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Strategy for the coupling of photochemical and biological flow reactors useful in mineralization of biorecalcitrant industrial pollutants

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Abstract

This study presents a combined photochemical (Fenton) and biological flow reactor for the degradation of *p*-nitrotoluene-ortho-sulfonic acid (*p*-NTS). This compound is contained in wastewaters coming from manufactures of dyes, surfactants and brighteners. The non-biodegradability of *p*-NTS in a fixed bed reactor (FBR) was proved under theoretically favourable conditions such as the presence of cosubstrates and adapted bacteria. From this ascertainment, *p*-NTS can be considered as a non-biodegradable compound. Afterwards, several experiments for sole photo-Fenton treatment were carried out in a laboratory scale photoreactor. By way of Dissolved Organic Carbon (DOC) and HPLC techniques, it was found that mineralization of *p*-NTS via photo-Fenton treatment in continuous or batch mode is not a cost-effective strategy. However, the chemical and biological characteristics studied for the phototreated samples showed that the Fenton system produced within a short time intermediates with very oxidised functional groups that are biodegradable and non-toxic. This thus could permit the integration of photochemical and biological processes. During treatments in continuous mode it was found that the main inconvenience of this application is related to the difficulty to control the H_2O_2 concentration. With this system, it was hard to avoid the inhibition of bacteria and hence a low biodegradation efficiency. To overcome the inconveniences of the process mentioned above, the semi-continuous mode was applied. The coupled photochemical-biological reactor was operated at five different treatment times (respectively 50, 70, 95, 110 and 125 min).

It was found that the most interesting zone for the coupled treatment is at the beginning of the photo-pretreatment when time is short enough to achieve a cost efficient process and high biological and overall efficiencies. However, if the pre-treatment time is too short (i.e., 50 min), the intermediates present in the solution are still structurally close to the initial biorecalcitrant compound and the efficiencies of both, the biological-and whole coupled process are dramatically diminished. Consequently, the optimal time to stop the photochemical treatment before leading the treated water to the biological reactor was found to be 70 min. At this moment, appropriate efficiencies were reached giving the best compromise between time and energy (71 $US per cubic meter) invested in both the biological and the overall treatment.

Keywords: *p*-NTS; Toxicity; Biodegradability; Photo-catalysis; Photo-Fenton reaction coupled photochemical and biological flow reactor

1. Introduction

The wastewater coming from numerous industrial processes contain organic toxic and/or non-biodegradable pollutants that are not eliminated by the conventional biological treatment systems.

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The biological treatments of the biodegradable residual waters are, at present, the most compatible with the environment and the least expensive. So, it is important for biologically recalcitrant compounds like *p*-NTS to develop efficient physique–chemical pre-treatment processes that reduce the toxicity and/or increase the biodegradability of the substances with a minimum impact over the environment and permit to lead the pre-treated water to a biological (low cost) treatment [1,2].

Previous studies have attempted some form of combined chemical oxidation and biological processes to treat contaminants in wastewater. The chemical processes utilised include ozone [3], as well as ozone/hydrogen peroxide [4], ozone/UV [5] electron beam with and without oxygen and hydrogen peroxide [6], potassium permanganate [7], UV-light [8], wet air oxidation [9] and natural sunlight [10], among others. Beneficial effects of such two-step treatments are commonly reported, these results, mainly from laboratory studies, suggest potential advantages for water treatment.

Surprisingly little basic engineering research has addressed the combining of chemical and biological processes and how this combination affects the global contaminant removal efficiency. Heinzle et al. [11] compared a variety of oxidation schemas for degrading pulp bleach plant effluents and in particular, reducing level of adsorbable organic halogens (AOX) in these waters. Aerobic pre-treatment followed by either (1) ozonation then bio-treatment or (2) cyclic ozonation/bio-treatment were deemed the preferable treatment options. In our knowledge, the only current commercial technology is the BioQuint® system that combines biological filtration and ozone/UV oxidation in a circulatory process for the degradation of a large diversity of wastewater [12].

In our group, special attention has been given to the non-expensive solar radiation [13–15]. Last year we have developed a coupled photochemical-biological reactor, which uses photo-Fenton treatment preceding biological process [16].

The present study shows an example of coupling advanced oxidation pre-treatment with bio-treatment. *p*-NTS has been chosen due to (a) the presence of nitro and sulphate substituents as electron withdrawing groups conferring biorecalcitrance to the molecule [17] (b) its presence in effluents from the Swiss chemical industry (c) previous work out of our laboratory reporting its relatively slow abatement via TiO_2/H_2O_2 in batch reactions [18]. Preliminary work with coupled photo-Fenton biological treatment indicated difficulties for *p*-NTS degradation [16]. Therefore, in the present work the pre-treatment strategy was modified with respect to the work presented in [16]. This modification allowed achieving high abatement efficiency in the subsequent biological as well as in the overall treatment.

An industrial photocatalytic-biological coupled process could take place at the exit of specific productions and/or in the mobile systems permitting itinerant treatment of the scattered low volume wastewater sources. The biological system (immobilised biomass reactor) which complete the photochemical pre-treatment should be compact, modular, flexible and resistant to the toxical shocks and to the charge and flow variations.

2. Experimental

2.1. Photoreactor

Annular geometry has been employed in the photochemical reactor as shown at the left hand side of Fig. 1. The glass spiral in the photochemical reactor is about 20 m long and 8 mm in diameter. The lamp is positioned in such a way that its centre line passes through the focal axis of the coil reactor. The lamp used was a 400 W medium pressure Hg-lamp, 40 cm long (Applied Photophysics). The predominant radiation was observed at 366 nm with 50% of the Hg lamp output (equivalent to ∼15 W). Care has been taken that all photons are absorbed in the optical thickness of the reactor coil since the scattering effects are less significant in a reacting medium having a high optical absorption. The reactor mixing flask 1 had a volume of 1 l. The runs were carried out at room temperature. The *p*-NTS solution was fed into the system from a 20 l reservoir and the H_2O_2 was automatically (control 1) added by means of a peristaltic pump 1 into the 1 l mixing flask 1 as shown in Fig. 1. The solution was continuously recirculated at 22 l/h through the illuminated part of the reactor by the pump 4. At the outlet of the photoreactor the pH was roughly neutralised by means of NaOH added via pump 3 (control 2).

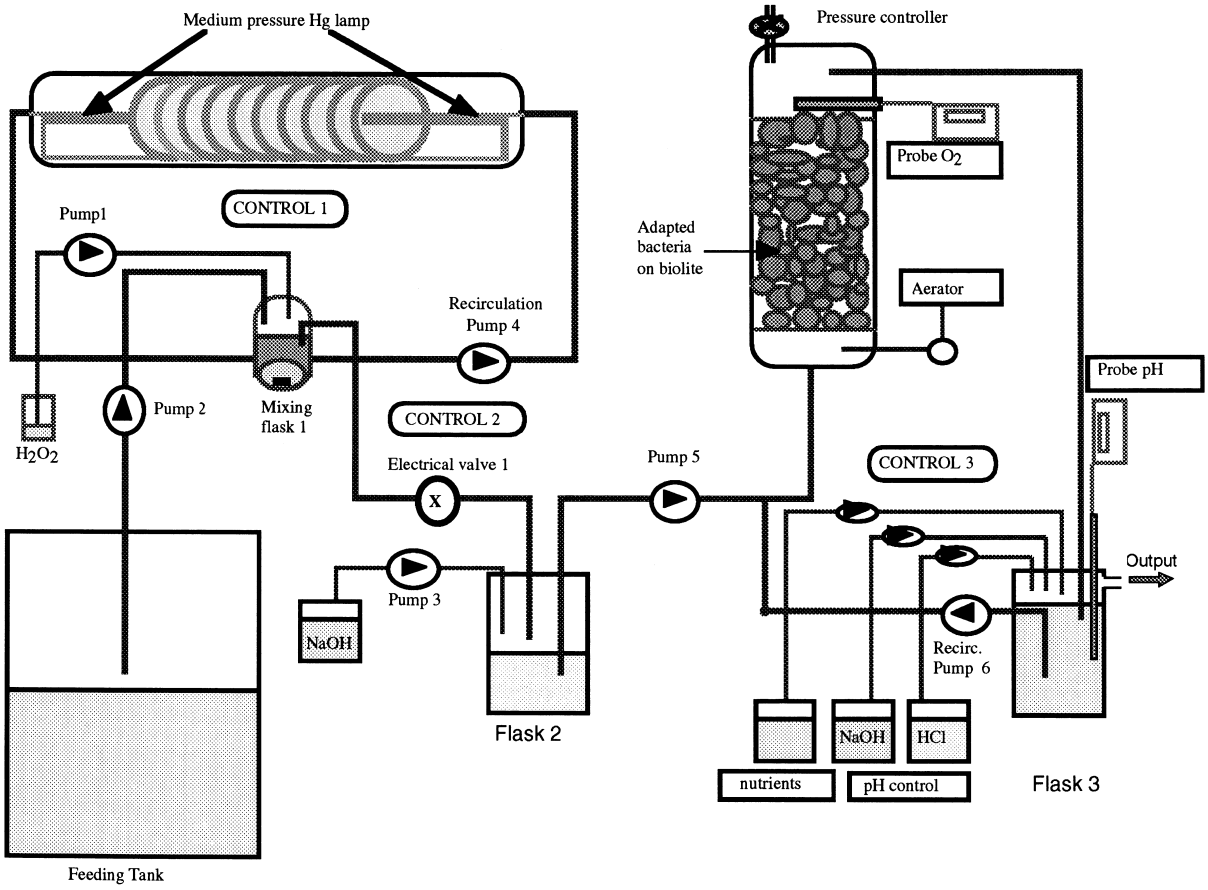

Fig. 1. Schematic drawing of coupled photo-Fenton-biological flow reactor.

2.2. Bioreactor

The fixed bed reactor (FBR) consisted of a column containing biolite colonised by activated sludge and having 1 l of water capacity. The effluent of the photochemical stage was circulated from flask 2 by the peristaltic pump 5 through the bottom of the column, which operated as an up-flow reactor. To assure a good contact of the phototreated solution with the biomass, the water was recirculated at 6 l/h through the column via the pump 6. The pH was controlled (control 3) and adjusted at 7.0 in flask 3 where the necessary nutrients (N, P, K and oligoelements) for the bacterial activity were also added. The aeration was about 150 l/h and the O_2 concentration was controlled by an O_2 probe at the top of the column. Other details for the second biological stage have been reported elsewhere [19,20].

2.3. Materials and procedures

p-NTS was a gift from Ciba (Monthey). $FeCl_3 \cdot 6H_2O$ and H_2O_2 were Fluka (30% w/w) analysis grade (p.a.) and they were used without further purification. In the biological reactor the nutrient salts used (P, N, K and oligoelements) were added from standard solutions during biological degradation. The mixture of these nutrients was added in the flask 3.

2.4. Chemical analysis

Dissolved Organic Carbon (DOC) measurements were performed using a TOC analyser (Shimadzu, model 5050A) provided with an automatic auto-sampler and with a solution of potassium phthalate as the calibration standard. Chemical Oxygen

Demand (COD) was carried out via a Hach-2000 spectrophotometer using dichromate solution as the oxidant in strong acid media. High performance liquid chromatography (HPLC) was carried out in a Varian 9065 unit (using diode array). A Spherisorb silica column ODS-2 was used and the mobile phase consisted of a solution Na-acetate in acetonitrile-water solution. This technique allows the measurement of the *p*-NTS concentration in solution and monitoring of the formation and decay kinetics of the aromatic and the aliphatic compounds during the process. The consumption of H_2O_2, during the reaction, was followed by the Merckoquant® test for peroxides.

2.5. Biological analysis

Biological Oxygen Demand (BOD) was performed by means of a Hg free WTW 2000 Oxytop unit thermostated at 20°C. The Zahn-Wellens Test [21] was used with high bacterial concentration of 1 g/l. The sludge from the biological activated sludge plant of Lausanne was aerated for a 24 h period and subsequently centrifuged. The centrifuged sludge was then suspended at 1 g/l in the Zahn-Wellens Test. During the photochemical pre-treatment, the toxicity was assessed using the Microtox® technique. The bioluminescence of *Photobacterium phosphoreum* in the presence of *p*-NTS was followed as a function of photochemical pre-treatment time [18].

3. Results and discussion

The biodegradability of *p*-NTS is practically zero. This negative result is deduced by lack of decrease of the dissolved organic carbon (DOC) observed by means of the Zahn-Wellens Biodegradability Test shown in Fig. 2. This test is carried out under conditions close to those of a wastewater treatment plant using activated sludge. DOC does not degrade (Fig. 2) even when using this test during a long period. This indicates that adaptation of bacteria did not occur. Two types of inoculum were tested. Samples 1 and 2 contained activated sludge from the urban wastewater treatment plant (Lausanne). Sample 3 contained activated sludge, which had previously been in contact with *p*-NTS during 35 days. Two concentrations were tested in order to discover if a toxicity effect is present.

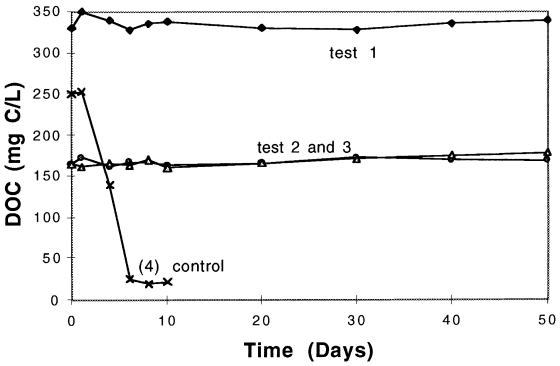

Fig. 2. Evolution of Dissolved Organic Carbon (DOC) in Zahn-Wellens biodegradability test of *p*-NTS solution (1) non-adapted biomass (2) non-adapted biomass and lower concentration of *p*-NTS (3) adapted biomass (4) control with diethylenglycol.

Sample 4 was a control experiment showing the activity of the activated sludge used since diethylenglycol (0.5 g/l) was degraded up to 98% within 6 days under the same conditions used during the test of *p*-NTS.

To conclude the biological part of the present work a large number of supplementary experiments attempting biodegradation of *p*-NTS were carried out in batch mode with the fixed bed reactor (FBR). The FBR was described in methods and shown at the right hand side of Fig. 1. Urban and industrial activated sludge was used in different aerobic culture media. The results summarised in Table 1 show no-biodegradation of *p*-NTS under several theoretically favourable conditions. Three methods were used to follow the tests reported in Table 1: (a) respirometry measurement with O_2 probe (b) determination of *p*-NTS concentration by HPLC and (c) Dissolved Organic Carbon (DOC) as a function of time.

3.1. Continuous versus batch photo-fenton treatment for mineralization of p-NTS

3.1.1. Continuous mode

The photoreactor shown at the left hand side of Fig. 1and described in methods was first operated in a continuous mode to attempt the mineralization of *p*-NTS. Fig. 3 shows the DOC of water leaving the photoreactor (into flask 2) as a function of time when the system is operated at different feeding rates (15, 10, 3 and 1 ml/min) via pump 2. The input concentration was in all cases 330 mg C per litre (or 1 g/l or 4.6 mmoles/l)

Table 1
Attempts to biodegrade *p*-NTS in fixed bed biological reactor

Number	Media used	Biodegradation
1.	Standard nutrient was used [8], *p*-NTS being the only source of carbon for the bacteria	Negative
2.	Standard nutrient, glucose added as cosubstrate	Negative
3.	Standard nutrient, yeast extract added as cosubstrate	Negative
4.	Standard nutrient without a source of nitrogen, *p*-NTS being the source of this element	Negative
5.	Standard nutrient as 4, but glucose was added as cosubstrate	Negative
6.	Standard nutrient without a source of sulphur, *p*-NTS being the main source of this element	Negative
7.	Standard nutrient as 6, but glucose was added as cosubstrate	Negative
8.	Sewage bacteria only, with the standard nutrient without a carbon source	Control
9.	Standard nutrient, *p*-NTS with glucose as the source of carbon. The concentration of *p*-NTS was progressively increased in order to attempt the adaptation of bacteria	Negative

Table 2
Performances of the photoreactor (shown at the left hand side of Fig. 1) operated in continuous mode at four different flow rates for degradation of a *p*-NTS solution. The concentration was 330 mg C per litre, 75 mg/l Fe^{3+}. One millilitre of H_2O_2 (30%) was automatically added in mixing flask 1 every 10 min. For details see text

	Flow rate (ml/min)			
	15	10	3	1
Flow rate (l/h)	0.9	0.6	0.18	0.06
Dilution rate, *D* (per h)	2.25	1.5	0.45	0.15
Residence time, t_r (h)	0.45	0.67	2.22	6.67
Input concentration (mg C per litre)	330	330	330	330
Output concentration (mg C per litre)	136	124	85	15
p-NTS removed (%)	100	100	100	100
DOC removed (%)	59	63	74	95
DOC degradation rate (mg C per hour)	175	124	44	19
Specific DOC degradation rate (mg C per hour per litre of photoreactor)	434	310	110	47
Energy consumption for 0.4 lamp (kW h/l)	0.45	0.67	2.22	6.67
Energy cost per cubic meter of treated water ($US)	54	80	267	800
Energy cost per kilogram of DOC removed ($US)	274	387	1091	2526

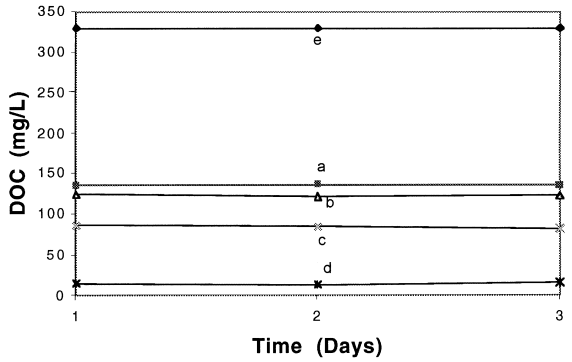

Fig. 3. DOC of solutions leaving the photochemical reactor operated in a continuous mode at different flow rates (a) 15 ml/min (b) 10 ml/min (c) 3 ml/min and (d) 1 ml/min. The input concentration (e) was in all cases 330 mg C per litre, 75 mg/l Fe^{3+}. One millilitre of H_2O_2 (30%) was automatically added in mixing flask 1 every 10 min.

of *p*-NTS and 75 mg/l of Fe^{3+}. The *p*-NTS solution was simultaneously recirculated by pump 4 at 22 l/h through the 0.4 l illuminated part of the photoreactor. The kinetics of photodegradation observed in this continuous mode treatment was obtained when the H_2O_2 (30%) was continuously added in mixing flask 1 (1 ml every 10 min) in order to assure a favourable H_2O_2/DOC ratio. The degradation was followed at least during 3 days after reaching the steady state. In all cases, some hours were needed at the beginning of the treatment to attain a steady state. Table 2 summarises the characteristics and performances of the system under each flow (feeding) rate operation (respectively 0.9, 0.6, 0.18 and 0.06 l/h). For all four flow rates, the primary degradation efficiency expressed as % of *p*-NTS removed (followed by HPLC analysis) was of 100%. In contrast, ultimate degradation effi-

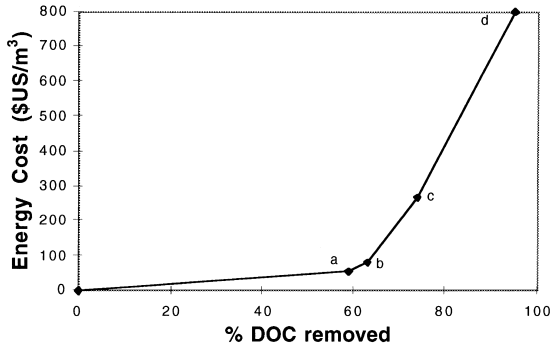

Fig. 4. Lamp energy cost in $US per cubic meter of phototreated water containing *p*-NTS as a function of DOC removal efficiency at different residence times (or continuous flow rates) (a) $t_r = 0.45$ h (15 ml/min) (b) $t_r = 0.67$ h (10 ml/min) (c) $t_r = 2.22$ h (3 ml/min) (d) $t_r = 6.67$ h (1 ml/min). The conditions are the same as in Fig. 3.

ciencies (mineralization followed by DOC analysis) were very different: respectively 59, 63, 74 and 95%. Table 2 shows that DOC degradation rates (respectively 175, 124, 44 and 19 mg C per hour) and flow rates decrease while residence time and energy cost for the lamp operation increase. The energy cost can be calculated knowing that the used light source is a 400 W lamp and that in Switzerland the energy cost is around 0.12 $US per kilowatt hour. These cost values are only useful to make comparisons and they can not be used to calculate the true energy cost because commercial lamps used for industrial systems are far more efficient than our laboratory lamp.

Fig. 4 shows the energy cost per cubic meter as a function of DOC removal (mineralization) attained at different residence times (or flow rates) applied. Decreasing of flow rate from 15 to 3 ml/min does not meaningfully enhance (from 59 to 74%) the DOC removal efficiency. DOC removal is close to total mineralization for only very low flow rate (1 ml/min) and for very high energy cost (800 $US per cubic meter of treated water). The energy cost necessary to eliminate the last 37% of DOC is dramatically enhanced and represents 90% of the cost to be invested for the total mineralization. From the observations presented above, one can conclude that intermediates formed during the initial stage of the photo-Fenton treatment are very photorecalcitrant and the decrease of the flow rate (or the increase of the retention time) is not a cost efficient strategy to reach mineralization of *p*-NTS solution in a continuous flow photoreactor.

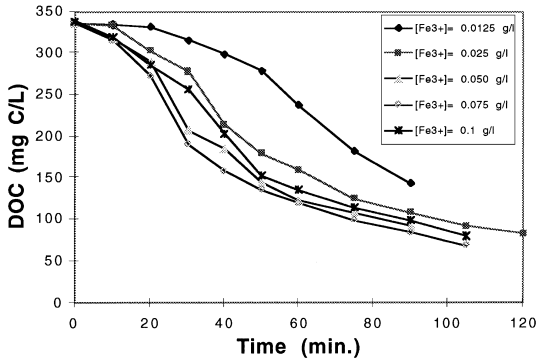

Fig. 5. Photo-Fenton batch degradation of a *p*-NTS solution (1 g/l) at different concentrations of Fe^{3+}. Three hundred microlitre of H_2O_2 (30%) were added every 5 min.

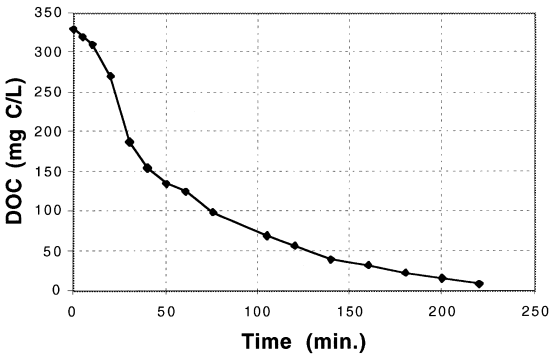

Fig. 6. DOC evolution during the photo-Fenton batch treatment of *p*-NTS solutions. The conditions are the same as in Fig. 5 with 75 mg/l of Fe^{3+} and the treatment is continued up to total mineralization.

3.2. Batch mode

The photoreactor shown at the left side of the Fig. 1 and described in experimental section was also operated in batch mode to attempt the photo-Fenton mineralization of *p*-NTS. 1.2 l of *p*-NTS solution (1 g/l or 4.6 mM) was recirculated from mixing flask 1 by pump 4 into the coil reactor ($V = 0.4$ l) at 22 l/h and 300 μl of H_2O_2 (30%) were added every 5 min. Different concentrations of Fe^{3+} were tested, and Fig. 5 shows that the best result was obtained with a Fe^{3+} concentration of 75 mg/l.

The latter concentration was selected to continue the treatment up to 220 min (Fig. 6) to reach almost total mineralization. In this case, the residence time (t_r) in illuminated part of photoreactor is 73 min and it

was obtained by: $V_i \cdot t \cdot V_t^{-1}$, where V_t is the total volume of treated water, t is the time necessary for mineralization (220 min) and V_i is the volume exposed to light into the photoreactor (400 ml). This system could only treat 1.2 l of solution (1200 mg or 5.5 mmoles or 400 mg of DOC) during 3 h 40 min that corresponds to a degradation rate of 0.33 l/h (or 108 mg C per hour). As the illuminated part of the reactor contains 400 ml, the specific degradation rate attained was 270 mg C or 820 ml/h per litre of photoreactor. The degradation rates, obtained with this batch mode, are also very low and the performances seem insufficient for a practical application. One could estimate the energy cost for the total mineralization of *p*-NTS contained in 1 m^3 of solution taking into consideration the following:

$$\frac{400\ (\mathrm{W\,h}) \times 1000}{0.328\ (\mathrm{l})} = 1250\ (\mathrm{Kw\,h/m^3}) \qquad (1)$$

Taking 0.12 $US as the cost per kilowatt hour in Switzerland, we can estimate 150 $US per cubic meter (or 450 $US per kilogram DOC removed). To obtain the same result using the continuous mode discussed above, the energy cost is 800 $US per cubic meter of treated solution. In the latter case, the treatment time is 5.4 times longer than in batch mode (see Table 2). Although the batch operation mode is more energy cost efficient than the continuous system described above, and an appropriate scaling up of the installation should decrease the running energy cost, the complete photomineralization obtained by this way is still too expensive and it is not a convenient strategy.

3.3. Strategy for the coupling of photochemical and biological treatments

If the photochemical treatment is stopped when 60% of the initial DOC value has been removed, the energy cost of the process is dramatically reduced. This is the case for both, continuous and batch operation modes. For the batch mode, the energy cost was 34 $US per cubic meter which represents 23% of the total cost of mineralization (150 $US). While in continuous mode, the energy cost to remove 60% of DOC was 54 $US per cubic meter representing 6.5% of 800 $US required for the total mineralization (Fig. 4 and Table 2). Therefore, the sole way to render photo-Fenton treatment economically attractive for the complete mineralization of non-biodegradable and/or toxic compounds like *p*-NTS is applying the photochemical reaction as pre-treatment preceding biological final treatment. The pre-treatment to modify the chemical structure of the biorecalcitrant *p*-NTS should be short enough and efficient. Thus, the chemical and biological characteristics of phototreated solutions were studied to determine the earliest moment when the photochemical (expensive) pre-treatment reduces the antiphysiological properties of *p*-NTS. This would permit transfer of phototreated water to a biological (low cost) treatment.

3.4. Chemical and biological characteristics of phototreated solutions

3.4.1. Chemical analysis

To be sure that the photochemical process can be used as pre-treatment preceding a biological treatment, it was very important to gain information concerning the chemical nature of the intermediates formed during the photo-pretreatment. A solution of *p*-NTS (1 g/l, 330 mg C per litre, 4.6 mM) was phototreated in batch mode in the presence of H_2O_2 (300 μl each 5 min) and Fe^{3+} (75 mg/l). Fig. 7(a) shows the results obtained by HPLC analysis where it can be seen that before 5 min of photochemical pre-treatment, the initial *p*-NTS (retention time: 5.9 min) has disappeared from the solution. The scanning by diode array detection of the other peaks corresponding to intermediates revealed the existence of a single aromatic compound different from *p*-NTS. This aromatic compound attained a maximum concentration before 5 min, and decayed within 20 min. Diode array detector also detected two main aliphatic compounds, but they could not be identified against commercial standards. Removal of the remaining H_2O_2 by a catalase enzyme was necessary to assure the stability of samples before HPLC analysis. The average oxidation state value of intermediates shown at the right hand side axis of Fig. 7(a) is a function of photo pre-treatment time. These values were estimated according to [1].

$$\text{Average Oxidation State} = 4 \times \frac{\mathrm{TOC} - \mathrm{COD}}{\mathrm{TOC}} \qquad (2)$$

Where TOC and COD are respectively expressed in moles of C per litre and moles O_2 per litre. Average oxidation state takes a value between +4 for CO_2 the most oxidised state of C and −4 for CH_4 the most reduced state of C. In Fig. 7(a) a plateau is observed for this

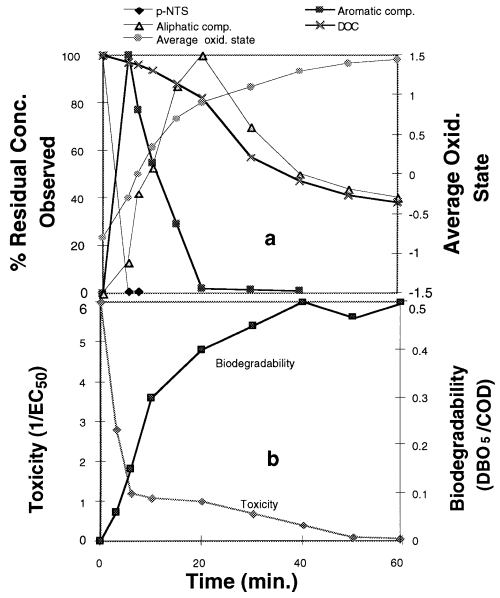

Fig. 7. (a) Relative concentration (expressed in % of DOC) of aromatic and aliphatic intermediates observed during the photo-treatment of a solution of *p*-NTS (1 g/l, 330 mg C per litre, 4.6 mM) H_2O_2 (300 μl each 5 min) and Fe^{3+} (75 mg/l). The average oxidation state evolution is shown at the left hand side axis. (b) Evolution of toxicity and biodegradability of the phototreated solution of *p*-NTS as a function of treatment time.

value after 20 min of photo-treatment. This suggests that the chemical nature of these photo-recalcitrant intermediates does not vary significantly after 20 min of reaction. Furthermore, the value of the plateau after 50 min (average 1.45) is characteristic of very oxidised and biocompatible aliphatic compounds like oxalic acid. Other details about both chemical characteristics of intermediates and hypothetical degradation schema were reported elsewhere [16].

3.4.2. Biological analysis

Chemical observations described above are validated by the concomitant decrease of the toxicity and increase of biodegradability shown in Fig. 7(b). Reduction in toxicity reflects the abatement of *p*-NTS up to 6 min. A slower decrease was subsequently observed until complete disappearance of toxicity (50 min). The results reported in Fig. 7(b) and obtained via Microtox® test show the efficiency of the pre-treatment applied for a short period of time. The pure *p*-NTS has a weak as well as an acute toxicity, and its most undesirable property is its recalcitrance to biodegradation leading to potential chronic effects in natural environment. The most important conclusion from Fig. 7(b) with respect to toxicity is that intermediates more toxic than the initial compound did not develop during the photo-assisted pre-treatment process. Moreover the beneficial effect of a short photo-treatment on the biodegradability of *p*-NTS solution is readily seen in Fig. 7(b) because the ratio BOD_5/COD attained is >0.4 within 20 min. Thus, after this short period of time the *p*-NTS solution reaches the biodegradability index for easily biodegradable wastewater. We can conclude this part of the work by the following statement: photo-assisted Fenton system generates in a very short period of time (30 min) intermediates with very oxidised functional groups which are non-toxic and as biodegradable as urban wastewater.

3.5. Coupling of photochemical-biological systems in continuous mode

3.5.1. Rough control of residual H_2O_2 concentration

H_2O_2 is known to induce detrimental physiological effects on bacteria. However, the lethal or critical concentration of H_2O_2 and the ability of bacteria to adapt can change for each bacterial consortium. Since the continuous elimination of residual H_2O_2 was technically difficult to install in our set up, we tried first to operate the system with high values (average 20 mg/l) and no strict control of residual H_2O_2 after the photochemical treatment. In addition, in this part of the work we wanted to make a compromise between the best conditions (i.e., H_2O_2/DOC ratio) for the photochemical process without affecting the optimal activity of the biological reactor. We also expected to induce adaptation of bacteria in the FBR to a high H_2O_2 concentration in order to operate the photochemical reactor with a high H_2O_2/DOC ratio (between 15 and 30 mole/mole) convenient to photo-Fenton process.

The coupled reactor shown in Fig. 1 was then operated in a continuous flow mode for the coupled photochemical-biological degradation of *p*-NTS. The feeding solution containing 330 mg C per litre (1 g/l or 4.6 mmoles of *p*-NTS) and 75 mg/l of Fe^{3+} were introduced from the feeding tank to the mixing flask 1 via the pump 2. The mixing flask 1 received, also

via pump 1, the desirable amount of H_2O_2 in order to maintain a favourable H_2O_2/DOC ratio in the photoreactor. The solution of the mixing flask 1 was continually recirculated at 22 l/h through the illuminated part of the reactor by the pump 4. The electrical valve 1 was in this case always open and the liquid reached the flask 2 by gravity. In flask 2 the pH was roughly neutralised, going from average 3 (optimal to Fenton reaction) to average 7 (optimal to biological work) by means of NaOH solution, automatically injected via pump 3 (control 2). After this, the pre-treated solution was brought to the bottom of the FBR by the pump 5. The FBR had previously been colonised by activated sludge from the aerobic municipal treatment plant of Lausanne (Vidy).

Table 3 shows the results obtained when the coupled photochemical-biological reactor was operated in a continuous flow mode without strict control of H_2O_2 at 10 and 3 ml/min of feeding flow rates. DOC measurements were performed during 5 days on samples drawn after both photochemical and biological reactors after reaching the steady state. When the system was operated at 10 ml/min ($t_r = 0.67$ h) photochemical, but not biological DOC removal efficiency, was relatively high (respectively 53 and 29%). Two different factors could explain this observation: (i) intermediates formed during the first step of photochemical treatment are still present in solution and structurally close to the initial biorecalcitrant compound (ii) residual concentration of H_2O_2 induces an inhibitory effect on the bacterial consortium in the biological part of the coupled reactor. However, if the residence time is extended from 0.67 to 2.2 h (or flow rate from 10 to 3 ml min/min) in order to eliminate biorecalcitrant intermediates, a very poor increase of DOC removal efficiency was observed in the biological part of the reactor. Table 3 shows the detrimental effect on biological and overall DOC removal efficiencies when the residual H_2O_2 concentration is not well controlled. Residual H_2O_2 concentration is very difficult to regulate precisely in continuous mode because of inertia of the system. Therefore, in our conditions it was difficult to avoid high concentrations of H_2O_2 going into the biological part of the reactor. This led to inhibition of bacteria and subsequent poor biodegradation efficiencies. Also the continuous elimination of H_2O_2 (i.e., by catalase) in flask 2 is not convenient and not cost efficient.

3.5.2. Strict control of residual H_2O_2 concentration

In run 3 (2 ml/min of flow rate) shown in Table 3, a slow H_2O_2 addition of 0.6 ml/h was carried out by pump 1. Strict and recurrent measurements were achieved in flask 2 in order to assure always a residual H_2O_2 concentration lower than 10 mg/l. In this way, the biological DOC degradation efficiency was strongly increased (78%). However, a reduction of residual H_2O_2 implies a decreasing of H_2O_2/DOC ratio and the concomitant diminishing of the photochemical efficiency. This was observed in this last run, where to attain 135 mg C per litre, the system was able to treat only 2 ml/min of *p*-NTS solution ($t_r = 3.33$ h). In contrast, to reach the same DOC by means of a continuous, sole photochemical treatment this value was 15 ml/min ($t_r = 0.45$ h). In the latter case shown in Table 2 and Fig. 3, no control of residual H_2O_2 concentration was necessary since the purpose was to maintain the best H_2O_2/COD ratio for fast COD removal, and coupling with a sensitive biological treatment to H_2O_2 was not present.

3.6. Coupling of photochemical-biological system in semi-continuous mode with strict control of residual H_2O_2 concentration

The first period of photochemical treatment is more efficient in batch than in continuous mode. Because the control of residual H_2O_2 and pH is easier in batch mode than in continuous mode, it was decided to work in sequential batch mode during a short period of time of photo-pretreatment. Eight hundred millilitre of *p*-NTS solution was automatically pumped by pump 2 (control 1) from feeding tank into the mixing flask 1 where the H_2O_2 was simultaneously added by pump 1 (control 1) in adequate amount. This amount was enough to assure a good H_2O_2/DOC ratio at the beginning of the photo-treatment when the photoreactivity is the highest. This ratio also allowed achievement of a DOC value ($\approx$135 mg C per litre) corresponding to easily biodegradable intermediates and less than 10 ml/l of H_2O_2 in flask 2 at the end of the fixed time (control 2) of batch treatment. When the chosen time of batch treatment is attained, the electrical valve 1 is opened to allow the 800 ml of treated solution to go into the flask 2. At the same time pump 3 is activated, pumping some NaOH solution into flask 2 to neu-

Table 3
Performances for *p*-NTS degradation (1 g/l, 75 mg/l of Fe^{3+}) by coupled photochemical-biological reactor operated in a continuous mode at three different flow rates with and without control of residual concentration of H_2O_2. For detail see text

	Photochemical treatment (in a 0.4 l reactor)			Biological treatment (in a 1 l reactor)			Coupled treatment		
	Input flow rate (ml/min)			Input flow rate (ml/min)			Input flow rate (ml/min)		
	10[a]	3[a]	2[b]	10[a]	3[a]	2[b]	10[a]	3[a]	2[b]
Residence time, tr (h)	0.67	2.22	3.33	1.67	5.55	8.3			
Input concentration (mg C per litre)	330	330	330	155	110	135			
Output concentration (mg C per litre)	155	110	135	110	60	30			
p-NTS removed (%)	100	100	100						
DOC removed (%)	53	67	59	29	45	78			
Overall efficiencies (% of DOC removed) in coupled reactor							67	82	91

[a] Without control of residual H_2O_2 concentration.
[b] With strict control of residual H_2O_2 concentration.

tralise the acidic water leaving the photo-Fenton treatment. This cycle is continuously repeated. For this reason this type of operation was named semi-continuous mode. Thereafter, the photo-treated water is led from the flask 2 to the biological reactor in a classical continuous mode.

The coupled photochemical-biological reactor shown in Fig. 1 and described in the experimental part was operated in semi-continuous mode at five different treatment times: 50, 70, 95, 110 and 125 min (corresponding respectively to the following flow rates: 0.96, 0.68, 0.50, 0.44 and 0.38 l/h). Each flow rate was maintained during at least 5 days after reaching steady its state to assure the stability of the system during a meaningful period of time. Photoreactor characteristics and performances of the coupled system are summarised in Table 4. Fig. 8 shows the percentage of DOC removed in a photochemical, a biological and a whole coupled photochemical-biological reactor as a function of treatment time (or flow rate) applied in the photoreactor.

In Fig. 8 it can be seen that the most interesting zone for the coupled treatment is at the beginning when the photo-pretreatment time is short enough to achieve a cost efficient process as well as high biological and overall efficiencies. This statement is supported in Fig. 8 by the observed accordance between a high contribution of the biological part of the process and a low energy cost of the photochemical treatment. However, if the pre-treatment time is too short, (i.e., 50 min) the intermediates present in the solution are still structurally close to the initial biorecalcitrant compound and the efficiency of both the biological and the whole coupled process is dramatically diminished.

Consequently, the optimal time to stop the photochemical treatment before leading the treated water to the biological reactor was found to be 70 min. At this moment appropriate efficiencies were reached for the best compromise between the time and energy (71 $US per cubic meter) invested in both biological and overall treatment. To our knowledge this is the first paper reporting a successful integration of photo-Fenton and biological processes for total mineralization of bio-recalcitrant compounds.

4. Conclusions

This study demonstrates the utility of the photo-Fenton pre-treatment for an aromatic and non-biodegradable compound (*p*-NTS) prior to biotreatment with a combined reactor concept. The non-biodegradability of *p*-NTS in a fixed bed reactor was proved under theoretically favourable conditions such as the presence of co-substrates and adapted bacteria. The photo-assisted Fenton system used as a pre-treatment generates in a very short period of time (30 min) inter-

Table 4
Performances for *p*-NTS degradation (1 g/l, 75 mg/l of Fe^{3+}) by coupled photochemical-biological reactor operated in semi-continuous mode at three different flow rates with strict control of residual concentration of H_2O_2. For detail see text

	Photochemical treatment 0.4 l reactor					Biological treatment 1 l reactor					Coupled treatment				
	Input flow rate (l/h)					Input flow rate (l/h)					Flow rate (l/h)				
	0.96	0.68	0.50	0.44	0.38	0.96	0.68	0.50	0.44	0.38	0.96	0.68	0.50	0.44	0.38
Treatment time (min)	50	70	95	110	125										
Dilution rate, *D* (per h)	2.4	1.7	1.25	1.1	0.95	0.96	0.68	0.50	0.44	0.38					
Residence time (h)	0.42	0.58	0.80	0.91	1.05	1.04	1.47	2.00	2.27	2.63					
Input concentration (mg C per litre)	330	330	330	330	330	200	136	100	80	76					
Output concentration (mg C per litre)	200	136	100	80	76	78	28	24	19	17					
p-NTS removed (%)	100	100	100	100	100										
DOC removed (%)	40	59	70	76	77	61	80	76	76	77					
DOC degradation rate (mg C per hour)	144	114	73	59	47	141	64	24	12	11					
Specific DOC degradation rate (mg C per hour per litre of reactor)	360	310	182	147	117	141	64	24	12	11					
Energy consumption for 0.4 W lamp (Kw h/l)	0.42	0.59	0.80	0.91	1.05										
[a]Energy cost per cubic meter in ($US)	50	71	96	109	126										
Energy cost per kilogram of DOC removed ($US)	333	420	657	813	1020										
Overall efficiencies (% of DOC removed) in coupled reactor											76	91	93	94	95

[a] In Switzerland 1 Kw h = $US 0.12.

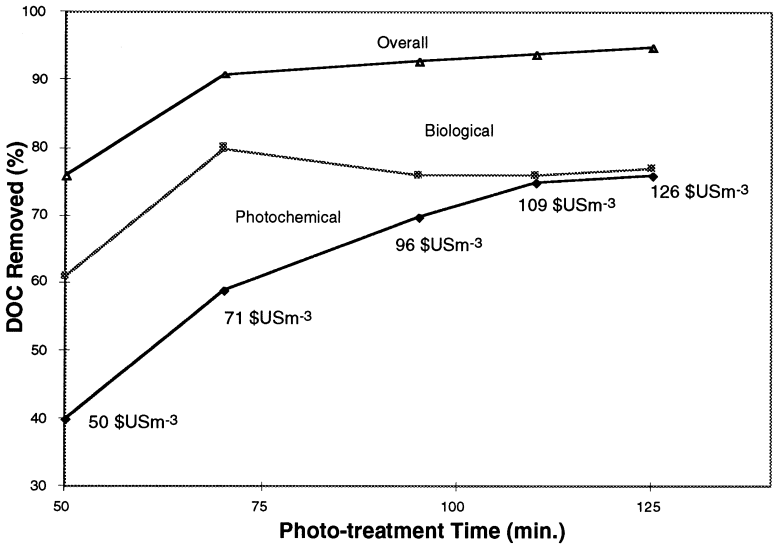

Fig. 8. Percentage of DOC removed after photochemical (with energy cost), biological, and coupled (overall) treatment for *p*-NTS solution.

mediates with very oxidised functional groups being not toxic and as biodegradable as urban wastewater.

Chemical and biological characteristics of phototreated solutions were studied to determine the earliest moment when the photochemical (expensive) pre-treatment reduces the antiphysiological properties of *p*-NTS. This would indicate when the phototreated water may be introduced into the biological (low cost) treatment.

The coupling of photochemical and biological flow reactor was operated in continuous and semi-continuos mode. The main parameters affecting the performance of the photo-assisted reactor in continuos mode is related to the high residual H_2O_2 concentration after the photochemical pre-treatment. The semi-continuos mode was applied to overcome this inconvenience.

Operating in semi-continuos mode, it was found that the optimal time to stop the photochemical treatment before leading the treated water into the biological reactor is 70 min. At this moment appropriate efficiency was reached for the best compromise between time and energy (71 $US per cubic meter) invested in both biological and overall treatment.

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