Research Article

TiO$_2$-Based Photocatalytic Treatment of Raw and Constructed-Wetland Pretreated Textile Wastewater

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Approximately, 15% of the total textile colorant production is estimated to be lost during dyeing and processing of textile fibres. If left untreated, these wastewaters can represent a serious environmental threat. In the present paper a combination of photocatalytic and biological degradation of prepared textile wastewaters (simulation of real textile effluent) is presented. Samples have been monitored through the course of photocatalytic experiments: change in UV-VIS absorbance spectra and complete decolouration were achieved for all three tested dyed wastewaters; however, only partial COD removal was achieved with photocatalytic oxidation (PCOx) and photocatalytic ozonation (PCOz). Toxicity test (*Vibrio fischeri*) of untreated and pretreated (constructed wetland, CW) samples showed a decrease in toxicity values only for the red-dyed wastewater. Comparison of efficiency of PCOx and PCOz for decolouration and mineralization of three structurally different dyes (anthraquinone and two azo dyes) has been done. CW pretreatment caused faster decolouration and substantial COD removal in PCOx (up to 45%). Pretreatment also accelerated decolouration during PCOz, but it accelerated COD removal only in the case of red-dyed wastewater due to short irradiation times applied.

1. Introduction

Textile dyes and other industrial dyeing agents represent one of the largest groups of organic molecules. High variety is characteristic for textile dyes' and auxiliary chemicals' composition used in the dyeing and finishing processes. In the world's dye market, azo dyes currently represent 60% share [1]. Due to incomplete dye exhaustion, the spent dye baths and water from washing operations constitute large volumes of dyed wastewaters [2].

Approximately, 15% of the total colorant production is estimated to be lost during dyeing processes [2]. Dyes reduce light penetration into the water, interfere with biological process (photosynthesis), and some exhibit toxic and carcinogenic effects [3]. Due to the complex, recalcitrant, and bioresistant character of textile effluents, a lot of attention has been dedicated to pollution abatement. Traditional physicochemical methods exhibit drawbacks such as secondary waste production (sludge), membrane fouling, and costly adsorbent regeneration [4]. In biological treatment approaches, the anaerobic phase is important for decolouration by the reductive cleavage of azo bond through which aromatic amines are formed, which are sometimes more toxic than the parent molecule itself [5].

Many new approaches to pollution abatement have been investigated like microbial or enzymatic decomposition and advanced oxidation processes (AOPs) [3, 6]. AOPs exhibit also disinfection action on treated wastewater [7, 8]. TiO$_2$-based heterogeneous catalysis' key advantages are absence of mass/phase transfer, possible operation at ambient conditions (under solar irradiation), and, importantly, likelihood of complete mineralization of organic carbon into CO$_2$. Efficient decolouration and partial or total mineralization of textile effluents by AOPs has been demonstrated [2–13]. Moreover, ozone introduction into the photocatalytically treated solution considerably increases the amount of highly reactive oxygen-based radicals in consequence increasing the rate of mineralization [14].

Constructed wetlands (CWs) are engineered systems mimicking natural conditions for wastewater treatment. They are considered as an inherently low cost method since

they use natural ability of vegetation, sand media, and its associated microorganisms for pollution removal [15]. The knowledge on effectiveness of CW for pollution removal has increased rapidly in last two decades; mainly, they are applied for municipal wastewaters, but proved to be successful also in storm, agricultural and industrial wastewaters' (acid mine drainage, dairy, and tannery effluent) pollution abatement [16–18].

A variety of pollutants found in the textile wastewaters can be removed by CW such as suspended solids, dyes, organic compounds, and heavy metals [19, 20]. Microbial transformations are prevailing in organic carbon degradation; they provide the majority of total nitrogen removal while plant uptake has a minor role [21]. The decolouration reaction which takes place in extracellular environment is a biological and chemical reaction.

Due to the environmental implications and limitations of each of the above named treatment processes, a lot of research is focused on combining biological and physicochemical treatment methods. A combination of anaerobic degradation and immobilised TiO_2 photocatalysis proved as feasible approach to treat dye-containing wastewaters [4, 22]. However, a combination of a CW and TiO_2-based photocatalysis was, to our knowledge, only applied for pesticide-polluted wastewaters [23].

The aim of the study was (1) to combine the two promising methods for textile wastewater treatment—CW treatment and TiO_2 photocatalysis—and to demonstrate advantages/disadvantages and (2) to use a complex matrix of simulated wastewater samples in the pretreatment and photocatalytic irradiation experiments since many studies so far have been performed on pure dye samples and with biodegradation in very low volume reactors.

A 250 L CW model was established (its performance will be published elsewhere) with the aim to obtain partial decolouration of the wastewater and COD removal. The CW pretreated and untreated samples were then subjected to photocatalytic degradation and photocatalytic ozonation in a Carberry-type photoreactor. The aim was to prove the presumption that the CW as the first-stage treatment can considerably shorten the irradiation time needed to meet the discharge limit values.

Simulated wastewaters were prepared according to the wastewater composition from a local textile plant. Three reactive dyes with different structure (monoazo, diazo, and anthraquinone dye) were used in order to establish colouration reduction and treatment efficiency for structurally different dyes. Efficiency in terms of colouration removal, COD reduction, and toxicity assessment was used to evaluate the effect of each treatment combination. The best strategy for a combination of the tested methods is discussed from efficiency point of view.

2. Materials and Methods

2.1. Prepared Wastewater Composition.
Wastewater was synthesized according to the local textile plants' parameters (Tekstina, Ajdovščina) where technological water is mixed with communal wastewater (E! 2983 "TEXTILE WET"

report). The same kind of dyes and textile auxiliaries were added as those used in "Tekstina": Reactive Blue 19, Reactive Red 22 or Reactive Black 5 (Figure 1); meat peptone was added (in experimentally established quantity to meet the BOD of the wastewater) as nutrient [24]. Concentrations of added auxiliaries were calculated from the dye dilution factor. All chemicals were purchased from Bezema Company, Switzerland and used without further purification. Prepared wastewater composition was the following: 100 mg/L dye of Reactive Red, Black or Blue, commercially available as Bezaktiv Blau V-RN SPE2, Bezaktiv Schwartz V-B 150 and Bezaktiv Rot V-BN (Bezema, Switzerland), 3.3 μL/L KOLLA-SOL DCA (sequestering agent), 13.2 μL/L COLORCONTIN SAN (wetting agent), 30 μL/L EGASOL SF (levelling agent), 250 g/L meat peptone (Fluka, 70174). Due to the fact that wastewater from the dyeing process in "Tekstina" is mixed with water from the rinsing stages and the companies' municipal wastewater, salt (which is normally added to dyeing solutions) was not added to be able to simulate the measured conductivity values.

2.2. Laboratory Scale CW Model Pretreatment.
An unplanted constructed wetland model was set up to treat prepared wastewater (its performance will be published elsewhere). The model had 2.5 m in length and 0.5 m in width and depth. The media used was washed sand of 8–11 mm particle size at the bottom 10 cm and 2–4 mm particle size in the upper 40 cm. The models' porous volume was 250 L and the hydraulic retention time (HRT) was 24 h with the constant flow of 175 mL/min. The CW model worked under continuous feed operation.

The following parameters were measured *in situ* at 4 measuring points—pH, temperature (T), electric conductivity, and dissolved oxygen (DO)—using the WTW MultiLine P4 portable universal pocket-size meter with pH electrode, SenTix 41 temperature probe, Cell Ox 325 dissolved oxygen probe, and TetraCon 325 standard conductivity cell. Samples from the influent and the effluent of the CW model were taken every 24 hours during the operation and directly analyzed. COD was determined photometrically on Nanocolor 500D photometer (Macherey-Nagel, Germany) using standard COD digestion solutions in the range 100–1500 mg/L (ISO 15705, measurement uncertainty = ±3%). BOD_5 was determined after incubation in WTW OxiTop measuring bottles (ISO 5815). Samples were also analysed with LUMIStox toxicity test (Dr. Lange, Germany) bioluminescence inhibition on *Vibrio fischeri* exposed to sample solutions for 30 min at 15°C. Results were compared to an aqueous control with colour correction (ISO 11348). For qualitative information on colouration reduction the absorbance was measured across the UV and VIS spectra (200–800 nm) in quartz cell with 10 mm optical length, on Hewlet Packard 8453 UV-VIS spectrophotometer (ISO 7887).

2.3. Photoreactor Setup.
Photocatalytic degradation was carried out in a Carberry-type photoreactor described elsewhere [25]. Duran glass reactor tube used in the experiments has
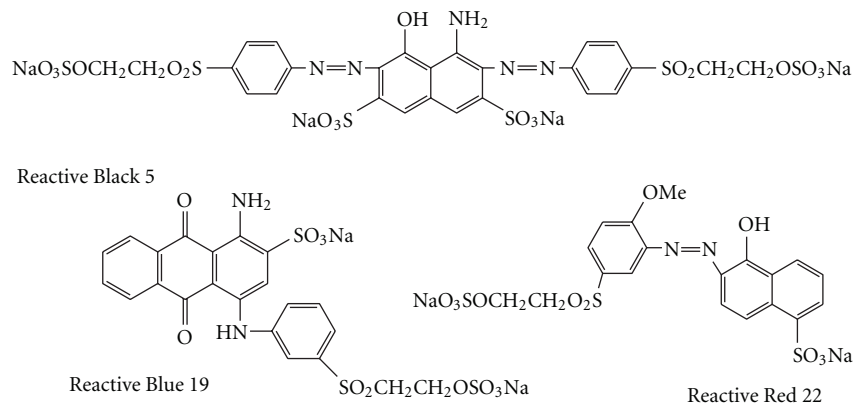
FIGURE 1: Chemical structures of dyes used in the experiments.

a frit with a valve at the lower end to allow the sample to be gas purged (Figure 2(a)). Initial volume of the irradiated sample was 280 mL. 6 low pressure mercury fluorescent lamps (CLEO 20 W, 438 × 26 mm, Philips; broad max at 355 nm) were used as UVA irradiation source.

Photocatalytic paper (Ahlstrom, France) was adjusted to a steel support and radially fastened with 24 thin bars to form a 12 angle star (Figures 2(b) and 2(c), [26]). The photocatalytic paper area was 0.069 m^2 and catalyst mass per unit area (paper + TiO$_2$) was 75 g/m^2, the total mass being 5.18 g. Commercially available paper is impregnated with Millennium PC-500 photocatalytic powder. Prior to fastening the paper onto the support, flowing water was used to rinse off the redundant catalyst.

2.4. Photocatalytic Degradation. Oxygen or ozone was bubbled through the lower end frit into the reactor tube. The gas flow was kept constant to keep the solution saturated. In the photocatalytic ozonation experiments the ozone was generated by Pacific Ozone Technology instrument, model LAB 21, fed with pure oxygen (99.5%). Gaseous concentration of ozone was determined by iodometric titration. The flow rate of ozone was calculated to be 0.13 g/h.

PCOx (Photocatalytic Oxidation): Dyed wastewaters with characteristics presented in the Table 1 were exposed to UVA irradiation under constant oxygen purging for 90 to 210 min, depending on the time needed to achieve decolouration.

PCOz (Photocatalytic Ozonation): Dye solutions were exposed to UVA irradiation under constant ozone purging for 20 to 30 min, depending on the time needed to achieve decolouration. Argon was introduced into the samples after sampling to prevent further oxidation of the sample.

Samples from both photocatalytic degradation experiments were taken in different time intervals (according to decolouration rate) and analyzed. The absorbance (at respective band wavelengths) was measured; the COD measurements and Lumistox toxicity tests were done to evaluate the toxicity and mineralization (degradation) efficiency.

Due to the very low concentrations of textile auxiliaries added to the prepared textile wastewater (see Section 2.1),

they exhibited a negligible contribution to COD and BOD values of the samples.

3. Results and Discussion

3.1. Changes of Absorbance Spectra after Pretreatment and during Photocatalytic Degradation. In Figures 3, 4, and 5 time-dependent UV-VIS absorbance spectra measured during PCOx experiment of Reactive Blue 19 (RBL19, Figure 3), Reactive Black 5 (RBK5, Figure 4), and Reactive Red 22 (RRD22, Figure 5) containing wastewaters are presented. Absorbance bands of all three dyes decrease with time of irradiation in the UV and VIS region. Measurements at their wavelengths of maximum intensity indicate degradation of dye molecules leading to a complete absence of wastewaters' colouration.

The same starting concentration of three commercial dyes (100 mg/L) exhibited significantly different absorbance at their characteristic absorbance bands (VIS spectra). RBL19 exhibited the lowest absorbance: 0.8, RBK5 the highest absorbance: 3.1, and RRD22: 1.9 on average. This is explained by the different structure of dyes under study, the RBK5 is a diazo dye, the RRD22 is a monoazo dye, and RBL19 is an anthraquinone dye (Figure 1). The goal to use the same concentration of commercial textile dyes (100 mg/L) was followed, even though the initial absorbance of RBK5 reached above 2.5. To verify the absorbance measurements the sample was diluted and calibration curve was done.

When spectra of the pretreated and untreated samples are compared (Figures 3, 4 and 5) it can be observed that the CW model pretreatment had a uniform effect on all dyes—it decreased VIS and increased UV absorbance—a consequence of aromatic amines' formation. This results from the azo bond reduction and chromophore cleavage in anaerobic conditions. The obtained results are in accordance with previous findings [6, 27].

The major difference between both sets of RBL19 degradation spectra (Figures 3(a) and 3(b)) lies in the fact that spectra of the pretreated sample exhibit simultaneous decrease in UV and VIS absorbing components (Figure 3(b)) (band at 592 nm), but in the untreated sample (Figure 3(a)) only minor decrease of UV absorbance is exhibited during

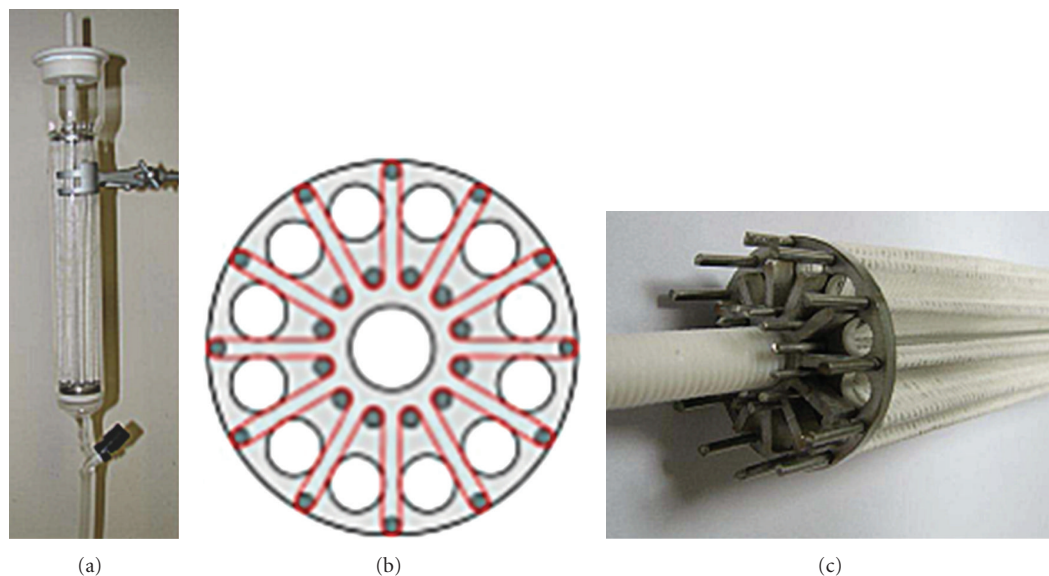(a)   (b)   (c)

FIGURE 2: (a) Photocatalytic cell with the glass tube. (b) Geometrical shape of the steel paper holder (top view). (c) Photocatalytic paper fixed to the steel holder.

TABLE 1: Characteristics of untreated and pretreated textile wastewater, subjected to photocatalysis.

Parameter	Untreated sample			CW-pretreated sample		
	Blue	Red	Black	Blue	Red	Black
Absorbance at max intensity in Vis	0.88 at 592 nm	1.99 at 520 nm	3.1 at 598 nm	0.55 at 592 nm	0.99 at 520 nm	1.1 at 598 nm
COD [mg/L]	372	351	360	280	215	245
BOD [mg/L]	183	185	187	148	93	100
pH	8.1–8.2	8.1–8.2	8.1–8.2	~7.3	~7.3	~7.3
Toxicity [%]	84	100	100	73	100	100

irradiation. During the pretreatment on average 35% of the dye molecules present in the wastewater is degraded into degradation products which exhibit absorbance in the UV part. These degradation products proved to be more susceptible to photocatalytic degradation compared to the parent compound.

The remaining UV absorbance of the untreated sample after photocatalysis (Figure 3(a)) is attributed to high resistance of anthraquinone dyes to degradation in this spectral range. Aromatic organic intermediates in the sample such as quinones and phenols cause the UV absorbance [28]. According to the references, different degradation products like quinones, phenols and mono- and diacids (maleic, acetic, oxalic) are formed under mild experimental conditions [28, 29].

Absorbance in the UV region is pronounced in both RBK5 (Figures 4(a) and 4(b)) spectra. On contrary to RBL19 (Figure 3), degradation of RBK5 in the untreated (Figure 4(a)) and pretreated (Figure 4(b)) samples is manifested simultaneously in the UV and VIS part of the spectra during irradiation.

In the untreated sample's spectra (Figure 4(a)) a new band is formed after 80 min of irradiation at 260 nm. The pretreated sample (Figure 4(b)) has two distinct bands in the UV, at 335 and 260 nm, the latter one is probably the main anaerobic degradation product [30]. In a photocatalytic study of the same dye (slurry TiO_2) temporal changes in spectra also showed a newly occurring band in the 260–280 nm region after 90 min of irradiation [31]. The GC-MS analysis revealed formation of aromatic and short chain aliphatic oxygenated hydrocarbon (like butanoic and propanoic acid) compounds [31]. Since the absorbance at 260 nm is present in both sets of spectra (Figures 4(a) and 4(b)) it can be assumed that the same degradation products are formed during anaerobic degradation and after 80 min of untreated sample irradiation.

Both RRD22 wastewater sample's spectra (Figures 5(a) and 5(b)) exhibit characteristic absorbance band at 520 nm. As in the case of RBK5 (Figure 4(b)), the RDD22 dye degradation during CW pretreatment is confirmed by a decrease in VIS and increase in UV absorbance, due to formation of aromatic products (Figure 5(b)). Again as in Figure 4, the RRD22 photocatalytic degradation occurs simultaneously in the UV and VIS part (Figure 5). Absorbance in the UV region at wavelengths between 260 and 300 nm is pronounced in both samples, indicating presence of aromatic compounds (Figures 5(a) and 5(b)). Unfortunately (to our knowledge) no scientific literature data on red dye of the same chemical structure is available, so no degradation products are suggested except those generally characteristic
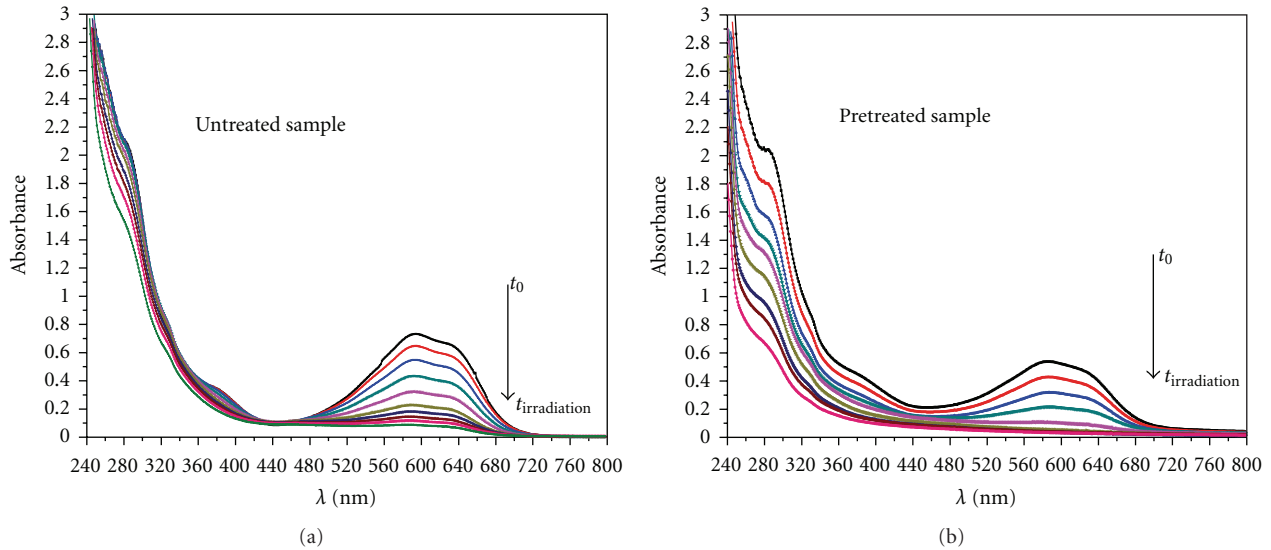
FIGURE 3: UV-Vis spectral changes as function of time of irradiation of untreated (a) and pretreated (b) Reactive Blue 19 textile effluent taken 5 to 15 min intervals, the irradiation time was 90 min.
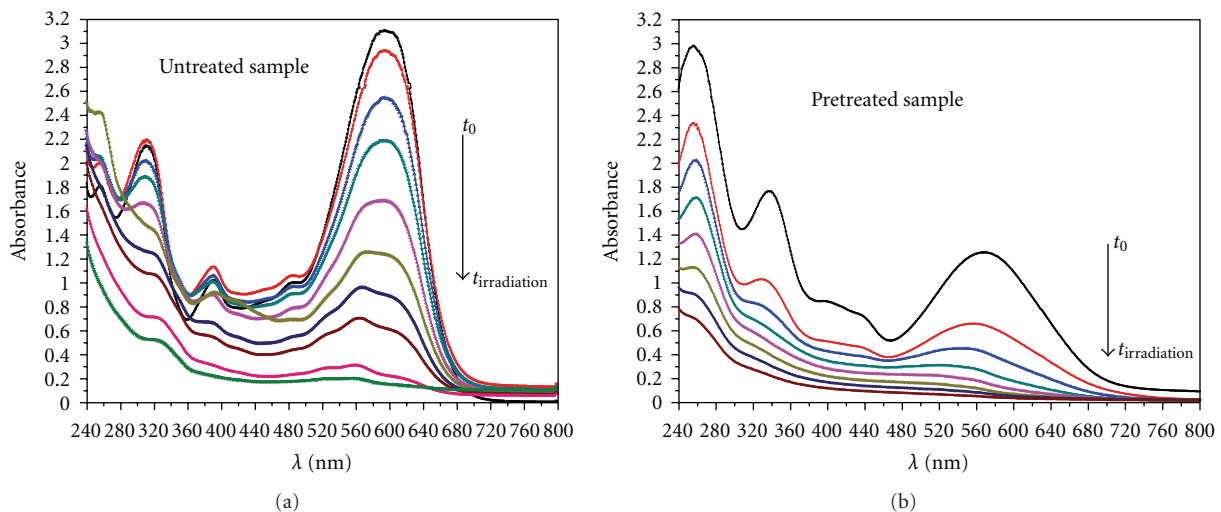

FIGURE 4: Temporal changes in absorption spectra of untreated (a) and pretreated (b) Reactive Black 5 textile effluent taken at 5–15 min intervals, the irradiation time was 210 min.

for textile dye degradation where formic and acetic acid are main degradation products followed by oxalic, glycolic and malonic acids [32].

The absorbance of dyes onto the photocatalytic paper was observed after 2-3 min immersion into the wastewater. By the end of the irradiation as the wastewater decolourised, also the photocatalytic paper discoloured. Since reversible adsorption would result in an unchanged spectrum after irradiation and spectra of all three dyes exhibited completely altered shape, this confirms the oxidative transformation rather than dye adsorption took place.

3.2. Comparison of Photocatalytic Degradation of Pretreated and Untreated Samples. In the following Figures 6, 7 and 8 normalised absorbance at the main VIS absorbance band and COD values of samples taken at the same irradiation intervals

are plotted as a function of time of irradiation (average values of 2–6 irradiation experiments). The difference in initial absorbance values between the untreated and pretreated samples is demonstrated. The irradiation time was chosen according to the time needed for each dye to be completely decolourized.

The lowest decrease in absorbance during pretreatment in the CW model was established for the RBL19 (Figure 6). Anthraquinonic dyes have already been reported as more recalcitrant under anaerobic conditions compared to azo dyes [33]. This was confirmed as the average decolouration percent was 35 for RBL19 (Figure 6) and much higher for both azo dyes up to 60% for RBK5 (Figure 7) and over 50% for RRD22 (Figure 8).

When photocatalytic reactions take place on the surface of the catalyst, the pH value of the wastewater is an important
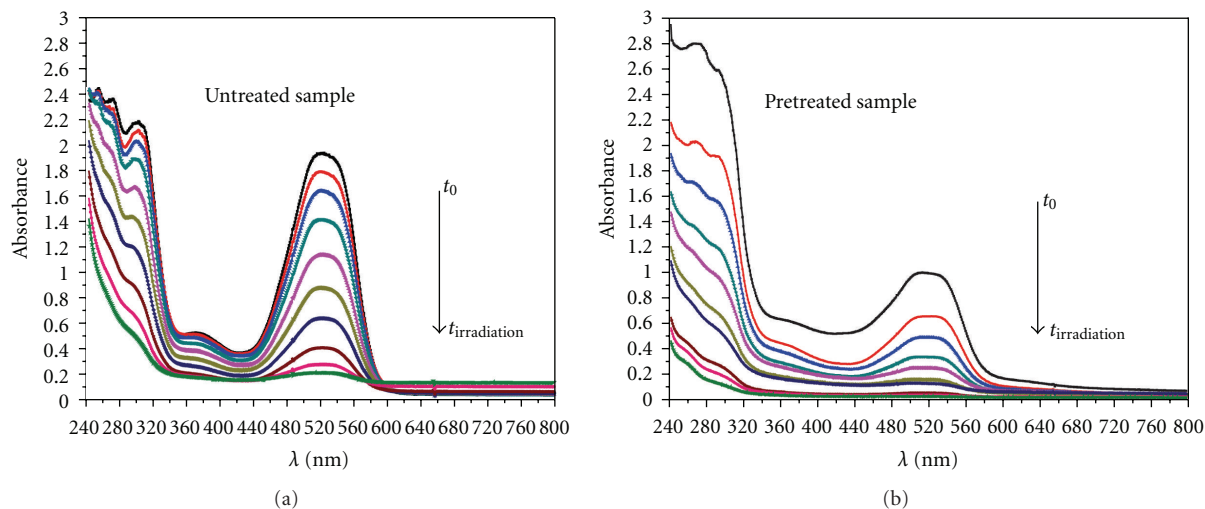
FIGURE 5: Temporal changes in absorption spectra of untreated (a) and pretreated (b) Reactive red 22 textile effluent taken at 5–15 min intervals, the irradiation time was 210 min.

factor since it dictates the surface charge properties of the catalyst. The starting pH of the untreated and pretreated wastewater (Table 1) was higher than the point of zero charge of TiO_2 and SiO_2 oxide surfaces (6.2 and 2.5, resp.), which creates electrostatic repulsive effect (ERL) which in turn hinders adsorption of the dye onto the photocatalyst surface. During degradation no significant change of pH was observed (up to 0.2 pH units oscillation), even though the pH values would be expected to decrease due to formation of acidic degradation products [32, 34]. However, it has to be taken into account that prepared wastewater samples beside dyes contained also high amount of organic material (see Section 2.1) which also influenced (buffered) wastewaters' pH values.

Electric conductivity of the pretreated samples was higher than that of the untreated samples, indicating partial organic material mineralization. Increased ion concentration proved to lower the ERL and promote further decolouration and degradation due to cations' negative charge neutralization and dye/catalyst surface interactions promotion. The effect of anions, which compete with the dye for surface adsorption sites is presumed to be less pronounced since negative and neutral sites on the semiconductor surface outnumber the positive ones [35]. Nevertheless, the acidic conditions proved to be more feasible for dye degradation in many studies, so under acidified conditions, the degradation rate would be expected to increase due to no ERL and more efficient electron-transfer process between the positive charged catalyst and negatively charged dye molecule [2, 36]. As in this study the aim was to mimic real conditions of industrial wastewaters' composition, the degradation in acidic media has not been tested.

Catalyst surface area proved to be an important parameter determining degradation rate due to dye/catalyst adsorption dependence [32, 35, 37, 38]. In the case of Degussa P25 aqueous suspension and lower dye concentration (compared to the concentration used in our experiment) PCOx the decolouration was achieved in 15 to 90 min, depending

on the catalyst load [31]. A complete mineralization was reached after 200 min of irradiation of an 85 mg/L RBK5 [39]. Literature data on photocatalytic paper application for dye degradation or mineralization is very scarce. Irradiation in a similar immobilised TiO_2 reactor with H_2O_2 addition reached complete removal of colouration in 30 to 60 min, depending on the concentration of H_2O_2 added [40]. A direct comparison is difficult since the reactor setup and the type of TiO_2 were different.

For RBL19 (Figure 6) the shortest irradiation time, that is, 90 min, was needed to achieve complete decolouration. This is attributed to its lowest initial absorbance indicating the lowest colouration intensity (anthraquinone structure). Nevertheless, 35% difference in initial colouration of the pretreated sample (Figure 6) did not shorten the irradiation time needed to reach complete decolouration and proved the recalcitrance of this anthraquinone dye.

Longer irradiation time (210 min) was needed to decolourise RBK5 (Figure 7) and RRD22 (Figure 8). As resulting from Figures 7 and 8, the PCOx decolouration course exhibits a clear difference in favour of the pretreated samples regarding the required irradiation time for decolouration (about 40% shorter time of irradiation).

Dye molecules colour the wastewater up to a degree which causes screening effect as they absorb UV irradiation, preventing it from reaching the surface of the catalyst and thus reducing reactive radicals formation and reaction efficiency. In Subsection 3.1 the initial absorbance values, which imply to the intensity of colouration, are presented. The substantial difference in initial absorbance and chemical structure (structural formulas in Figure 1) among azo and anthraquinone dyes resulted in almost 60% shorter time needed for RBL19 decolouration. Retardation in light penetration with increasing dye concentration requires higher catalyst surface for the same degradation rate to be achieved [10, 39].

When decolouration curves of untreated samples are compared, it can be ascertained that the RBL19 (Figure 6)
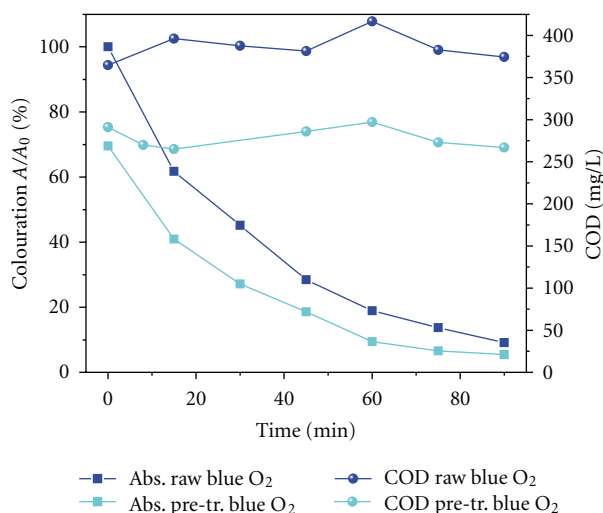
FIGURE 6: Colouration expressed as A/A_0 and COD values of Reactive Blue 19 wastewater samples at different times of PCOx irradiation. Square symbols in all graphs represent absorbance values of untreated and pretreated samples; sphere symbols represent COD values of the same samples.
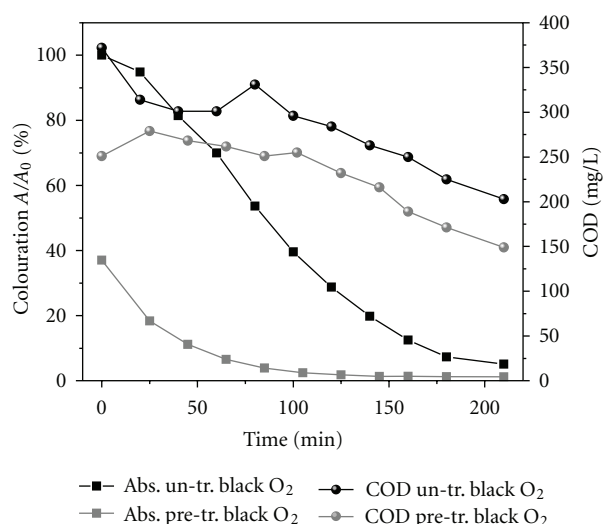

FIGURE 7: Colouration expressed as A/A_0 and COD values of Reactive Black 5 wastewater samples at different times of PCOx irradiation.

FIGURE 8: Colouration expressed as A/A_0 and COD values of Reactive Red 22 wastewater samples at different times of PCOx irradiation.

curve exhibits first order exponential decay; but RBK5 (Figure 7) and RRD22 (Figure 8) curves exhibit more of a sigmoid shape in the first part of the irradiation experiment. Only after 60 min of irradiation, when initial absorbance decreases for 30%, the curves acquire exponential decay shape. Exhibited characteristic of the curves is attributed to the screening effect of the red and black dye during first part of irradiation due to high initial colouration intensity. When colouration intensity decreases for a certain percent, screening effect is no longer present and further decolouration proceeds exponentially. These findings are in accordance with the published results [34]. Additionally, the screening effect is confirmed by the fact that none of the pretreated samples' decolouration curves has sigmoid shape.
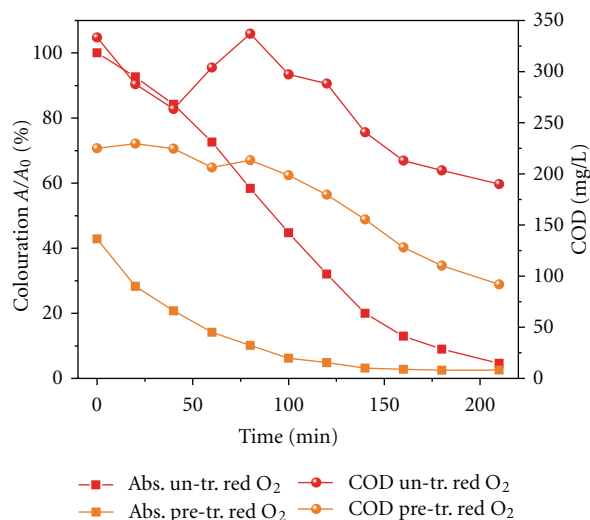
Toxicity of the untreated and pretreated samples towards the *Vibrio fischeri* test organism prior to irradiation was very high (only for the blue-dyed wastewater was lower than 100%) (Table 1). This is attributed to the established textile dyes' toxicity; mother compounds or degradation products are many times found to be carcinogenic or mutagenic [41].

During textile wastewaters' photocatalytic degradation only in the case of pretreated RRD22 a pronounced decrease in toxicity occurred. In all cases the toxicity during the irradiation first increased and later started to decrease. As also the COD values showed sigmoid shape (Figures 6, 7, 8) during irradiation, the toxicity of the samples can be attributed to toxic intermediates formed during first stages of reaction. This confirms the published results by [42]. Prolonged irradiation would be expected to result in further toxicity abatement since COD values started to decrease during the second half of irradiation.

3.3. COD Concentration and Sample Mineralization. From Figures 6, 7, and 8 it can be concluded that decolouration was achieved much faster compared to the mineralization. Since the irradiation time was chosen according to the time needed for disappearance of visible colouration, the obtained mineralization rate is not significant. During dye degradation the intermediate products were formed and partial mineralization as final compound degradation was achieved only at longer irradiation time.

No COD decrease was achieved at RBL19 (Figure 6) untreated wastewater irradiation. This is attributed to the short irradiation time applied. Average COD decrease for untreated wastewaters is similar for black (Figure 7) and red dye (Figure 8), reaching 169 and 143 mg/L, respectively (45 and 43% decrease). These numbers are in agreement with the published data for similar irradiation lengths [43]. Irradiation in a similar immobilised TiO_2 reactor, but with H_2O_2 addition reached 50 mg/L after 240 min of irradiation, in our experiment the COD decrease was higher [40]. After

decolouration of the wastewater is achieved, the COD is reported to decrease sharply [6].

In all untreated water samples an increase in the COD concentration is exhibited in the first 60–80 min of irradiation. After 60 min irradiation of the untreated RBL19 wastewater sample (Figure 6—dark sphere symbol) a peak occurs and no correlation with decolouration can be established. The RBK5 and RRD22 COD curves (Figures 7 and 8—dark sphere symbol) of untreated wastewater samples exhibit an increase in COD concentration, a peak occurring after 80 min which is followed by a decrease. COD curves' sigmoid shape indicates formation of more tolerant intermediate products, which temporarily increase COD of the wastewater [44].

CW pretreatment contributed to COD decrease after photocatalysis of all the wastewater samples ranging from only 24 mg/L (RBL19, Figure 6) to 108 mg/L (RBK5, Figure 7) and 121 mg/L (RRD22, Figure 8). It can be concluded that the pretreatment increases the overall mineralization rate which for real scale textile wastewater treatment plants means shorter irradiation time in order to meet the effluent limits (COD under 120 mg/L) [43]. In the case of pretreated samples, the sigmoid shape of the curve is far less pronounced (Figures 6, 7, 8—light sphere symbol). COD value starts to decrease in the second half of irradiation.

It has to be taken into account that when the wastewater is irradiated, the COD decrease does not depend solely on the dye degradation but is rather influenced by many additional photocatalytic decomposition processes taking place in the irradiated wastewater.

3.4. Photocatalytic Ozonation.

When ozone molecule is adsorbed onto the surface of the semiconductor an ozonide radical anion is formed, resulting in hydroxyl radical formation. Another pathway of its formation through ozone mediation is the reaction of superoxide anion with the ozone, again leading to hydroxyl radical formation [45, 46]. Furthermore, a synergy effect of TiO_2-based photocatalysis combined with ozonation has been reported. It results from a series of reactions which are often conditioned by preceding reactions' products [47, 48].

As in PCOx also in PCOz the absorbance spectra of untreated wastewater samples and CW pretreated samples (not shown) indicated a decrease in the absorbance bands in UV and VIS region with time of irradiation and no new absorbance bands occurred. After PCOz the spectra show absence of VIS wavelengths absorbing molecules, while some absorbance in the UV persists and is more pronounced in the untreated samples.

All the untreated and pretreated wastewater samples reached complete decolouration in much shorter time with PCOz compared to PCOx, as following from Figures 9, 10 and 11. The untreated RBK5 (Figure 10) and RRD22 (Figure 11) samples were decolourised in 20 min and RBL19 (Figure 9) in only 10 min. Faster decolouration is attributed to the action of ozone which increases the rate of decolouration [14].

For both RBL19 (Figure 9) wastewater samples the same irradiation time was needed to reduce visible colouration; for
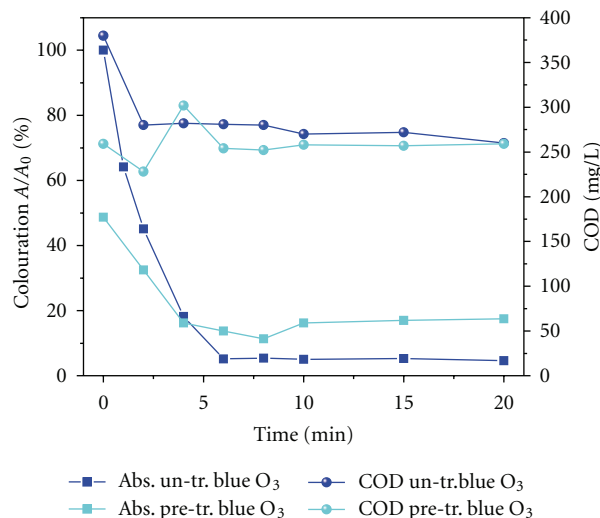
FIGURE 9: Colouration expressed as A/A_0 and COD values of Reactive Blue 19 wastewater samples at different times of PCOz irradiation. Square symbols in all graphs represent absorbance values of untreated and pretreated samples; sphere symbols represent COD values of the same samples.
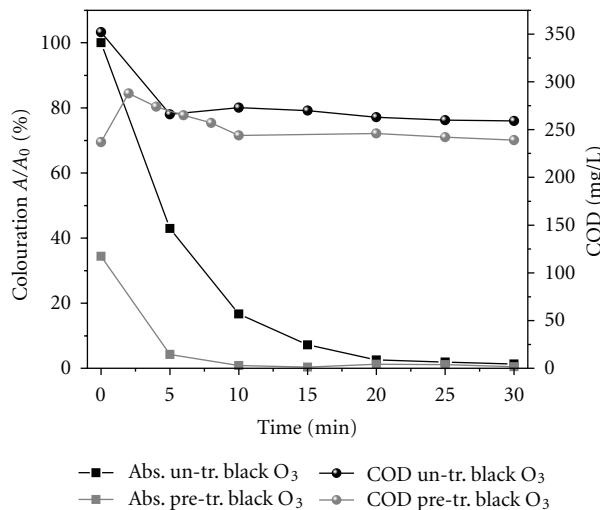
FIGURE 10: Colouration expressed as A/A_0 and COD values of Reactive Black 5 wastewater samples at different times of PCOz irradiation.

RRD22 (Figure 11) the difference between the untreated and pretreated one was only 5 min. Only in the case of RBK5 (Figure 10) the pretreated samples needed considerably shorter (50%) irradiation time.

Since ozone molecule adsorption to the semiconductor surface is an inevitable step for hydroxyl radical formation, the catalyst type, load, and surface area play an important, rate determining role [49, 50]. This was also proven by Wu et al., 2008 [51], where addition of different amounts of TiO_2 did not considerably improve decolouration. To our knowledge, so far there are no publications yet on the dye decolouration with PCOz using Ahlstrom photocatalytic paper as catalyst. The data on PCOz irradiation with

TABLE 2: Irradiation times given in minutes needed to obtain decolouration of different samples and the difference between both methods and between untreated (UN-T.) and pretreated (PRE-T.) samples within each method (PCOx and PCOz).

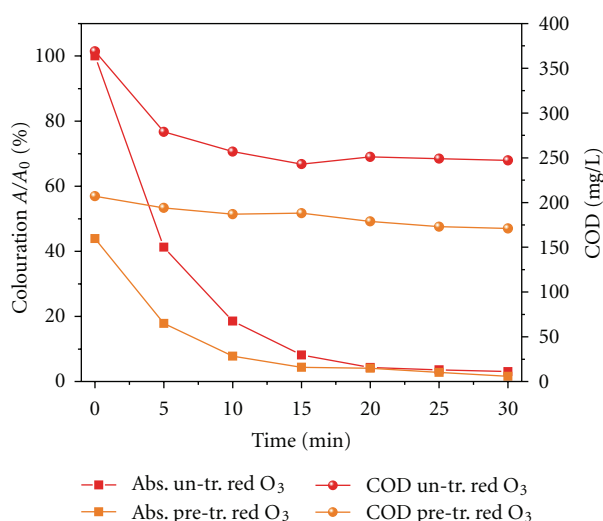| Colour	Treatment/sample	PCOx (O$_2$ purging) [min]	PCOz (O$_3$ purging) [min]	Difference between PCOx and PCOz [%]	Difference between UN-T. and PRE-T. PCOx [%]	Difference between UN-T. and PRE-T. PCOz [%]
Blue, RBL19	Untreated	90	6	93	0	0
	Pretreated	90	6	93		
Red, RRD22	Untreated	210	20	90	43	25
	Pretreated	120	15	88		
Black, RBK5	Untreated	210	20	90	69	50
	Pretreated	65	10	85		

FIGURE 11: Colouration expressed as A/A_0 and COD values of Reactive Red 22 wastewater samples at different times of PCOz irradiation.

P25-Degussa TiO$_2$ catalyst for monochloroacetic acid and pyridine degradation [46] has proven to be 4 times and 5 times more efficient respectively, compared to the PCOx.

Ozone-mediated dye degradation was established to be the fastest at alkaline pH values since alkaline environment promotes ozone decomposition in favour of hydroxyl radical formation [52, 53]. Thus, the samples' pH values are in favour of radical formation (Table 1). In more alkaline wastewaters degradation rate would be further increased since the difference between pH 2 and 12 was found to be 32% [53].

In Figures 9, 10, and 11 the COD values of the samples obtained during 20 to 30 min irradiation time are also shown (right side scale). For the RBL19 pretreated sample (Figure 9, light sphere symbol) no decrease is exhibited while the untreated sample (Figure 9, dark sphere symbol) exhibits 32% COD decrease. For RBK5 (Figure 10) the COD concentration decrease is evident for untreated samples (26%, 93 mg/L, Figure 10, dark sphere symbol) but was again absent in the pretreated samples (Figure 10, light sphere

symbol). Only in the case of RRD22 wastewater (Figure 11) the PCOz proved to be successful in COD abatement in both sets of samples (33% and 17% for untreated and pretreated samples). Moreover, the more or less pronounced sigmoid COD curves indicate formation of degradation reaction products which can act as ozone scavengers thus decreasing the rate of mineralization. Again it has to be kept in mind that all samples were actually wastewater and not dye solution samples, containing also organic material (see Section 2.1).

Study done by authors in [54] shows that PCOz treatment (P25-Degussa) of textile effluents resulted in almost complete decolouration after 60 min of irradiation and more than 60% decrease in TOC values [54]. This implies to the competition of reaction intermediates with pollutant molecules in O$_3$ scavenging and only their further degradation to mineralization eventually decreases the overall TOC values. In simulated textile wastewaters prolonged irradiation time would be needed to reach not only decolouration but also higher degree of COD removal.

As in PCOx also in PCOz high toxicity of the samples was exhibited during and after irradiation. Again only toxicity of the untreated RRD22 samples decreased to 82% and of the pretreated RRD22 samples below the toxicity limit (20%).

Large differences are exhibited between the PCOx and PCOz irradiation (decolouration) times (Table 2). The PCOz irradiation time of the RBL19 untreated and pretreated samples was shorter for 93% and of the RRD22 and RBK5 samples between 85 and 90%, compared to PCOx. Again the RBL19 pretreatment did not shorten the decolouration irradiation time but the RRD22 and RBK5 pretreatment shortened it for 25–69%.

For RBL19 was the COD decrease substantial only in untreated samples' PCOz (Table 3); in RRD22 and RBK5 PCOx it accounted for 41–60% and was much lower (or absent) in PCOz. This confirms that the length of irradiation played a crucial role in COD decrease.

4. Conclusions

In the paper a comparison between the photocatalytic decolouration and mineralization of untreated and pretreated samples of three prepared textile wastewaters is presented.

TABLE 3: COD removal of samples during irradiation treatment.

Sample/colour	COD removal [%] during irradiation	PCOx irradiation [%]	PCOz irradiation [%]
Blue, RBL19	Untreated	0	32
	Pretreated	8	0
Red, RRD22	Untreated	43	33
	Pretreated	60	17
Black, RBK5	Untreated	45	26
	Pretreated	41	0

During the CW pretreatment of simulated textile wastewater considerable level of decolouration and partial decrease in the COD levels was achieved. It can be concluded that the pretreatment proved to be successful in shortening the decolouration irradiation time for both azo dyes, RRD22 and RBK5 in PCOx and PCOz experiments. This was not the case for RBL19 since the irradiation time is exactly the same regardless of the samples' origin. Overall irradiation time was found to be dependent on the initial colouration intensity due to screening effects at high initial colourations.

Regarding the irradiation time scale, PCOz proved to be more efficient in terms of much shorter decolouration time compared to the PCOx. However, due to shorter irradiation time the COD removal was lower or absent.

To meet the technical water effluents' legislative limits, both experiments would have to be prolonged, due to the insufficient COD removal. Since intermediate products' degradation follows the decolouration step and catalytic decolouration is much faster with ozone purging, photocatalytic ozonation is proposed as a more favourable of the two procedures. But longer ozonation experiments would have to be tested for a COD removal.

A combination of the CW and photocatalytic techniques proved to be a promising approach in increasing cost efficiency in textile wastewater treatment.

Abbreviations

CW: Constructed wetland
PCOx: Photocatalytic oxidation
PCOz: Photocatalytic ozonation
RBL19: Reactive Blue 19
RBK5: Reactive Black 5
RRD22: Reactive Red 22.

Conflict of Interest

There was no conflict of interest present regarding the use of commercial products; all products used in this study were purchased on the market.

Acknowledgments

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