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Comparison of photocatalytic degradation of dyes in relation to their structure

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Abstract The photocatalytic degradation of a series of six acid dyes (Direct Red 80, Direct Red 81, Direct Red 23, Direct Violet 51, Direct Yellow 27, and Direct Yellow 50) has been tested compared in terms of color removal, mineralization, and toxicity (*Lactuca sativa* L. test) after photocatalysis on immobilized titanium dioxide. The dyes were examined at their natural pH and after hydrolysis at pH 12. Results show that hydrolysis decreases strongly the efficiency of color removal, that full mineralization takes much longer reaction time than color removal, and that toxicity is only very partially reduced. Some structural parameters, related to the structure and the topology of the dye molecules, could be correlated with the apparent color removal rates at natural pH.

Keywords Acid dyes · Photocatalysis · Titanium dioxide · Mineralization · Molecule topology · Toxicity

Introduction

Textile dyes present in dyehouse wastewater have been a growing concern for many years, especially because many

of the textile plants are installed in water-stressed countries where reclaimed water reuse would be beneficial. Part of the dyes used in the dyeing process is released in the wastewater and the loss can reach 50 % for reactive dyes (Laing 1991). Besides the aesthetic impacts they have when they are released without treatment in a water body, they are also linked to health hazards (Bafana et al. 2011). If the acute toxicity of azo dyes is rather low according to the European Union definition (Verma 2008), their (bio)transformation products and their impurities, such as aromatic amines, can present acute and chronic toxicity as well as carcinogenicity (Alves de Lima et al. 2007; Golka et al. 2012), mutagenicity (Chequer et al. 2011), genotoxicity (Sweeney et al. 1994; Chequer et al. 2009), cytotoxicity (Ferraz et al. 2011), estrogenicity, and anti-estrogenicity (Bazin et al. 2012). Not only the dyes themselves but also dyehouse wastewater treated by classical methods (i.e., activated sludge) are exhibiting these sources of annoyance (Oliveira et al. 2007; Carneiro et al. 2010) that can be transferred to the aquatic environment (Umbuzeiro et al. 2005; Alves de Lima et al. 2007). Moieties such as aniline, toluidine, benzidine, and naphthalene (Zhou et al. 1997; Møller and Wallin 2000; Bae and Freeman 2007; Baan et al. 2008; Kawakami et al. 2010; Turesky and Le Marchand 2011; Lizier et al. 2012; Manzetti 2012; Talaska et al. 2012) are potentially carcinogenic. It is therefore crucial to investigate techniques to remove these harmful pollutants safely before discharging the wastewater in the aquatic environment or re-using it. As the dyes should be stable and resistant, their biological degradation remains difficult (Saratale et al. 2011; Tan et al. 2012). Current methods for their removal either require their adsorption onto a material (Forgacs et al. 2004) or chemical degradation (Anjaneyulu et al. 2005). Many low-cost adsorbents often based on waste materials (Mittal et al. 2009) have been proposed: potable water treatment sludge (Moghaddam et al. 2010), feather (Mittal et al. 2012), cotton stalk (Kahraman et al. 2012), marine macroalgae (Daneshwar et al. 2012; Kousha et al.

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2012), bottom ash (Gupta et al. 2006), chitosan (Ignat et al. 2012; Sánchez-Duarte et al. 2012), de-oiled soya (Gupta et al. 2006), pumice stone (Samarghandi et al. 2012), wood (Hossein et al. 2012) and its sawdust (Ansari et al. 2012), and fruit seeds or shells (Doulati Ardejani et al. 2008; Kahraman et al. 2012; Toprak et al. 2012; Zahra et al. 2012) are among the last ones which have been successfully tested. Carbon-based materials such as activated carbon (Gupta et al. 2011; Wang 2012) or slurry (Gupta et al. 2007) give also good results. Gupta et al. (2006) has shown that dye recovery could be possible but generally such a process generates secondary pollution that requires disposal that can be costly. Coagulation techniques have the same kind of disadvantages. The main advantage of adsorption and coagulation techniques is that they do not involve chemical reactions able to produce harmful by-products. More recently advanced oxidation processes such as ozonation (Tehrani-Bagha et al. 2010), anodic oxidation (Petrucci and Montanaro 2011), combined action of persulfate and zero-valent iron (Le et al. 2011), or photocatalysis have been proposed.

Although other photocatalysts might be used (Huang et al. 2012) most researchers are employing photoactivated titanium dioxide (TiO₂) (Hashimoto et al. 2005). Exposing TiO₂ in water to near UV-light produces hydroxyl radicals on the surface of the catalyst and these reactive radicals can completely oxidize organic compounds found in the water (Vautier et al. 2001). Therefore ultimately the dyes themselves are oxidized into simple species such as carbon dioxide, nitrogen (as N₂), and water leaving behind no harmful by-product.

A recent literature survey has revealed that among the about 12,400 papers devoted to photocatalysis that are listed in the Web of Science, 39 % deal with titanium dioxide and 17 % with dye removal. However, a limited number of these papers (<1 %) seem to be related to the treatment of a real textile wastewater. Furthermore, only a small number of dyes have been tested, with dyes such as Methylene Blue (47 %) and Methyl Orange (36 %) receiving a lot of interest. Now thousands of dyes are available on the market and a given textile shade is often the result of a mixture of dyes. In spite of attempts to assess the efficiency of AOPs on some of them (Zayani et al. 2009) it seems unrealistic to test the performance of any treatment process on such a number of substances, both in terms of time and cost. Therefore its prediction based on the structural characteristics of the dyes is an approach that should be considered. Hachem et al. (2001) have indeed tested the photocatalytic degradation of several dyes but came to the conclusion it was difficult to compare the performances. Lachheb et al. (2002) and Guillard et al. (2003) have compared the photocatalytic disintegration of five dyes with very different structures (namely Methylene Blue, Orange G, Alizarin S, Azo-Methyl Red, and Congo Red) while Khataee et al. (2010) have discussed the effect of the structure on three similar

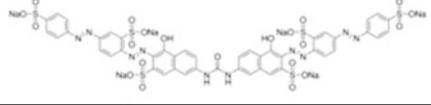
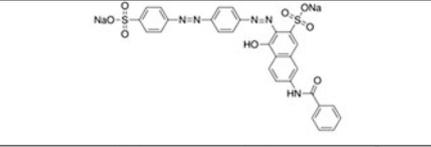
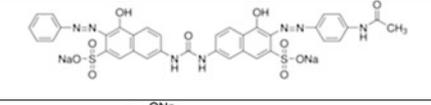
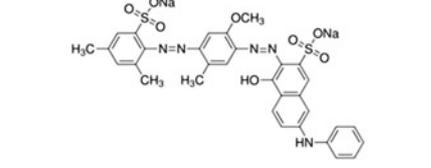
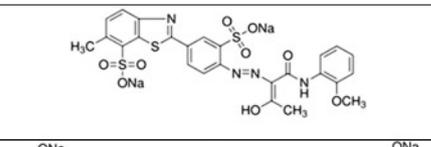
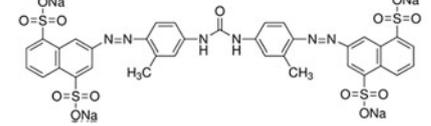
dyes (Acid Orange 8, 10, and 12). A statistical analysis of ozone/UV/H₂O₂ treatment of four dyes (Acid Orange 7, Acid Orange 10, Acid Red 73, and Acid Red 88) has been proposed by Muthukumar et al. (2005). In these three cases, the importance of structural elements such as sulfonic acid groups, benzene, and naphthalene rings or methyl groups has been underlined. Khataee and Kasiri (2010) have discussed the importance of various auxiliary groups found in dye molecules, based on literature data. Unfortunately, it is very difficult to compare results obtained under different experimental conditions (type of titanium dioxide, pH, type of reactor). Recently, Wols and Vries (2012) have proposed a quantitative structure–activity relationship (QSA) approach to predict the degradation of priority compounds by UV/H₂O₂ processes but no dye was considered. Such methods have also been proposed to predict the toxicity of chemical substances (Greene et al. 1999; Khadikar et al. 2002; Jain and Agrawal 2007; Jensen et al. 2008; Benigni and Bossa 2012). The prediction is based on molecular descriptors aiming at the quantification of various structural and physicochemical characteristics. The molecular descriptors are calculated on representations of the molecules based on the graph theory (Natarajan 2011).

In the textile industry, dyeing occurs generally at high temperature in an alkaline or acidic pH range in order to increase the hydrophobicity and flexibility of the fibers to be dyed (Khouni et al. 2011). The dye molecule is transformed under these harsh conditions. Ancillary substances such as salts, wetting agents, and softeners are also added to improve the dyeing process. Therefore a textile wastewater is more complex than a simple dye solution and this might affect the efficiency of treatment processes, as observed by Alinsafi et al. (2007).

It should also be remembered that color removal is not the ultimate goal of applying advanced oxidation processes: improved biodegradability (when the photocatalytic process is run prior to a biological treatment), mineralization, and destruction of any toxic molecules (when the effluent is discharged in a water body or used for irrigation) should be sought after. Depending upon the final destination of the reclaimed water, effluent toxicity could be tested on living organisms (*Daphnia magna*, *Pimephales promelas*) or plants (duckweed, lettuce seeds). The results are indeed sometimes surprising: decrease (Kumar et al. 2007; Gupta et al. 2007; Abd El-Rahim et al. 2008; Osugi et al. 2009; de Andrade et al. 2012) or increase (Işik and Sponza 2004; Oliveira et al. 2010) of toxicity have been reported depending upon the treatment and the dyes.

Our goal has been to compare the effect of structure for six acid dyes (either natural or hydrolyzed) in terms of color removal, mineralization, and toxicity. The selected dyes (Direct Red 23, Direct Red 80, Direct Red 81, Direct Violet 51, Direct Yellow 27, and Direct Yellow 50) have a

Table 1 List of the dyes tested in the present work and some of their properties

Name	Empirical formula	CAS number	Color Index	Purity (%)	Chemical formula	M _w (g/mol)	λ _{max} (nm)
Direct Red 80 (DR80)	C ₄₅ H ₂₆ N ₁₀ Na ₆ O ₂₁ S ₆	2610-11-9	C.I. 35780	25		1373.07	528
Direct Red 81 (DR81)	C ₂₉ H ₁₉ N ₅ Na ₂ O ₈ S ₂	2610-10-8	C.I. 28160	50		675.60	397
Direct Red 23 (DR23)	C ₃₅ H ₂₅ N ₇ Na ₂ O ₁₀ S ₂	3441-14-3	C.I. 29160	30		813.72	507
Direct Violet 51 (DV51)	C ₃₂ H ₂₇ N ₅ Na ₂ O ₈ S ₂	5489-77-0	C.I. 27905	50		719.70	549
Direct Yellow 27 (DY27)	C ₂₅ H ₂₀ N ₄ Na ₂ O ₉ S ₃	3214-47-9	C.I. 13950	N.A.		662.62	393
Direct Yellow 50 (DY50)	C ₃₅ H ₂₄ N ₆ Na ₄ O ₁₃ S ₄	3214-47-9	C.I. 29025	40		956.82	390

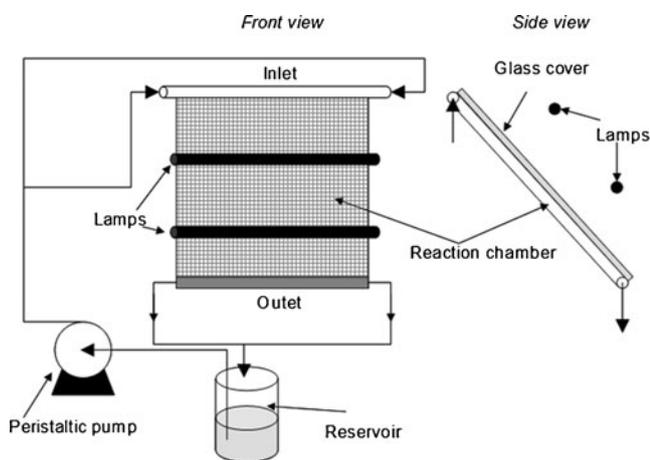
more complex structure than those previously investigated by Lachheb et al. (2002), Khataee et al. (2010), and Muthukumar et al. (2005). Direct Red 81, Direct Violet 51, and Direct Yellow 50 belong to the “Subset of the Aromatic Azo- and Benzidine-based Substances” included in Section 71 by Environment Canada (2012). Direct Violet

51 has been found to be toxic to *Daphnia similis* (LC₁₀₀=400 mg/mL) (Corso et al. 2012).

Materials and methods

Dyes solutions

The dyes (Table 1) were obtained from Sigma Aldrich (Saint-Quentin Fallavier, France) and used without further purification. All solutions were prepared at a concentration of 25 mg/L. Dilution in ultra-pure water was used to produce the so-called “natural” solution, whose pH ranged between 5.8 and 6.9 depending upon the dye. Hydrolyzed solutions were obtained by adjusting the pH of the “natural” solution to 12 using sodium hydroxide, heating the alkaline solution at 80 °C for 90 min, and adjusting back the pH to the desired value (5.5, 6, 7, or 8) with hydrochloric acid. Light dyehouse effluents (Alinsafi et al. 2007) were simulated by mixing the dye (25 mg/L) with ammonium sulfate (5.56 mg (NH₄)₂SO₄/L), sodium monohydrogen phosphate (5.56 mg Na₂HPO₄/L) and potato starch (Sigma Aldrich; 2.78 mg/L) and hydrolyzing the mixture as previously described.

**Fig. 1** Photocatalytic reactor

Photocatalytic tests

The photocatalytic tests were performed in a lab-built reactor (Fig. 1) made out of stainless steel with a $30 \times 30 \text{ cm}^2$ workable area (Fig. 1). The solution to be treated was falling

as a thin film from the top of the chamber onto titanium dioxide (Millenium—PC 500, >97 % anatase) immobilized by means of a silica-based binder on a mat made of cellulose fibers (Ahlstrom, Pont-Evêque, France). The angle of slant was set at 37° to achieve a homogeneous distribution of the

Table 2 Dyes tested by Lachheb et al (2002) and Khataee et al. (2010)

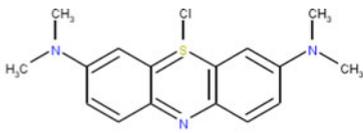
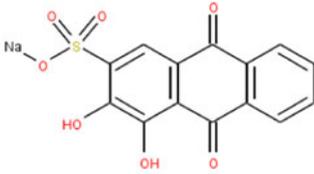
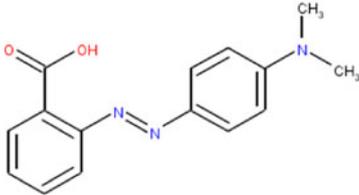
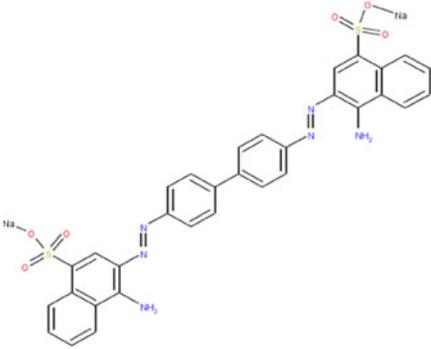
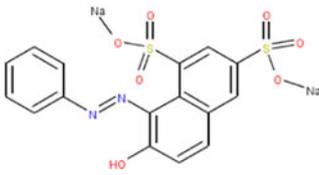
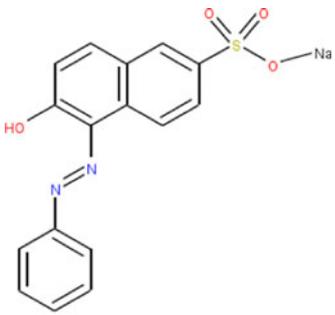
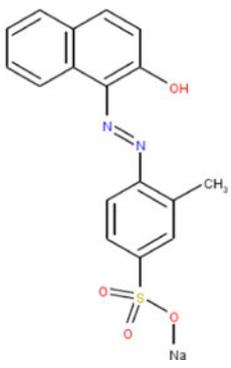
Name	Empirical formula	Chemical formula	M_w (g/mol)	λ_{max} (nm)
Methylene Blue (MB)	$\text{C}_{16}\text{H}_{18}\text{N}_3\text{Cl}$		356	660
Alizarin S (AS)	$\text{C}_{14}\text{H}_7\text{NaO}_7\text{S}$		360.28	520
Azo Methyl Red (MR)	$\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_2$		269.3	540
Congo Red (CR) (also Direct Red 28)	$\text{C}_{32}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2$		696.68	510
Acid Orange 10 (AO10) (Orange G)	$\text{C}_{16}\text{H}_{10}\text{N}_2\text{Na}_2\text{O}_7\text{S}_2$		452.4	480

Table 2 (continued)

Acid Orange 12 (AO12)			350.3	488
Acid Orange 8 (AO8)	$C_{17}H_{13}N_2NaO_4S$		363.4	490

liquid onto the paper. The reacting chamber was covered by a transparent glass sheet to avoid evaporation of the solution. The sample (initial volume=500 mL) to be treated was stored in a reservoir and was continuously circulated in the system by a peristaltic pump at a constant flow rate of 110 mL/min. PTFE tubings were used to avoid adsorption. The reservoir was open to air to insure sufficient oxygenation. Artificial irradiation was provided by two UV lamps (F15T8, BLB 15W, Duke, Essen, Germany) emitting around 365 nm, positioned parallel to the reactor. At the start of each experiment, the reactor was stabilized with the dye solution for 30 min with the UV lamps off. After 30 min, a sample was collected ($t=0$) and the lights were turned on. The reactor was left to run for 24 h. Samples were collected from the reservoir periodically for UV-vis measurements through the duration of testing. The reactor was washed after every test by circulating ultrapure water for 24 h with the UV lamps on. The tests were run in triplicate.

Analytical procedures

UV-vis spectra were collected on a Secomam (Domont, France) Anthelie Light spectrophotometer, between 200 and 700 nm using a quartz cuvette (path length=1 cm). Ultra-pure water was used as blank. For each dye a calibration curve was obtained for concentrations ranging between 0 and 25 mg/L.

Ammonia concentration in the final samples was determined using a micro-Nessler method on a HACH DR2400 spectrometer (Hach Co., Colorado, USA). Nitrates were measured by ion chromatography (Dionex (Sunnyvale, California) fitted with a IonPac AS18 column) and dissolved organic carbon (DOC) was determined on a Shimadzu (Kyoto, Japan) TOC-VCSH device.

Toxicological assessment

The toxicity of the dye solutions (before and after photocatalysis) was compared after selection of the lettuce (*L. sativa* L.) test (Banks and Schultz 2005), adapted from Palácio et al. (2009). Two mineral water samples (Evian and Vittel) were tested as positive controls: they differ mainly according to their calcium, magnesium, and sulfate contents (On-line material). A 5-g NaCl/L solution was used as a negative control. Each sample was tested in its own container. A piece of absorbent paper was placed at the bottom of the container and 3 mL of the sample to be tested was added to the container. Lettuce seeds were placed on the absorbent paper. The container was covered with aluminum foil in which four small holes were made then placed in a sealed plastic bag which was maintained at 25 °C. After 5 days the number of germinated seeds was counted and the length (sum of radicle and hypocotyl lengths) of each

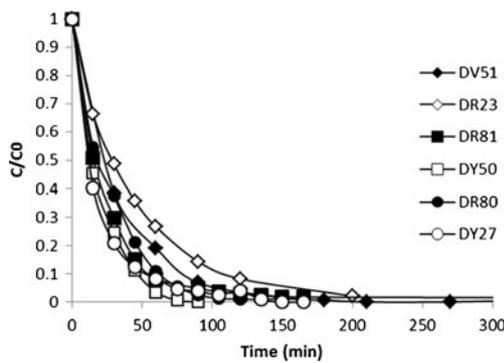


Fig. 2 Color removal kinetics of the six dyes (natural pH)

germinated seed were measured. The absolute germination index (AG), the germination index (GI), and the relative toxicity (RT) were computed using the following formulae:

$$AG = \frac{N_{germ}}{N_{seed}}$$

$$GI = \frac{N_{germ}}{N_{Posit_control}} \times \frac{L_{germ}}{L_{Posit_control}}$$

$$RT = \frac{L_{Posit_Control} - L_{Sample}}{L_{Posit_Control} - L_{Negat_Control}}$$

N_{seed} is the number of seeds placed in the container, N_{germ} and L_{germ} are the number and the average radicle length of germinated seeds in the tested sample, respectively. $N_{Posit_Control}$ and $L_{Posit_Control}$ are the number and the average length of germinated seeds in the positive control solution, respectively. $L_{Negat_Control}$ is the average length of germinated seeds in the negative control solution.

Descriptor calculation

The dye molecules were drawn using USEPA T.E.S.T. (Toxicity Estimation Software Tool) version 4.0.1. (2012), which provided 793 2D descriptors for each structure. The procedure was also applied to the dyes used by Lachheb et al. (2002) and Khataee et al. (2010) (Table 2).

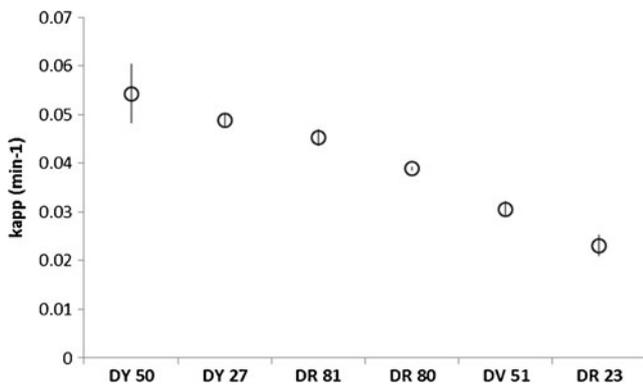


Fig. 3 Apparent color removal constants at natural pH. Open symbols average values. Vertical bar standard deviation

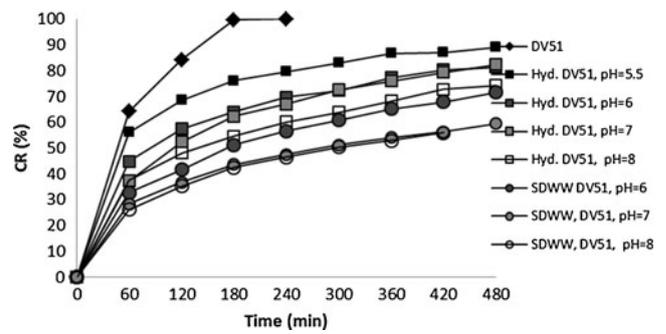


Fig. 4 Color removal kinetics of DV51 after hydrolysis or in synthetic dyeing wastewater (SDWW)

Results and discussion

Color removal

As shown in Fig. 2, color was removed rapidly for the six dyes under natural conditions, i.e. pH=5.82 (DR81), pH = 5.96 (DR80), pH = 5.92 (DR23), pH = 6.06 (DV51), pH = 5.98 (DY50), and pH = 6.75 (DY27).

A Langmuir–Hinshelwood approach was selected to calculate color removal rates.

$$r = \frac{dC}{dt} = k\theta = -\frac{kKC}{1 + KC}$$

Where:

- r Degradation rate
- k Degradation rate constant
- θ Occupation coverage of adsorption sites
- K Adsorption equilibrium constant (defined by the ratio between adsorption and desorption rate constants $K = k_{ads}/k_{des}$)
- C Equilibrium concentration (after adsorption)
- t Time

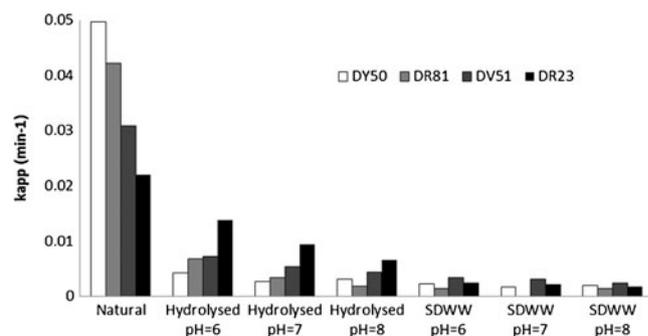


Fig. 5 Apparent color removal rates of the different dyes depending upon the type of solution (SDWW synthetic dyeing wastewater)

Table 3 DOC removal during photocatalysis of natural dye solutions for 24 h

Dye	Initial DOC (mg/L)	% removed
DR23	2.19	61
DR80	2.97	87
DR81	4.67	82
DV51	4.09	82
DY27	4.47	92
DY50	2.77	79

It was assumed that the term KC was negligible, because at low concentrations $kC \ll 1$ and the model follows a first-order kinetics, so the integrated reaction rate can be determined by apparent rate constant:

$$\ln \frac{C}{C_0} = -k_{app} \cdot t$$

where C_0 is the initial concentration of dye solution. The apparent rate constant k_{app} contains the degradation rate constant and the adsorption constant K , and that might be different from one dye to another according to their affinities toward the catalyst surface. Figure 3 summarizes the apparent color removal rate constants under natural pH.

The color removal efficiency, expressed by $CR(\%) = \left(1 - \frac{C}{C_0}\right) \cdot 100$, decreases when the dyes are hydrolyzed. The decrease is more important in the case of the synthetic dyeing wastewater, as shown in Fig. 4 for DV51. Similar results were obtained with the three other dyes that were subject to hydrolysis (DY50, DR81, and DV23). DR23 appears to be less sensitive to a simple hydrolysis, but the color removal rate decreases sharply when the dye is incorporated in the simulated dye house effluent. These results indicate how difficult it is to forecast the efficiency of a photocatalytic process on a real dye house wastewater based on simple dye solutions (Fig. 5).

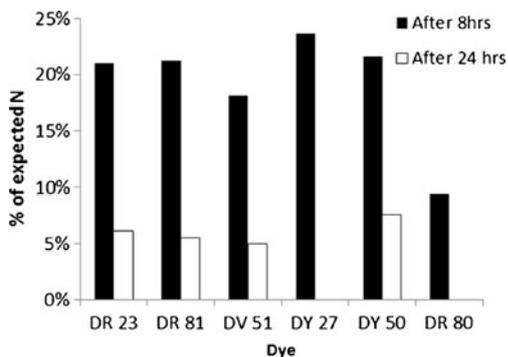


Fig. 6 Recovery of N as ionic species (NH_4^+ and NO_3^-) after 8 and 24 h of photocatalysis for natural dye solutions

Mineralization

Table 3 summarizes the efficiency of the photocatalysis in terms of organic carbon removal after 24 h. After 24 h, the mineralization cannot be considered as complete except for DY27. However, the impurities content of these dyes is rather high (Table 1) and it is difficult to know which part (dye or impurities) was recalcitrant. After hydrolysis similar C removal yields were obtained except for DY27, for which the C removal rate decreased to 22 % at pH 7 and 10 % at pH 8. Nitrogen atoms present in the dyes molecules were partially found as NH_4^+ and NO_3^- , with slightly more NO_3^- than NH_4^+ . A smaller amount of nitrogenous ions was found after 24 h than 8 h (Fig. 6). N recovery was in the same

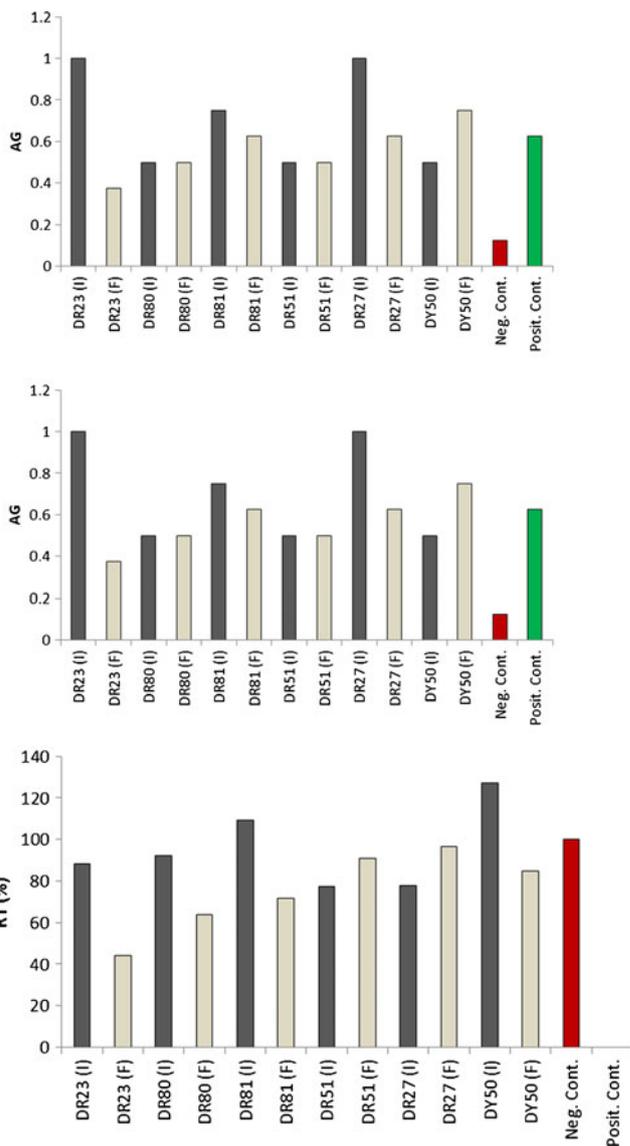


Fig. 7 Toxicological tests for natural dye solutions before (I) and after (F) photocatalysis. Positive control=Vittel mineral water. Negative control=5 g NaCl/L of Vittel mineral water

range in the case of hydrolyzed dyes. According to Guillard et al. (2003), the nitrogen atoms of the azo-bonds evolved towards N_2 when the nitrogen atom present in amino groups will first be transformed into NH_4^+ and later oxidized towards nitrates.

Toxicological tests

Figure 7 summarizes the results of the toxicological tests run with the “natural” dye solutions before and after photocatalysis, using Vittel mineral water as positive control. The absolute germination index was lower after treatment than before for three dyes (DR23, DR81, and DR27) and higher for only one dye (DY50). No change was observed for DR80 and DR51. The germination index was similar before and after photocatalysis except for DR23 and DR27 (it decreases) and DY50 (it increased). Overall the relative toxicity remained high after treatment.

Figure 8 compares the relative toxicity for four dyes (at “natural” pH, as hydrolyzed and included in a synthetic wastewater) before and after photocatalysis. For these tests, the positive control was Evian mineral water. AG was between 0.9 and 1 for all tests, except for the negative

control (0.75). The lettuce seeds were not from the same batch as the first series. This could explain the overall lower levels of toxicity observed. The average germination index was also high (0.93 with a standard deviation of 0.14) but was significantly lower for the negative control (0.29). Under these conditions the relative toxicities were always lower after treatment than before. However, except for DR23 at pH 7, the residual relative toxicity was larger than 10 %. One reason for such limited effect on toxicity removal is that reaction by-products, which are not fully mineralized after 24 h, could be as toxic (if not more) as the initial molecules. Even if this point is not yet fully investigated, it has been reported previously in literature (Fatta-Kassinos et al. 2011; Michael et al. 2012).

Relation with structure

Table 4 lists the dyes fastest to slowest in terms of the apparent color removal constant (“natural” pH) as well as significant structural features of the dyes. It is clear from the data that one single structural feature does not control the rate of color removal and that it was rather a combination of features that determined this rate. One of these features was

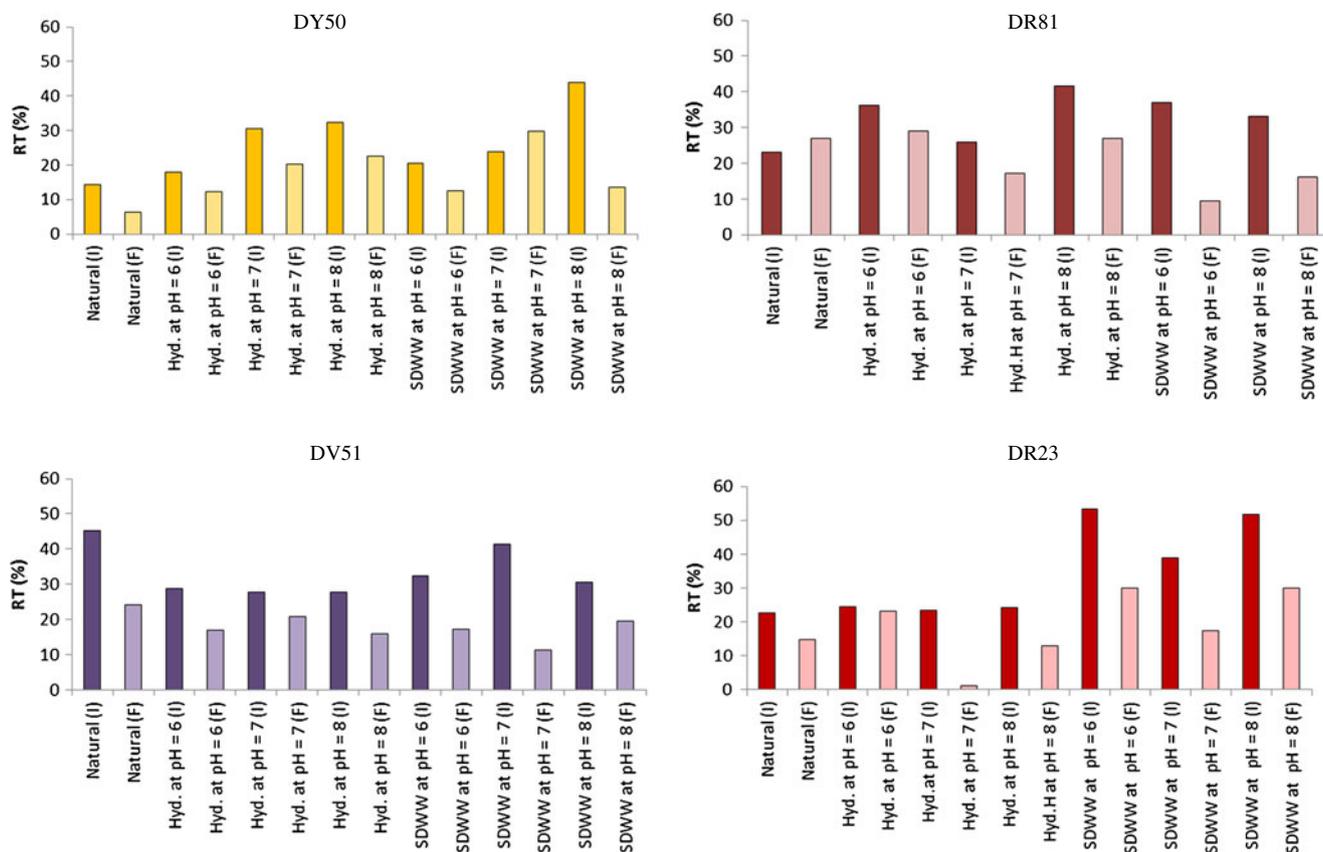


Fig. 8 Comparison of the relative toxicity before and after photocatalysis for four dyes (“natural” solutions, hydrolyzed solutions, and included in synthetic wastewater (SDWW)). Positive control=Evian mineral water. Negative control=5 g NaCl/L of Evian mineral water

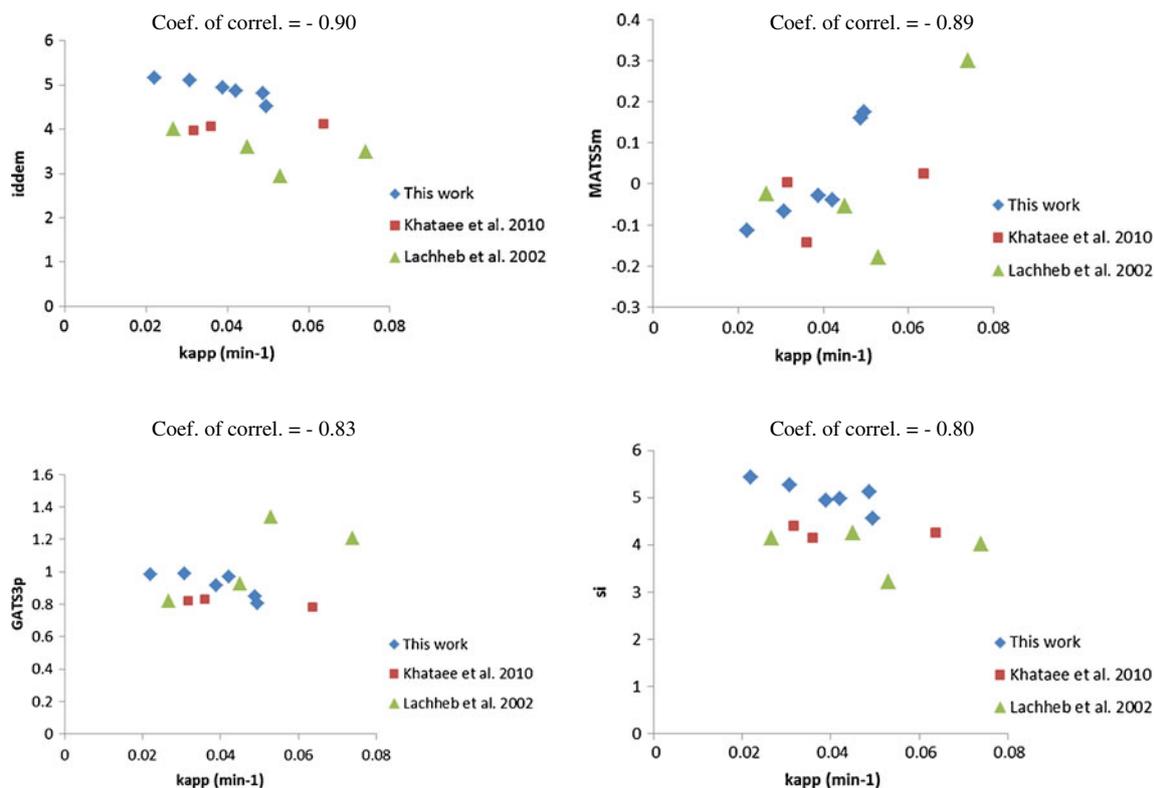
Table 4 Comparison of simple structural features with the apparent color removal rate

Dye	K_{app} (min^{-1})	Number of					$\text{SO}_3/\text{aromatic rings}$
		Sulfonic acid groups	Azo bonds	Aromatic rings	Benzene rings	Naphtalene rings	
DY 50	0.0543	4	2	6	2	2	0.67
DY 27	0.0488	2	1	4	3	0	0.5
DY 81	0.0453	2	2	5	3	1	0.4
DR 80	0.0389	6	4	8	4	2	0.75
DV 51	0.0306	2	2	5	3	1	0.4
DR 23	0.0231	2	2	6	2	2	0.33

the sulfonic groups which increase the solubility of the organic molecule in water and favor its interaction with hydroxyl radicals. The apparent color removal rate increases with the ratio of the number of sulfonic groups over the number of aromatic rings (defined as the number of benzene rings plus twice the number of naphthalene rings), except for DR80. But DR80 counts four azo bonds, instead of one or two for the five other dyes. These findings agreed with a previous study on acid azo dyes (Muthukumar et al. 2005). This would explain why DR80, the largest dye molecule, was still faster in degradation than some of the smaller molecules, and why DY50 was the fastest in discoloration.

The simple structural analysis provided by the parameters described in Table 4 does not allow taking into account the

full complexity of the tested dye molecules. The 793 2D descriptors provided by the T.E.S.T. software contain more details. However, it does not seem reasonable to run a multivariable data mining procedure based on them as our experimental data base is limited to six substances. Wols and Vries (2012) include 153 compounds in their data base. In a first step simple correlations were looked for between the apparent color removal rates obtained with the natural dye solution and the 409 non-zero 2D descriptors that were computed. The correlation coefficients ranged between ± 0.9 and ± 0.003 . Twenty percent of the 2D descriptors have a correlation coefficient higher than 0.5 with the experimental k_{app} values. In Fig. 9, the four 2D descriptors providing the highest coefficients of correlation have been plotted. The

**Fig. 9** k_{app} values plotted versus 2D descriptors values

data points corresponding to the dyes investigated by Lachheb et al. (2002) and Khataee et al. (2010) have been plotted, although they cannot be used in the experimental database as they were not obtained under the same experimental conditions. The information contents in *iddem* (mean information content on the distance degree magnitude), *MATS5m* (the Moran autocorrelation of a topological structure-5 weighted by atomic masses), *GAT33p* (the Geary autocorrelation of a topological structure-3 weighted by atomic polarizabilities), and *si* (mean information content) are related to the topology of the molecule (size and distances between atoms). *GAT33p* contains also information on how the molecule will react under an external electric field. Detailed information on these descriptors can be found in (Todeschini and Consonni 2009).

Conclusions

The structure of dye molecules affects the efficiency of advanced oxidation processes such as photocatalysis in terms of color removal, mineralization, and toxicity reduction. Facing the very large number of available dyes, efforts should be pursued in order to collect experimental data, obtained in similar experimental conditions, that can be compared. Normalization of photocatalytic tests should be encouraged. Such a database could be then confronted with structural parameters reflecting the structure and the topology of molecules and use to predict the behavior of other dyes. However, these descriptors do not take into account the actual state of the dye molecule in the wastewater (hydrolyzed molecule, presence of additives) that can modify the molecular structure. If color removal rate constants are easy to obtain, one should not forget that the ultimate goal of degradation is full mineralization (or at least transformation into harmless by-products) so that the reclaimed water could be either discharged into the aquatic environment or re-used (directly on-site for industrial purpose, for irrigation, etc).

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