised animals after 24 h. and 48 h according to Eq.1.

$$\% \text{immobilization} = \frac{((\text{Number of immobilized organisms}) * 100)}{\text{Total number of tests organisms}} \quad (1)$$

2.5. Analysis

For the aim of wastewater characterization, chemical oxygen demand (COD), Total organic carbon (TOC) and dissolved organic carbon (DOC) (Shimadzu TOC analyzer (6KVA model), total suspended and volatile solids (TSS and VSS), metals (ICP-OES, Spectro blue Model), conductivity (WTW Cond 3210 Set 1 (2005), total kjeldahl nitrogen (Eflab), ammonia-nitrogen (Eflab), alkalinity, and pH (WTW pH 315i) parameters of the effluents were determined according to Standard Methods (2005). Color (German standards, UV₄₃₆₋₅₂₅₋₆₂₀), and aromaticity (UV₂₅₄) were also determined by a UV-vis spectrophotometer (Shimadzu UV-2401). Residual Zn and Ti concentrations after photocatalytic oxidation experiments were also measured by ICP-OES (ICP-OES, Spectro blue Model). All analyses and treatment studies were performed at NKU Environmental Engineering Department and Central Laboratory (NABİLTEM).

3. Results and discussion

3.1. Wastewater characteristics

Characterization of secondary treated effluent samples is given in Table 1. The characteristics of the samples varied in wide range by means of COD, TKN and ammonia parameters. A part those WW1 and WW2 samples represented the interval of textile finishing industry wastewater (Villegas-Navarro *et al.*, 2001; Meriç *et al.*, 2005a), the gradual decrease in almost all parameters from WW1 to WW2 was obtained by adding a natural polymer in the biological treatment to control ammonia before discharge. TSS, which is an important factor causing light penetration block during photocatalytic oxidation, was still high in WW2 sample (Rizzo *et al.*, 2014). The high ratio between VSS/TSS showed to create a TOC increase potential after oxidation in accordance with the other oxidation process application results (Meriç *et al.*, 2005b). Total COD of the samples was measured in the order of approximately 1>1/4 from WW1 to WW2. Lower soluble COD content of WW2 seems to be proportional with its lower visible UV absorbance value too. Alkalinity which is another parameter to influence efficiency of photocatalysis process due to the hydroxyl radicals scavenger capacity of carbonates (Pelaez *et al.*, 2012) decreased by 44% from WW1 to WW2 sample.

Unionized ammonia concentration was reported to be a function of pH (decreases as pH increases) and temperature (% increases as temperature increases) (USEPA, 2002). Accordingly, ammonia concentration

(18-39 mg l⁻¹) measured yields around 0.3 mg l⁻¹ unionized ammonia concentration at 7-7.5 pH and 25 °C. In the case of the samples studied unionized ammonia concentration was expected to be much lower than 0.5 mg l⁻¹ concentration which was reported toxic to *D. magna* (Meriç *et al.*, 2005b). As seen in Table 1, both biologically treated samples WW1 and WW2 did not result in toxic when they were tested as 50% diluted. However, WW2 tested without dilution was found 55% toxic although it was the least strong treated effluent. This is attributed to the other components of the sample which should contain toxic organics (Arslan Alaton *et al.*, 2002; Correia *et al.*, 1994; Dulekgurgen *et al.*, 2007; Eremektar *et al.*, 2007; Khan and Malik, 2014; Meriç *et al.*, 2005a and b; Sharma *et al.*, 2007; Selçuk *et al.*, 2006; Villegas-Navarro *et al.*, 2001)

Table 1. Characterization of treated textile wastewaters

Parameter	Unit	WW 1	WW 2
pH	-	7.94	7.65
Conductivity	Ms cm ⁻¹	5.15	4.50
Alkalinity	mg CaCO ₃ l ⁻¹	436	246
TSS	mg l ⁻¹	92±4	84±3
TVSS	mg l ⁻¹	70±2	57±3
Total COD	mg l ⁻¹	370±74	90±9
Soluble COD	mg l ⁻¹	230±15	70±4
TOC	mg l ⁻¹	61	60
TKN	mg l ⁻¹	48±3	24±3
Amonnia Nitrogen	mgNH ₃ -N l ⁻¹	39±1	18±3
Ti	ppb	196	14
Al	ppb	462	85
Zn	ppb	79	368
Cd	ppb	0.86	0
Cr	ppb	14	13
Cu	ppb	68	107
Fe	ppb	236	416
Mn	ppb	33	22
Ni	ppb	4.2	3.5
Se	ppb	2.1	0
Color			
UV ₄₃₆	cm ⁻¹	0.176	0.196
UV ₅₂₅	cm ⁻¹	0.258	0.267
UV ₆₂₀	cm ⁻¹	0.118	0.165
UV-vis at 254 nm	cm ⁻¹	1.853	1.036
Acute toxicity-48 h*	%	ND	55±0.5
Acute toxicity-48h* (50% diluted)	%	5±0.5	10±0.6

ND: not determined; WW: number of the sample, * acute toxicity to *Daphnia magna*

3.2. Photocatalytic treatment at varying TiO₂ loadings and pH values on WW1 sample

The effect of TiO₂ catalyst concentration on the treatment of WW1 sample was investigated during 3 h of oxidation varying TiO₂ loading in the range of 0.5–2.5 g l⁻¹ and at pH 8.0 which was as the closest value to the original pH of the sample (Fig. 1a). The increase in the amount of TiO₂ increased *versus* COD and UV₂₅₄ removal up to 2 g l⁻¹ TiO₂ concentration and COD and UV₂₅₄ removal slightly decreased at 2.5 g l⁻¹ TiO₂ concentration. This phenomenon could be due to the light scattering and reduction in light penetration through the treated textile wastewater (Pelaez *et al.*, 2012; Rizzo *et al.*, 2014). The COD efficiencies were obtained as 21%, 32%, 43%, and 39% after 3 h of photocatalytic oxidation using TiO₂ concentrations of 0.5, 1, 2, and 2.5 g l⁻¹, respectively. Decolorization was also observed at all TiO₂ concentrations in parallel to COD removal.

The effect of pH on the performance of the photocatalytic treatment is related to pH_{PZC} of TiO_2 (close to 6.5-6.8). In basic conditions, TiO_2 surface is negatively charged while the TiO_2 surface is positively charged in acidic solutions. Among the investigated pH values, COD removal was drastically decreased at pH 3 and 11. Furthermore, the decolorization was not observed at pH 3 and 11. Maximum COD (49%) and UV_{254} removal (85%) are obtained at pH 5 condition (Fig. 1b). Relatively higher COD removal at pH 5.0 than at pH 8 (43%) is attributed to be still close to PZC of TiO_2 which was not covered by TSS having negative charge to adsorb on TiO_2 nanoparticles (Fernandez-Ibanez *et al.*, 2003; Pelaez *et al.*, 2012; Rizzo *et al.*, 2014). Furthermore, because of high total COD and VSS values of WW1 (Table 1), a soluble COD contribution from the oxidation of VSS could contribute to have lower COD removal than expected (Selçuk *et al.*, 2006). Besides, carbonates could decrease the process efficiency (Rizzo *et al.*, 2014; Selçuk *et al.*, 2011). As for the case of color removal, UV_{436} , UV_{525} and UV_{620} removals were achieved by 35%, 61% and 69% at 0.5 g l^{-1} TiO_2 loading. Color removal increased to 100% at 2 g l^{-1} TiO_2 loading during 3 h irradiation time in accordance with the highest COD removal obtained (Fig. 1b). According to results shown in Fig.1, the optimum TiO_2 concentration for efficient decolorization and COD degradation was concluded to be 2 g l^{-1} at pH 5.0 for 3 h oxidation. UV spectra changes of WW1 sample in those conditions are given in Fig. 2. After 90 min, decolorization was observed in textile wastewater.

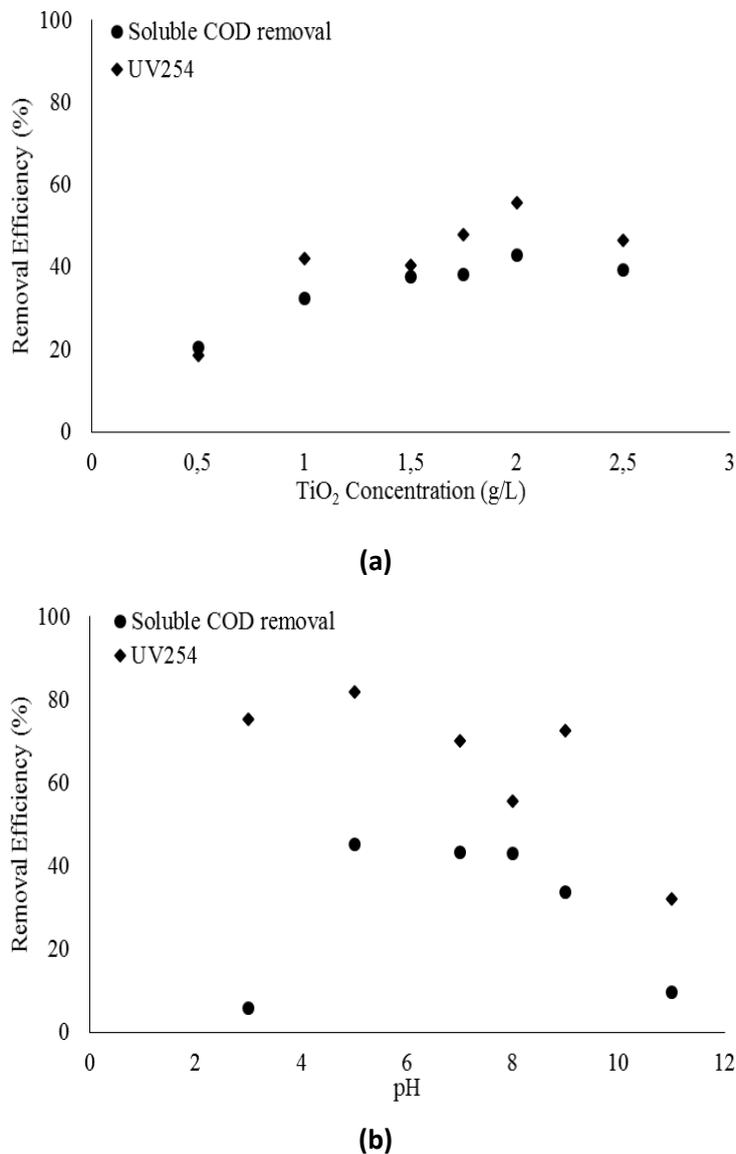


Figure 1. Evolution of COD and UV_{254} of the WW1 sample at varied TiO_2 (a) and pH (b) values during 3 h photocatalytic oxidation

In order to determine the kinetics for the reproducibility of TOC, COD and UV₂₅₄ removals and toxicity optimization the experiments were repeated at optimum oxidation conditions mentioned above. Fig. 3 shows that TOC, COD and UV₂₅₄ removals increased gradually by time. Removal of efficiencies of TOC and COD were found to be 62% and 45% respectively. A slightly lesser COD removal determined in the previous experiments can be attributed to the hardness of the repeatability of the same conditions during oxidation (non-automatic controlled reactor and environmental conditions).

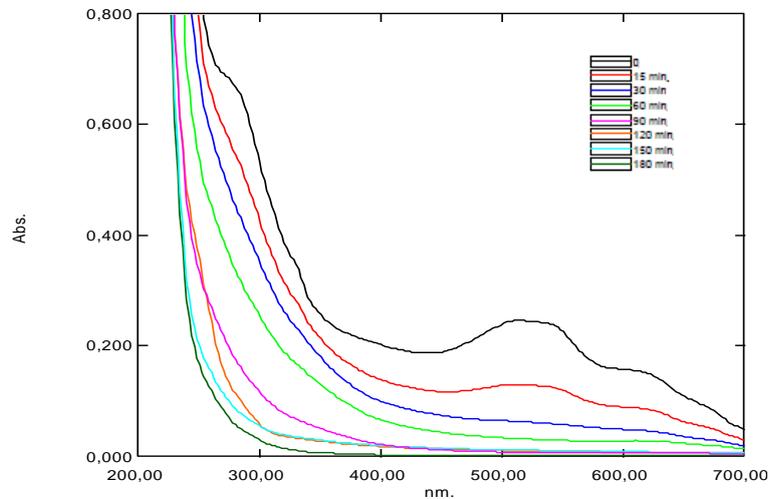


Figure 2. UV spectra changes of the WW1 sample at 2 g l⁻¹ TiO₂ dose and pH 5 during 3 h of irradiation time

A higher TOC removal than COD removal should be due to the calculation done on the basis DOC measurements in the treated samples because a significant increase of soluble COD occurred after oxidation from decomposition of VSS parameter while DOC may represent a lesser portion of that soluble content, thus, promoting higher TOC removal in the treated samples. This contribution is well seen in Figure 3 as TOC first decreased after 2 of irradiation time indicating the mineralization of large molecular organics which can indicate also the increase of toxicity, and it increased after 3 h due to the contribution of new soluble products from VSS destruction. Dearomatization (UV₂₅₄ removal) started to increase in parallel to TOC and COD removals and it continue to increase during oxidation reaching around 82% removal after 3 h irradiation.

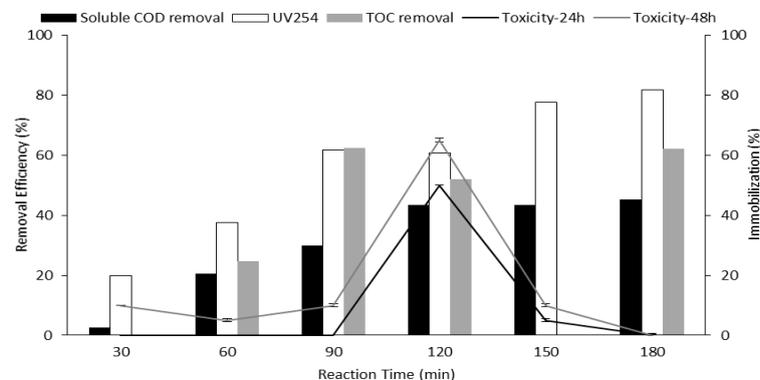


Figure 3. The effect of photocatalytic oxidation time on COD, TOC, UV₂₅₄ and toxicity removals of the WW1 sample at 2 g l⁻¹ TiO₂ dose and pH 5 during 3 h irradiation time

The toxicity increase after 120 min irradiation could be due to the formation of long chain by-products after breaking down of aromatic structured chemicals (Meriç *et al.*, 2005a; De Moraes *et al.*, 2000). While

oxidation continued those by-product should degrade to smaller molecules or more stabilized oxidation products which can be related to the not observed immobilization of *D. magna* after 180 min. photocatalytic degradation (De Moraes *et al.*, 2000; Rizzo *et al.*, 2014).

3.3. Photocatalytic treatment of WW2 at varying ZnO loadings and pH values

The efficiency of ZnO photocatalyst to abate COD and color in WW2 sample was investigated at varying ZnO loadings and original pH value of the sample during 3 h irradiation time. The plot of percent COD and UV₂₅₄ removals vs. catalyst dose is shown in Fig. 4a. Although a lower COD removal efficiency than the case of TiO₂ use (10-15%) was obtained higher removals of UV₄₃₆, UV₅₂₅ and UV₆₂₀ were achieved (73%, 87% and 82% respectively) at 2 g l⁻¹ ZnO loading and pH 9.

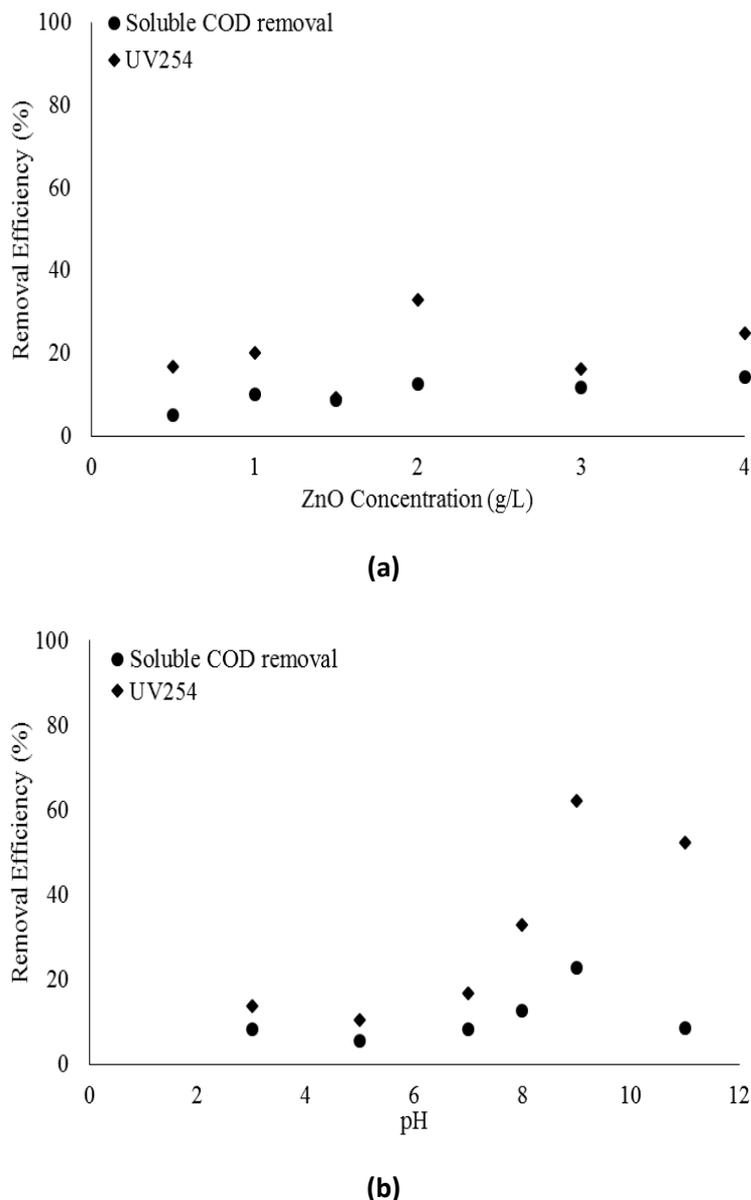


Figure 4. Evolution of COD and UV₂₅₄ of the WW2 sample at varied ZnO (a) and pH (b) values during 4 h photocatalytic oxidation

While increasing ZnO concentration, blocking effect of the radiation was observed in the photocatalytic degradations (Pelaez *et al.*, 2012). Dearomatization increased slowly (up to 38% removal) by gradual catalytic dose increase up to 2 g l⁻¹. The effect of pH on the performance of the photocatalytic treatment

with ZnO is shown in Fig 4b. The COD and UV₂₅₄ removals were not largely influenced by the pH up to pH 9 (Abdollahi *et al.*, 2014). At pH 9, the percent of UV₂₅₄ degradation was a significantly increase however the COD removal was obtained 23% during 3 h irradiation. Figure 5 shows that UV spectra changes of textile wastewater with time at 2 g l⁻¹ ZnO concentration and pH 9. Since pH of zero point charge for ZnO is about 9 and at the pH below 9, surface of ZnO is positively charged. To treat the COD and color simultaneously, the optimum ZnO concentration and pH were chosen to be 2 g l⁻¹ and 9, respectively. As shown in Figure 6 a low COD removal of 23% and a higher dearomatization (UV₂₅₄ removal) efficiency to be 62% were observed during repeated experiments at the optimized conditions.

A slight TOC removal was obtained after 1 h irradiation at which maximum toxicity level was observed. This phenomenon can be explained similar to the TiO₂ catalyst based experiments as explained above and it is clear to see the results after 90 min at which both soluble COD and DOC increased, thus their removals decreased. UV₂₅₄ removal increased in parallel between 90 and 120 min time intervals. Slight toxicity observed to *D. magna* after 150 min irradiation should indicate the increase of destruction of aromatic molecules to more toxic long chain by-products (Meriç *et al.*, 2005b; Pelaez *et al.*, 2012; Rizzo *et al.*, 2014). No significant increase of Zn or Ti concentrations was determined in the optimized samples for the concern of ecotoxicity to be caused by nanoparticles (Aruoja *et al.*, 2009).

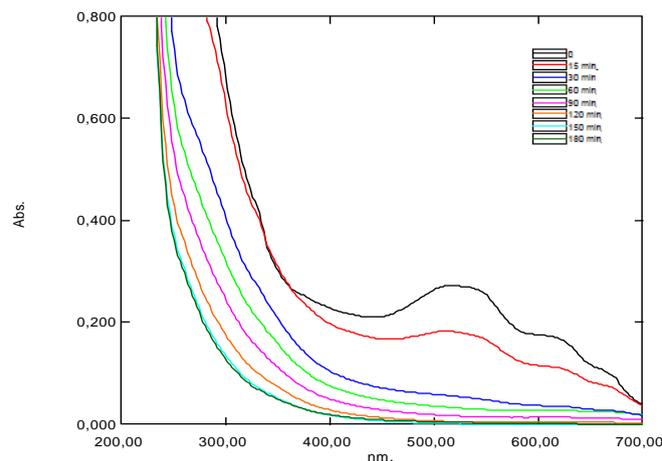


Figure 5. UV spectra changes of the WW2 sample at 2 g l⁻¹ ZnO dose and pH 9 during 3 h irradiation

3.4. Kinetics and reuse evaluation

The photodegradation and decolorization of treated textile wastewaters followed pseudo-first order kinetics with regression coefficients over 90%, except the case of ZnO experiments (Table 2). According to photodegradation coefficients, WW2 was found to be less oxidizable by ZnO at the experimental conditions.

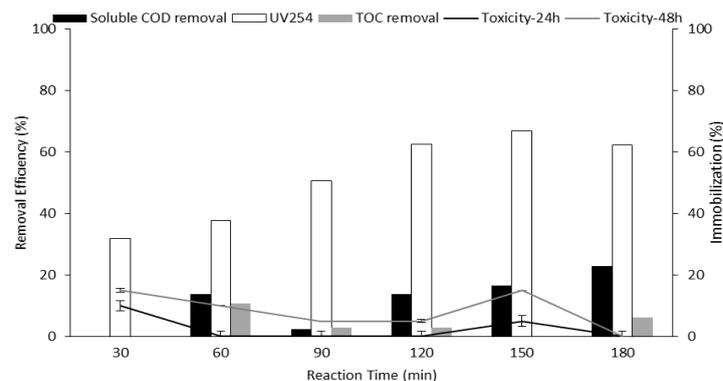


Figure 6. The effect of photocatalytic oxidation time on COD, TOC, UV₂₅₄ and toxicity removals of WW2 sample at 2 g l⁻¹ ZnO dose and pH 9

British Textile Technology Team recommended guideline values for reuse of treated textile wastewater (BTTG, 1999) to contain 80 mg l⁻¹ of COD, 100 mS cm⁻¹ of conductivity and 20 Pt-Co of color. An average COD removal of 45% obtained at the optimum conditions (2 g l⁻¹ TiO₂, 5.0 pH, 3 h irradiation) provided an effluent COD of 170 mg l⁻¹ which was sufficient for discharge limits (<200 mg l⁻¹) but not for reuse purpose. On the other hand, even that low COD removal (23%) obtained at the optimum conditions ZnO catalyst application (2 g l⁻¹ ZnO, pH=9, 3 h irradiation) exhibited an effluent COD concentration lower than 70 mg l⁻¹ meaning that WW2 could be treated properly for reuse. German Federal Ministry of Environment published wastewater discharge limits (2001) for color parameter by means of absorbance measurements which were set as 7-5-3 m⁻¹ for 436 (yellow), 525 (red) and 620 (blue) nm wave bands of sunlight spectrum respectively. These absorbance values were respected by the effluents treated at optimum conditions using both catalysts in this study.

Table 2. Kinetic parameters of photocatalytic treated textile wastewaters using TiO₂ and ZnO catalysts

	TiO ₂ [WW1]			ZnO [WW2]		
	TOC	UV ₂₅₄	Soluble COD	TOC	UV ₂₅₄	Soluble COD
k (min ⁻¹)	0.0056	0.0071	0.0038	NC	0.0061	0.0011
t _{1/2} (min)	124	98	182	NC	114	630
R ²	0.9866	0.9134	0.9318	NC	0.9638	0.8646

NC: not calculated due to the lack of proper data sets.

4. Conclusion

Photocatalytic oxidation of biologically treated textile wastewaters indicated that removal rates of TOC, COD and color are severely dependent on catalyst concentration and pH. Both TiO₂ and ZnO catalysts displayed to provide a satisfying efficiency of decolorization at 2 g l⁻¹ catalyst loading and 3 h irradiation time considering their effective pH values around isoelectrical charge points. Acute toxicity significantly varied in both TiO₂ and ZnO treated samples during 3 h irradiation. Both catalysts were found to be effective for complying with strict discharge limits and reuse of treated textile wastewaters. However, it is important to determine the optimum parameters for the degradation of the textile wastewater.

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