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Biodegradability enhancement of textile dyes and textile wastewater by VUV photolysis

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Abstract

Photo-degradation and biodegradability have been studied for three different families of non-biodegradable textile dyes (Intracron reactive dyes, Direct dyes and Nylanthrene acid dyes) and a textile wastewater, using VUV photolysis. Ninety percent of color removal of dye solutions and wastewater is achieved within 7 min of irradiation. Biological oxygen demand (BOD) was found to increase during discoloration process while chemical oxygen demand (COD) decreased. The biodegradability index (BOD_5/COD) increases up to 0.40 for most of the dye solutions when total discoloration is obtained. It implies that VUV photolysis tends to enhance the biodegradability of dye containing solutions. Thus, this technique could be used as a pre-treatment step for conventional biological wastewater treatment.

Keywords: Photo-degradation; VUV photolysis; Dyes; Biodegradability; Textile wastewater

1. Introduction

Dyes contamination constitute a group of organic substances that are introduced into the environment as a result of several man-made activities. Considerable amount of these pollutants draw off during the textile dyeing and finishing operations [1]. Nowadays, colored water is unattractive and generates more and more complaints. Dyes have obtained notoriety as hazardous substances, because most of them are toxic and persistent in the environment [2,3]. Environmental pollution by dyes also set a severe ecological problem which is increased by the fact that most of them and their degradation by-products are difficult to discolour and degrade using standard biological methods [4,5]. This enables dyes to go through wastewater treatment plants without being eliminated [6].

Previous studies have demonstrated that traditional physical and chemical techniques such as coagulation, adsorption on activated carbon, ultra filtration, reverse osmosis can be generally used efficiently to remove dyes from textile wastewater [7,8]. However, these processes are considered as non-destructive since they merely transfer the dye from liquid to solid wastes. Consequently, the regeneration of the adsorbent material and post-treatment of solid wastes, which are expensive operations, are needed [9].

Biological treatment of wastewater and aqueous hazardous wastes is often the most economical alternative when compared with other treatment options [10]. Although many organic molecules are readily degraded, many other synthetic and naturally occurring organic molecules are bio-recalcitrant. Textile dyes are considered to be resistant to biodegradation [11]. The hazardous potential on bacterial strands of dyes has been reported elsewhere [12,13].

Recently, there has been considerable interest in utilization of advanced oxidation processes (AOP's) for destruction of organic compounds [14,15]. AOP's is based on the production of hydroxyl radicals as oxidizing agents to mineralize many synthetic organic chemicals. The chemical processes used include: H_2O_2/UV [16], ozone [17], photo-Fenton [18], Fenton, UV, wet air oxidation and natural sunlight. However, costs associated with chemical oxidation alone can often be prohibitive for wastewater treatment. Previous studies attempt some form of integration of chemical and biological treatment processes as an economical mean for treating bio-recalcitrant organic chemicals in wastewater [19–23]. The chemical process would be used as a pre-treatment in order to increase the biodegradability of wastewater. In these combined processes, it is necessary to determine the variation of biodegradability as a function of the chemical reaction conditions (time of pre-treatment,

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concentration of the oxidizing agent, temperature, etc). Many authors use the ratio BOD/COD as biodegradability index [24,25]. Other biodegradability measurements such as BOD, BOD/TOC, oxygen uptake, inhibition of oxygen consumption by activated sludge and EC_{50} toxicity have been reported [26].

Between these oxidation processes, direct photolysis of organic dyes has been proved difficult in the natural environment because the decay rates strongly depend on the dye's reactivity and photosensitivity [27]. Despite, most of commercial dyes are usually designed to be light resistant, recent effort has been directed at investigating the photo-degradation of organic dyes by UV-irradiation systems. For example, Chun and Yizong [28] studied the photocatalytic degradation of several azoïc dyes in TiO_2 suspension. Herrera et al. [13] examined the photochemical discoloration of non-biodegradable reactive dyes in the presence of Fe^{2+} ions and H_2O_2 and different irradiation wavelengths.

This work reports the VUV photo-degradation and discoloration of textile dyes in batch annular reactor. Three different models textile azoïc dyes (Intracron reactive dyes, Direct dyes and Nylanthrene acid dyes) were used. The aim of this work was to explore the effect of VUV light photolysis in the biodegradability of the treated solutions. The following topics are also studied in this paper (a) the biodegradability of initial and final dye solutions, (b) the inhibition of oxygen consumption by activated sludge for initial and final dye solution, (c) a case study for biodegradability improvement of textile industrial water.

2. Materials and methods

2.1. Chemicals

Reagents used for biological oxygen demand were $FeCl_3{\cdot}6H_2O$ (98%, PROBUS), $CaCl_2$ (95%, PANREAC), NH_4Cl (99,5%, PANREAC), $NaH_2PO_4{\cdot}H_2O$ (98%, PROBUS), $MgSO_4$ (97%, PANREAC) and NaOH (97%, MERCK). For COD analysis, digester and catalysis solutions were purchased from HACH, H_2O_2 (30%, CARLO ERBA). Reagents used for inhibition test are peptone (99.8%, SIGMA), beef extract (99.5%, DIFCO), urea (99.5%, ACROS), NaCl (99.8%, CARLO ERBA), $CaCl_2.2H_2O$ (98%, PRDABO), $MgSO_4{\cdot}7H_2O$ (98%, LABOSI) and K_2HPO_4 (97%, MERCK).

2.2. Analytical methods

UV-Vis spectra have been acquired between 200 and 800 nm with a secomam ANTHELIE spectrophotometer (Suprasil quartz cell; pathlength, 2 mm, scan speed, 1800 nm min^{-1}).

Analysis of samples for 5 days biochemical oxygen demand (BOD_5) were performed according to the procedures stipulated in Standard Methods (1985) Section 5210D with the use of an Oxitop system (VELP Scientifica). Inoculum used was taken from the municipal wastewater treatment plant in Ales (Ales, France).

Chemical oxygen demand (COD) was also measured using spectrophotometer (DR/2000 direct reading spectrophotometer) according to the Standard Methods (1985) Section 5220D.

Conductivity measurement was carried out with WTW LF330 conductivity hand-held meter (TertaCon 325).

The test for inhibition of oxygen consumption by activated sludge were carried out following the guidelines given by the international organisation for standardisation ISO 8192–1986.

2.3. Photolysis procedure

Photolysis has been tested as color removal process. Experiments were carried out in batch operation via an annular type reactor as shown in Fig. 1 (reactor capacity: 2 l, irradiated volume: 420 ml). The reaction zone consists of a cylindrical quartz tube (length: 85 cm, external diameter: 1.5 cm, irradiation thickness: 5.5 mm). The reactor is equipped with a low pressure mercury lamp (Pen Ray UV-P) emitting principally at 253.7 and 184.9 nm (VUV). The lamp

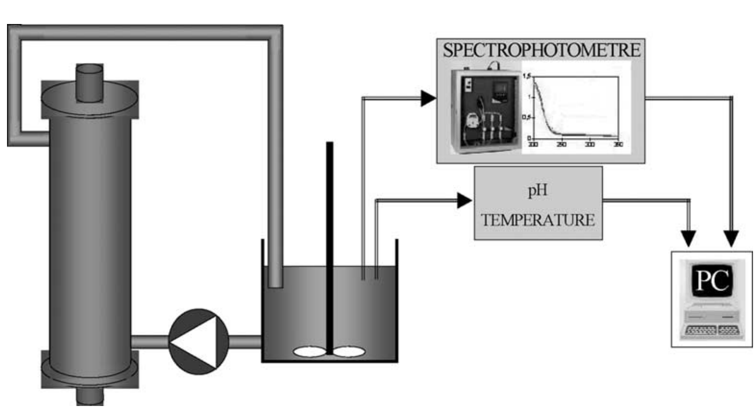

Fig. 1. Photolysis system.

is surrounded by a Suprasil quartz tube. The lamp nominal power is 120 W. Liquid re-circulates through a centrifugal pump at a flow rate of 180 l h^{-1}.

The reactor was charged with a 100 mg l^{-1} dye aqueous solution. No pH buffer solution was added to the reaction mixture. All experiments were performed at ambient temperature (21–25 °C). UV-Vis spectra were acquired on line and samples were periodically withdrawn for pH and COD analysis. The final discolored solutions were used for BOD tests and inhibition of oxygen consumption, after neutralization (pH 7).

3. Results and discussion

Physico-chemical characteristics of studied dyes (100 mg l^{-1}) and textile wastewater, before and after VUV photolysis, are summarized in Table 1. The chosen concentration is the maximal concentration that can be observed in most discharge textile wastewater.

3.1. Biodegradability tendency

In order to investigate the ability of the original dye to go through biodegradation, in addition to biodegradability index (BOD_5/COD), inhibition of oxygen consumption by activated sludge for the studied dyes has been tested. Indeed, inhibition test allows a rapid indication of the toxicity of water medium for non-acclimated biomass population. Moreover, it may advantageously take place of BOD_5 measurement. Domestic wastewater can be considered substantially biodegradable if it has a BOD_5/COD ratio between 0.4 and 0.8 [29]. The biodegradability index shows that all the studied dyes are non-biodegradable (Table 1). The inhibition effect on activated sludge for one dye of each family is presented as shown in Fig. 2, the sludge used in this test is taken from the municipal wastewater plant in Ales (Ales, France).

As it can be seen in Fig. 2, the presence of these dyes in small concentration leads to the inhibition of oxygen consumption by the activated sludge. This fact can be imputed, either to the toxicity of the dyes for the bacterial culture which leads to bacteria death, or to the non-biodegradable character of the organic load. Textile dyes, azoïc or not, were studied and have been classified as hardly biodegradable pollutants [31,32], so the second hypothesis could account for BOD_5 and inhibition test behaviour.

3.2. VUV photolysis

During photo-degradation experiments, UV-Vis spectra have been acquired according to irradiation time. Fig. 3 shows the evolution of UV-Vis spectra for Intracron Red dye. Total color removal occurs after 4 min of irradiation and, in the same time, only 23% of COD is eliminated.

Table 1 collects the results obtained for all studied dyes and the irradiation time required for 90% decoloration. It can be observed that Nylanthrene dyes require the same irradiation time for colour removal while different times are needed for the other two dyes families. Further investigations should be done to identify the functional groups the dyes involved in this behaviour. For the three dye families, an acidification of the medium can be noticed which can be imputed to the formation of mineral and organic acids by mineralization.

3.3. Biodegradability improvement

After photolysis, the treated dye solutions have been tested for their BOD, COD, conductivity (Table 1) and inhibition of oxygen consumption. As shown in Fig. 4 for Intracron Red and Nylanthrene Red dyes, BOD_5 of the dye solution is increased after photolysis, while COD decreased during the reaction. Table 1 shows the biodegradability index of all studied dyes when colour removal is 90%, and

Table 1
Physico-chemical characteristics of studied dyes (100 mg l^{-1}) and textile wastewater before and after VUV photolysis

Dyes	pH_i	pH_f	COD_i ($mgO_2\,l^{-1}$)	COD_f $mgO_2\,l^{-1}$	COD removal (%)	C_i (μS.cm^{-1})	C_f (μS.cm^{-1})	BI_i [a]	BI_f	I_t (min)[b]
Nylanthrene Yellow	6.3	2.8	128	90	30	40	66	0.09[c]	0.27	7.5
Nylanthrene Red	6.1	2.7	110	77	30	20	21	0.03	0.31	7.5
Nylanthrene Blue	7.9	2.8	140	88	37	23	46	0.05	0.21	7.5
Intracron Red	5.1	2.7	112	86	23	23	27	0.0	0.22	3.4
Intracron Orange	5.5	2.9	133	88	33	38	155	0.02	0.23	5.1
Intracron Black	5.5	2.8	71	58	18	26	109	0.0	0.26	2.5
Intracron Yellow	5.8	2.9	88	54	39	105	186	0.01	0.27	2.5
Direct Yellow	5.4	3.0	90	62	31	57	116	0.09	0.42	4.5
Direct Red	5.3	3.0	122	90	22	30	78	0.02	0.41	5.2
Direct Blue	5.5	2.9	100	77	23	18	63	0.09	0.42	4.0
Textile wastewater	6.8	3.0	325	267	18	1730	1730	0.0	0.22	13

[a] BI: biodegradability index $(BOD_5/COD)_i$.
[b] I_t: irradiation time required for 90% decoloration.
[c] BOD_5: result presented is the average of four repeated sample.

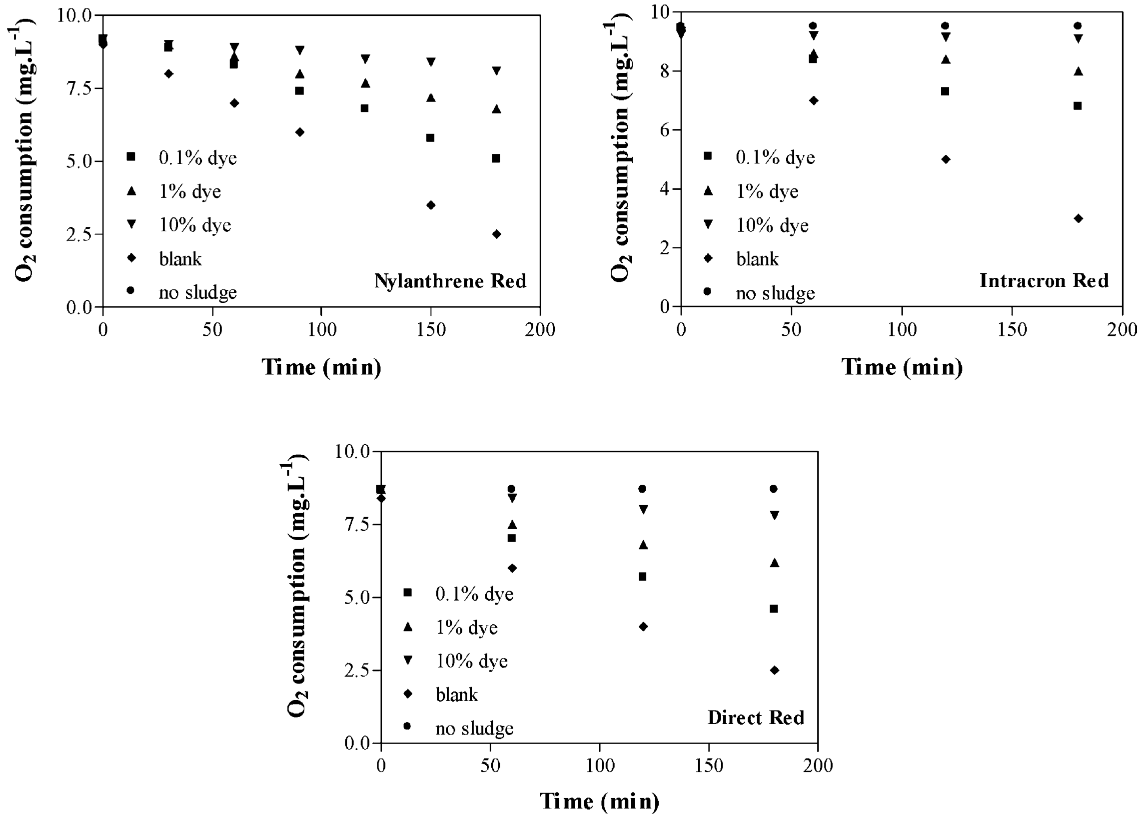

Fig. 2. Inhibition of O_2 consumption by activated sludge for three dye solutions (100 mg l^{-1}, pH: 7.0 ± 0.2).

the COD abatement. The increase of BOD_5 may imply that the biodegradability can be enhanced by the photolysis oxidation converting the non-biodegradable organic substrates into more biodegradable compounds.

Fig. 5 shows the BOD_5/COD ratio for initial and treated solutions changed from 0 to 0.42, depending on the structure of initial chemicals. It can be seen that using the VUV light, as pre-treatment step, leads to noticeable improvement in the biodegradability index (BOD_5/COD) for the three dyes families. This improvement in biodegradability is reached

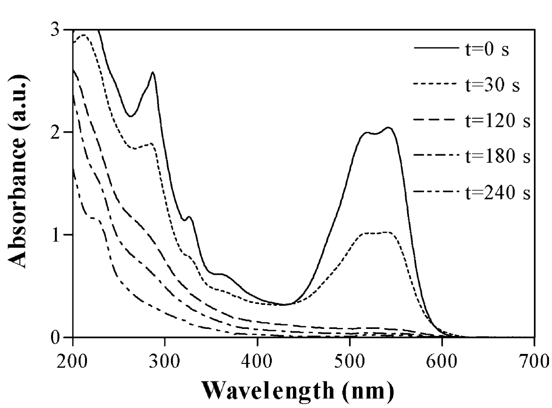

Fig. 3. Evolution of UV-Vis spectra vs. irradiation time for Intracron Red reactive dye solutions (100 mg l^{-1}).

with moderate COD conversion and short irradiation time. As mentioned previously, a wastewater sample is considered as readily biodegradable when a BOD_5/COD value is in the range of 0.40–0.80. This limit was reached easily for Direct dyes, which indicates that this family is degraded into intermediates that are readily biodegradable. Modern dyes are known to contain high composition ratio of aromatic rings in the dye molecules. These molecules are degraded into toxic compounds such as aromatic amines [33]. As an increase of biodegradability is observed after phtoloysis, it can be assume that this process do not generate such compounds. For the other two families (Nylanthrene acid dyes and Intracron reactive dyes), results show that dyes by-products may have inhibition for biodegradation.

So, it was decided for these families to go further more in photolysis, to see if the final BOD_5/COD ratio could be increased. The results shows that the index is increased for Intracron Red and Nylanthrene Red until, respectively, 0.39 and 0.38 with 2.0 min and 2.5 min overtime of irradiation. This effect is combined with COD removal of 28% and 40%, respectively, and a total discoloration. Other studied dyes show the same tendency in increasing the biodegradability index as the colour disappeared completely.

The by-products arising from total discoloration were tested for inhibition on activated sludge: no inhibition in oxygen consumption for activated sludge is observed during the 3 h test and the sludge behaviour is the same as

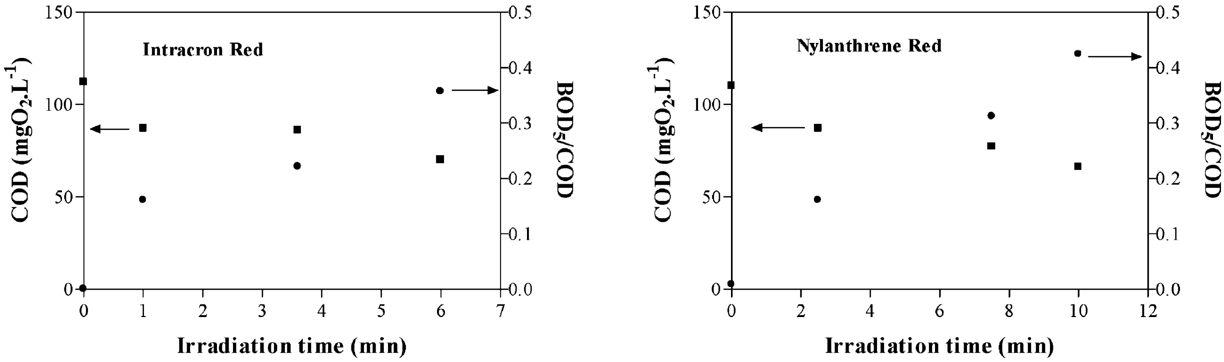

Fig. 4. Evolution of BOD_5/COD index and COD vs. irradiation time for Intracron Red and Nylanthrene Red ($100\,mg\,l^{-1}$).

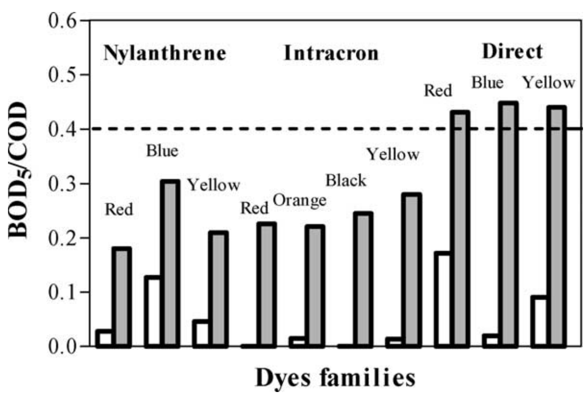

Fig. 5. BOD_5/COD evolution for initial and photolysed dyes solutions ($100\,mg\,l^{-1}$).

for the blank solution, but with more oxygen consumption due to the presence of biodegradable organic compounds (Fig. 6).

In order to see the effect of the absence of VUV light, same experiments were done with Infrasil quartz. In fact, this quartz prevents VUV irradiation (184.9 nm) to reach the reaction zone. Experimental results show that VUV irradiation is more efficient in degradation of textile dyes

Table 2
Comparison between UV and VUV photolyzed solutions

Dye	VUV COD removal (%)	UV COD removal %	UV BI_f	VUV BI_f	I_t (min)
Nylanthrene Red	30	24	0.2	0.31	7.5
Nylanthrene Blue	37	24	0.16	0.21	7.5
Intracron Red	23	15	0.15	0.22	3.5
Intracron Orange	33	28	0.15	0.23	5.0
Direct Red	22	26	0.3	0.41	5.2
Direct Blue	23	20	0.39	0.42	4.0
Textile wastewater	18	14	0.16	0.22	13.0

(Table 2). However, the tendency depends on the dye family: for Direct and Nylanthrene groups, the difference between Infrasil and Suprasil quartz is not so important since COD% and BOD_5/COD are in the same order of magnitude. While it can be noticed a valuable difference for Intracron family. In this case, the BOD_5/COD value decreases by 40% by changing the photolysis process from VUV to UV. More efforts should be done to investigate the degradation mechanism and by-products identification.

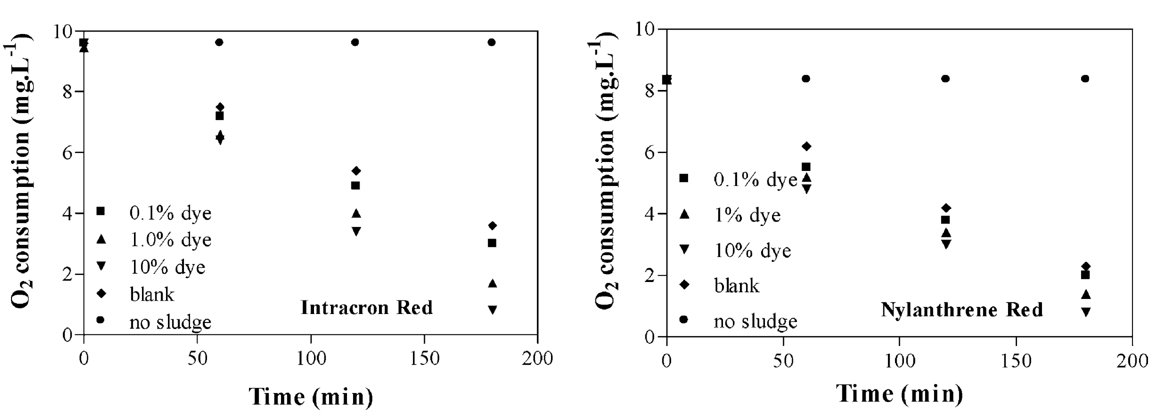

Fig. 6. Inhibition of O_2 consumption by activated sludge for photolyzed Nylanthrene Red dye and Intracron Red dye ($100\,mg\,l^{-1}$; pH 7.0 ± 0.2; irradiation time, 7.5 min, and 3.4 min, respectively).

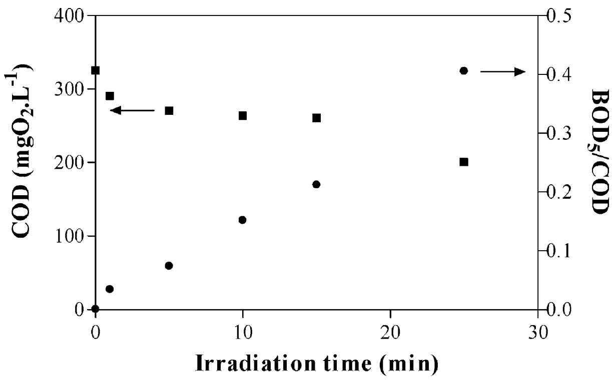

Fig. 7. Evolution of BOD_5/COD and COD vs. irradiation time for textile industrial water.

3.4. *Industrial textile wastewater*

The same treatment has been applied to an industrial wastewater coming from textile industry that uses the same studied dyes for specific applications. Clearly, this wastewater cannot be biodegraded according to its BOD_5/COD value equal to zero (Table 1). However, colour and COD have been removed by VUV photolysis. Total discoloration is achieved for about 13 min of irradiation. At the same time, the COD conversion of the wastewater was 18%. Concurrently, the ratio BOD_5/COD increased up to 0.22 (Fig. 7). It is interesting to note that the BOD_5/COD with irradiation time follows a linear tendency. It can be explained by the fact that more biodegradable by-products are generated during organic matter oxidation. The biodegradability has been enhanced up to the previous limit (BOD_5/COD >0.40) by further photo-degradation. The limit was reached after 28 min of irradiation and, during this time, 39% COD conversion is obtained. The difference between VUV and UV irradiation is about 25%. Previous study of industrial wastewater gives the same order of magnitude [30].

4. Conclusion

Ten textile commercial dye solutions among which acid, direct and reactive dyes, were successfully discolored by VUV photolysis. Greater than 90% colour removal of most dyes solutions was achieved after 7.5 min treatment. During the same time, 30% in average of COD is eliminated. Moreover, it was found that the BOD_5 of the dye solution increases after photolysis. This indicates that the biodegradability of textile dyes can be enhanced after only few minutes of treatment. The BOD_5/COD of dyes was increased up to the value for which organic matter is considered readily biodegradable (BOD_5/COD >0.40) when colour disappeared totally. For the tested industrial wastewater, an 20% abatement of COD and total colour removal were obtained after 13 min of irradiation. During this time, biodegradability enhancement of 0.22 was reached.

These results suggest that VUV photolysis can be used as a pre-treatment combined to an existing biological treatment.

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