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COMBINING A SEQUENCING BATCH REACTOR WITH HETEROGENEOUS PHOTOCATALYSIS (TiO_2/UV) FOR TREATING A PENCIL MANUFACTURER'S WASTEWATER

R. N. Padovan and E. B. Azevedo*

Molecular Physics and Chemistry Department, Institute of Chemistry of São Carlos, University of São Paulo (USP), Av. Trabalhador São-Carlense 400, Centro, P.O. Box 780, 13560-970, São Carlos - SP, Brazil.
Phone: + (55) 16 3373 9962, Fax: + (55) 16 3373 9975
E-mail: rodrigopadovan@yahoo.com.br, *bessa@iqsc.usp.br

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Abstract - A Sequencing Batch Reactor (SBR) was combined with heterogeneous photocatalysis (TiO_2/UV) as a tertiary treatment for a pencil manufacturer's wastewater. The SBR removed almost all Chemical Oxygen Demand (COD) from the wastewater, although color was barely removed. Photocatalysis was optimized using a factorial design. Final COD, Dissolved Organic Carbon (DOC), and color removals were 95%, 80%, and 93%, respectively. Treated wastewater showed no ecotoxicity towards *Lactuca sativa*. Color removal kinetics (photocatalysis) followed a pseudo-first order model. The SBR + AOP (Advanced Oxidation Process, TiO_2/UV) combination was a feasibility choice for removing both COD and color from this wastewater.
Keywords: SBR; AOP; Photocatalysis; TiO_2; Color removal; Toxicity.

INTRODUCTION

Biological processes are the best choice for treating high concentrations of organic matter and high volumes of wastewater. There are many kinds of biological processes, one of them being the Sequencing Batch Reactor (SBR). SBRs are a kind of Activated Sludge Process (ASP), where all steps (feed, reaction, settling, decantation, and inactivation) are carried out in the same compartment in a cyclic operation (Khouni *et al*., 2012).

On the other hand, ASPs present limitations for treating compounds with low biodegradability and their efficiency can be drastically reduced by toxic compounds (Mantzavinos and Psillakis, 2004). A possible tool for minimizing this effect is combining ASRs with another treatment, such as Advanced Oxidation Processes (AOPs).

AOPs are based on the *"in situ"* generation of hydroxyl radicals ($^{\bullet}OH$). This radical is the second best oxidant in nature, fluorine being the first one (Legrini *et al*., 1993; Hoffmann *et al*, 1995). The most studied AOP is heterogeneous photocatalysis. Many kinds of photocatalysts have been studied, among them: TiO_2, ZnO, CeO_2, CdS, and ZnS (Gogate and Pandit, 2004). Titanium dioxide is the most used photocatalyst due to its low cost and toxicity, photo-stability, and the wide range of pHs in which it can be used (Nakata and Fujishima, 2012).

Several papers have studied the degradation of dyes by TiO_2/UV. However, a single, universally applicable end-of-pipe solution is unrealistic, so that a combination of different techniques is required to devise a technically and economically feasible option

*To whom correspondence should be addressed

(Hai *et al*., 2007). Such combinations may present a synergistic effect rather than an additive one (Oller *et al*., 2011).

There are few studies regarding the combination of those two technologies. Most of them use the biological reactor only to observe the wastewater biodegradability increase after photocatalysis (Hincapié *et al*., 2005; Arques *et al*., 2007; García-Ripoll *et al*., 2007; Oller *et al*., 2007). Studies that assessed both processes in tandem showed promising results for organic matter removal, ranging from 90-100% (Essam *et al*., 2007; L'Amour *et al*., 2008).

According to Scott and Ollis (1995), there are four major groups of wastewaters whose degradation could be potentially improved by combining those processes: wastewaters with (1) recalcitrant or non-biodegradable compounds; (2) a large share of biodegradable compounds, but with compounds that require a final polishing; (3) toxic or inhibitory compounds; and (4) non-biodegradable organic metabolites. For types (1) and (3), the best approach is to use chemical oxidation as a pretreatment. For type (2), it should be used as a post-treatment. For type (4), chemical oxidation between biological processes is indicated.

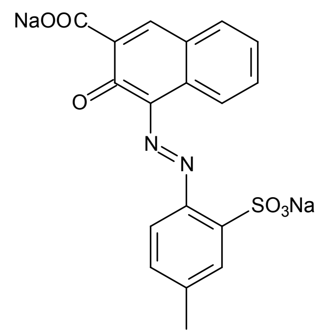
The wastewater studied in this work came from a pencil manufacturer − Chemical Oxygen Demand (COD) ≅ 670 mg O_2 L^{-1} and Dissolved Organic Carbon (DOC) ≅ 105 mg C L^{-1}. It is a mixture between cleaning procedure wastewaters from the production room and the sanitary wastewater produced by over 2,200 employees. It comprises a 1:1 mixture of industrial and sanitary sewage with a typical flow rate of approximately 30 m^3 h^{-1}. It presents biodegradability, with more than 90% organic matter removal in the industrial SBR. However, removing color is a real challenge. This is a type 2 wastewater (Scott and Ollis, 1995).

The main goal of this work was to remove color from this wastewater by combining an SBR with an AOP (photocatalysis, TiO_2/UV), as well as optimizing the AOP regarding photocatalyst content, temperature, and pH. That is the first step in developing a sound coupled treatment for this kind of wastewater.

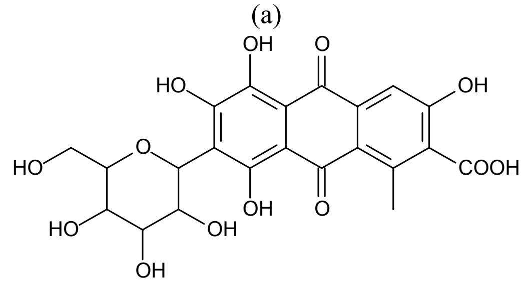
MATERIALS AND METHODS

Wastewater

Ten samples of the wastewater were collected at the entrance of the biological reactors in decontaminated 4-L glass bottles and immediately refrigerated at 5 °C on different days, then mixed together to obtain a composite sample. After collection, the pH was adjusted to less than 2, using H_2SO_4, to avoid microbial degradation. Sanitary sewage was collected at the same plant and stored at 5 °C. The studied wastewater comprised a 1:1 mixture of wastewater and sewage, which simulates the plant procedure when feeding the biological reactors. The wastewater contained, mainly, the following dyes: Red 6 (C.I. 15850), Carmine (C.I. 75470), and Orange 5 (C.I. 45370:1) (Figure 1).



(a)



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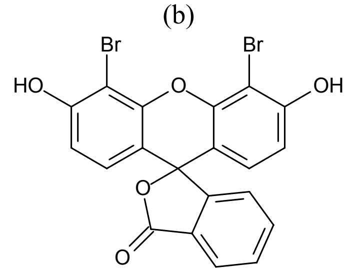


(c)

Figure 1: Structures of the dyes: (a) Red 6 (C.I. 15850), (b) Carmine (C.I. 75470) and (c) Orange 5 (C.I. 45370:1).

Sequencing Batch Reactor

The operational conditions used at the industrial site were reproduced in the laboratory. The SBR was a 500 mL graduated cylinder with a working volume of 400 mL. A sludge amount equal to one third of the reactor working volume was used throughout the experiments. Air was provided by an air compressor, with a flow rate of 100 L h^{-1}.

The reactor Hydraulic Residence Time (HRT) was 3 h (react phase). The sludge was obtained from the plant biological reactors, presenting proper features, such as: few filamentous microorganisms, well-formed flakes, and feasible settling characteristics.

To assess reactor performance, the following analyses were performed: Total Solids (TS), Volatile Solids (VS), Settled Sludge Volume (SSV), and Sludge Volume Index (SVI) (APHA, 2005).

Photocatalytic Reactor

The experiments were performed in a 250 mL open cylindrical Pyrex® reactor. 100 mL of the SBR effluent were irradiated with a Philips HPL-N 250 W medium-pressure mercury-vapor lamp, with the outer bulb removed. The lamp was positioned 20 cm above the liquid layer. Figure 2 shows its emission spectrum measured with a StellarNet EPP2000C spectroradiometer. Temperature was controlled at the desired levels and air was continuously pumped into the suspension at approximately 100 L h^{-1}. The TiO_2 photocatalyst used in this work was P25 from Evonik.

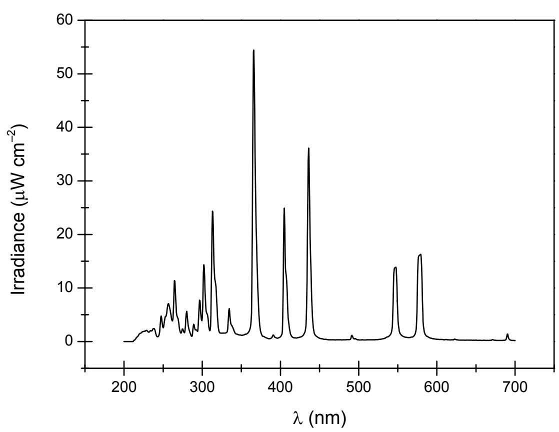


Figure 2: Emission spectrum of the medium-pressure mercury-vapor lamp used.

Wastewater Assays

COD and DOC analyses followed standard protocols (APHA, 2005), the latter using a Shimadzu Vcph TOC-Total Organic Carbon Analyzer. Prior to analyses, samples were filtered (0.45 μm).

By using COD and TOC analyses, it is possible to calculate the Mean Oxidation Number of Carbon (MOC) (Eq. 1). With this number, the average level of oxidation of the organic matter remaining in solution is estimated (Vogel *et al*., 2000). Because the photocatalyst is removed by filtration after photocatalysis, DOC was used instead of TOC, yielding a slightly modified MOC.

$$\mathrm{MOC} = 4 - 1.5 \times \frac{\mathrm{COD}}{\mathrm{TOC}} \quad (1)$$

Color removal was monitored with a Varian Cary Win UV/Visible spectrophotometer. Spectra from 400 to 700 nm were obtained and integrated, therefore producing an indirect measure of color.

Ecotoxicity tests (120 h) were performed to assess the possible generation of ecotoxicity after photocatalysis. The methodologies proposed by Ortega *et al*. (1996) and Beltrami and Rossi (1998) were followed, where the test organisms are seedlings of lettuce, *Lactuca sativa*. The half maximal effective concentration (EC_{50}) was calculated using the adjusted Spearman-Karber method (Hamilton *et al*., 1977).

RESULTS AND DISCUSSION

Sequencing Batch Reactor

The SBR achieved good organic matter removals, with average COD and DOC removals of 90 and 75%, respectively, within 3 hours of aeration (COD from 670 to 63 mg L^{-1} and DOC from 105 to 27 mg L^{-1}, approximately). Operational conditions were: TS 8.1 g L^{-1}, VS 4.6 g L^{-1}, SSV 350 mL, and SVI 76 mL mg^{-1}. SSV and SVI complied with the suggestions of Grady *et al*. (1999) for good sedimentation conditions. TS and VS were slightly lower; however, other authors achieved good results with similar VS values (Jungles *et al*., 2014). Table 1 presents the full characterization of the wastewater after the biological reactor.

However, the SBR achieved only 22% color removal. That performance is also observed during plant operation. One must bear in mind that artificial dyes are xenobiotic molecules designed to be resistant. Kapdan and Oztekin (2005) reached 95% color removal, in an aerobic-anaerobic-SBR, but all decolorization was achieved in the anaerobic phase. Despite the high color removal, the anaerobic degradation of azo-dyes can produce potentially carcinogenic amines (Chen and Zhu, 2007). To avoid this problem, feed, settling, decant, and inactivation phases were kept at a minimum (30 min) and photocatalysis with TiO_2/UV was used to remove color.

Table 1: Full characterization of the wastewater after the biological reactor.

Parameters	Values (mg L^{-1})
pH*	6.70
COD	70
Oils and grease	27
Phenols	< 0.001
Ag	0.021
As	< 0.0001
B	0.2
Ba	< 0.001
Cd	0.010
Cr (hexavalent)	< 0.001
Cr (total)	0.016
Cu	0.012
Cyanides	< 0.001
Fe (soluble)	< 0.005
Fluorides	0.05
Hg	< 0.0001
Mn (soluble)	0.093
Ni	0.039
Pb	0.08
Se	< 0.01
Sn	0.008
Sulfides	< 0.001
Sulphates	39
Zn	0.109

* dimensionless

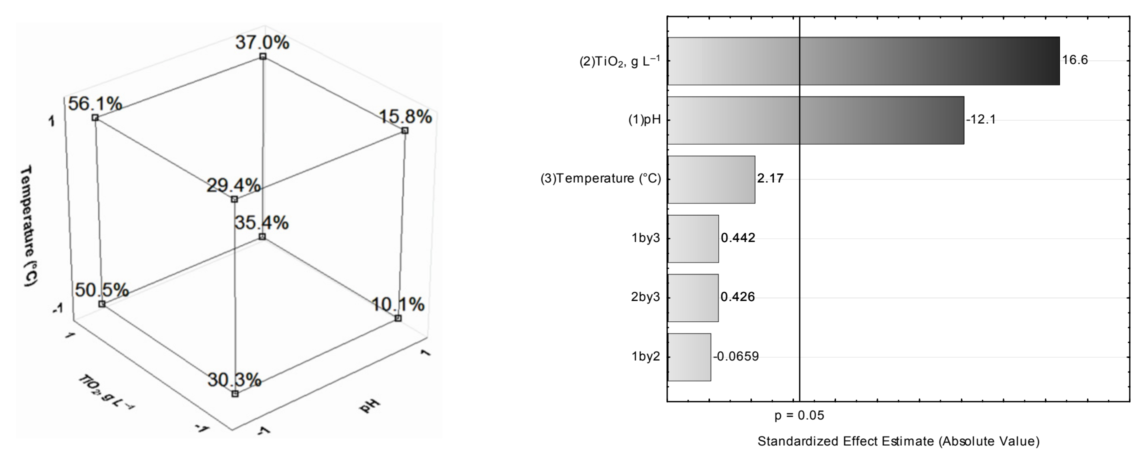
TiO_2/UV

Heterogeneous photocatalysis was then assessed, as a post-treatment, for color removal purposes. A factorial design was performed. Temperature levels were: 30 °C (–1), the usual wastewater temperature and 40 °C (+1), the maximum legal discharge temperature; TiO_2 contents were: 0.1 (–1) and 1.0 (+1) mg L^{-1} (common range observed in the literature); and pH 5.0 (–1) and 9.0 (+1), acidic and basic pHs around 7.0.

Figure 3a shows the results of the factorial design performed. The greatest color removals were obtained in acidic pH and with 1.0 g TiO_2 L^{-1}. All samples were irradiated for 25 min. Adsorption (dark) experiments showed no statistically significant removals.

Temperature presented a statistically insignificant effect on the process (Figure 3b) and, within the studied range, high TiO_2 content and low pH favor color removal. Additional photocatalytic experiments were then performed varying only the pH (5.0, 7.0, and 9.0) and TiO_2 content (0.1 and 1.0 g L^{-1}). Temperature was set at 25 °C, which is the average temperature of the wastewater. No significant differences were observed in the process efficiency from neutral to acidic pH. So, pH 7 was chosen, since: (a) it is the secondary wastewater pH and (b) there would be no need for pH adjustments for final disposal. Finally, the studied range of TiO_2 contents was expanded (0.25, 0.5, 1.0, 1.5, 2.0, and 2.5 g L^{-1}) with 2 g TiO_2 L^{-1} being the best value.

At the fixed treatment conditions (pH = 7, T = 25 °C, and 2 g TiO_2 L^{-1}), kinetic experiments were performed (Figure 4). All experiments were performed in triplicate (18 independent experiments). After 10 min, color removal followed a pseudo-first order model: $k = (5.4 \pm 0.92) \times 10^{-2}$ min^{-1}, $R^2 = 0.991$. In the first 10 min of photocatalysis, there is only a very small color removal (5%, approximately). That fact can probably be ascribed to the preferred degradation of colorless organic compounds.



(a) (b)

Figure 3: Results of the 2^3 experimental design: (a) cube plot of predicted means (confidence interval at a 95% confidence level: ± 7.8%) and (b) Pareto chart.

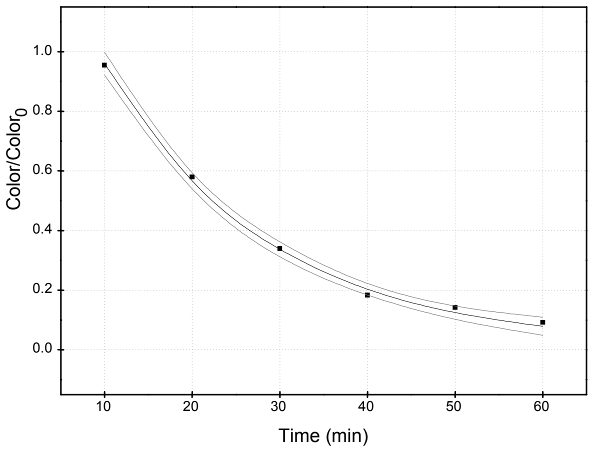


Figure 4: Color removal kinetics (photocatalysis) with the 95% confidence interval (gray). Conditions: pH 7.0, T = 25 °C, 2.0 g TiO_2 L^{-1}; kinetic parameters: $k = (5.4 \pm 0.92) \times 10^{-2}$ min^{-1}, $R^2 = 0.991$.

After 60 min of irradiation (photocatalysis), color removal increased approximately 71%. Photolytic tests (without catalyst) for the same period of time were performed. Only 20% of color removal was achieved.

Figure 5 shows the visible absorption spectra of the raw wastewater (COD_0 = 700 mg L^{-1}) after the SBR, and after coupling the SBR to photolysis (pH 7.0, T = 25 °C) or to photocatalysis (pH 7.0, T = 25 °C, 2.0 g TiO_2 L^{-1}), for 60 min of irradiation. One can easily observe the huge improvement obtained for the coupling SBR + photocatalysis, regarding color removal.

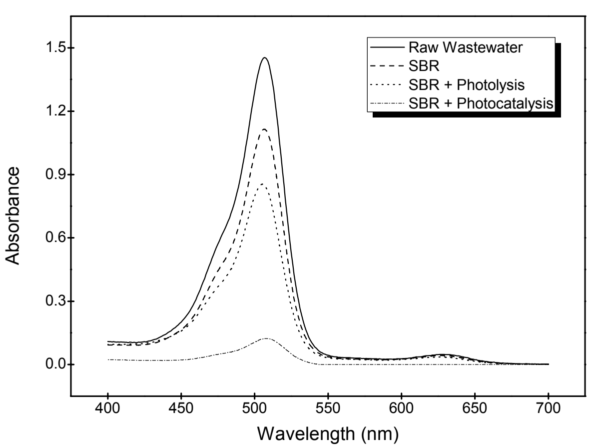


Figure 5: Absorption spectra of the raw wastewater, after the SBR, photolysis (pH 7.0, T = 25 °C), and photocatalysis (pH 7.0, T = 25 °C, 2.0 g TiO_2 L^{-1}). COD_0 = 700 mg L^{-1}.

As the dyes were degraded, the occurrence of photosensitization is possible, which would increase the efficiency of the excitation process (Linsebigler *et al*., 1995). No works dealing with TiO_2 photosensitization by Red 6 or Orange 5 were found. On the other hand, Carmine does sensitize titanium dioxide. The band-gap energy is reduced from 3.16 to 2.99 eV, promoting a red shift and increasing visible light excitation (Rosu *et al*., 2013).

Organic Matter Removal

Figure 6 shows the results from COD and DOC analyses during the photocatalytic treatment. While color removal increased 71%, COD and DOC removals increased 40 and 30%, approximately. Those differences are probably due to the fact that removing color requires only the degradation of the dyes' chromophore groups, while COD (and especially DOC) removal requires an extensive oxidation of the whole molecules.

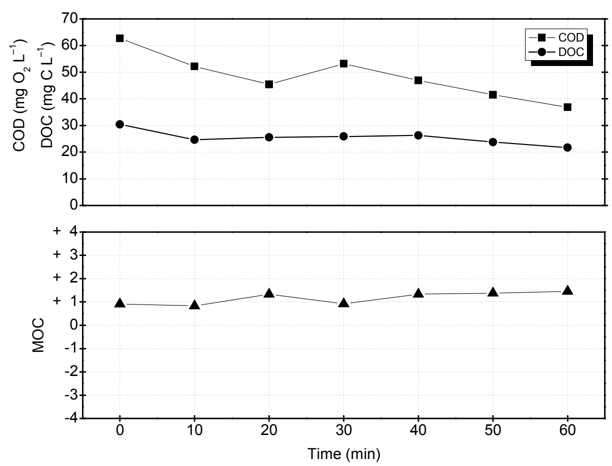


Figure 6: COD and DOC removals and MOC evolution during photocatalysis.

The MOC slightly increased (from +0.9 to +1.5). The photocatalyzed wastewater was already biologically treated. Therefore, the present compounds were somewhat stabilized (oxidized). Nevertheless, the MOC clearly indicates the wastewater oxidation during photocatalysis. Moreover, there is no use in extending the treatment time beyond 60 min, since the MOC is relatively stable from 50 min on.

Comparison with Previous Works

To our knowledge, only two other works specifically dealt with combining SBR with photocatalysis for treating real wastewaters (Table 2). None of them aimed at color removal.

Table 2: Comparison between previous works and the present one.

Authors	Wastewater	Processes and Conditions ①	Processes and Conditions ②	Removals
Elmolla and Chaudhuri (2011)	Type[a]: 3 AMX and CLX[c]	Photocatalysis: • 1 g TiO_2 L^{-1} • 250 mg H_2O_2 L^{-1} • pH 5 • 5 h	SBR[b]: • 48 h	• 100% AMX/CLX • 57% sCOD[d] (670 to 236 mg L^{-1})
Xu *et al*. (2012)	Type[a]: 1 Dyes	Photocatalysis: • 2 g SDS[e]-CuO/TiO_2 L^{-1} • 40 min	SBR: • 12 h	• 94% COD (1,134 to 71 mg L^{-1}) • 95% BOD[f] (384 to 18 mg L^{-1})
Silva *et al*. (2013)	Type[a]: 1 Leachate	Solar photo-Fenton: • 13 h	AS[i]: • 450 h	• 90% DOC (1,000 to 90 mg L^{-1})
Bustillo- Lecompte *et al*. (2014)	Type[a]: 2 Slaughterhouse Wastewater	ABR[h]-AS[i]: • 46 h	UV/H_2O_2: • 3 h	• 92% DOC (1,000 to 80 mg L^{-1})
This work	Type[a]: 2 Dyes	SBR: • 3 h	Photocatalysis: • 2 g TiO_2 L^{-1} • pH 7 • 1 h	• 95% COD (700 to 37 mg L^{-1}) • 80% DOC[g] (105 to 27 mg L^{-1}) • 93% color

[a] According to Scott and Ollis (1995); [b] SBR: Sequencing Batch Reactor; [c] AMX: amoxicillin; CLX: cloxacillin; [d] sCOD: soluble Chemical Oxygen Demand; [e] Sodium dodecyl sulfate; [f] BOD: Biochemical Oxygen Demand; [g] DOC: Dissolved Organic Carbon; [h] Anaerobic Baffled Reactor; [i] Activated Sludge

Elmolla and Chaudhuri (2011) studied the treatment of a wastewater containing antibiotics (amoxicillin and cloxacillin). Although long treatment times (5 h of photocatalysis + 48 h of SBR), additional oxidant (H_2O_2), and acidic pH (5) were used, organic matter removal (COD) was low (57%). They concluded that the feasibility of using the combined UV/H_2O_2/TiO_2-SBR process for treatment of this wastewater was limited.

Xu *et al*. (2012) achieved high organic matter removals (94% COD and 95% BOD) from a dyestuff wastewater. However, the SBR stage took 12 h.

Other works can be found in the literature using different kinds of coupled treatments and wastewaters, as the one studied by Silva *et al*. (2012) that used solar-photo-Fenton on a pre-industrial scale coupled with activated sludge to treat sanitary landfill leachate (Type 1, COD = 1,000 mg O_2 L^{-1}). The process presented promising results, achieving more than 90% of DOC removal.

Bustillo-Lecompte *et al*. (2014) studied the degradation of a slaughterhouse wastewater (COD = 1,000 O_2 mg L^{-1}), coupling an anaerobic-aerobic reactor with the UV/H_2O_2 process. That combination removed 92% of COD in 46 h with a total cost of \$1.25/kg of TOC removed and \$11.60/m^3 of treated wastewater. In that case, the AOP was used after the biological process (Type 2).

Elmolla and Chaudhuri (2011) and Xu *et al*. (2012) dealt with type 1/3 wastewaters, requiring the sequence: Photocatalysis → SBR (Scott and Ollis 1995). On the contrary, this work studied the treatment of a type 2 wastewater (SBR → Photocatalysis). Nevertheless, high organic matter removals were also achieved (95% COD and 80% DOC), along with an almost complete decolorization. The use of short treatment times (3 h of SBR + 1 h of photocatalysis) and neutral pH must be emphasized.

Figure 7 compares the efficiency of combining the SBR to photocatalysis regarding COD, DOC, and color removals. One can see the successful combination of two complementary processes: SBR removes carbon and the AOP removes color, substantially improving the wastewater quality, making it probably safe to be discharged.

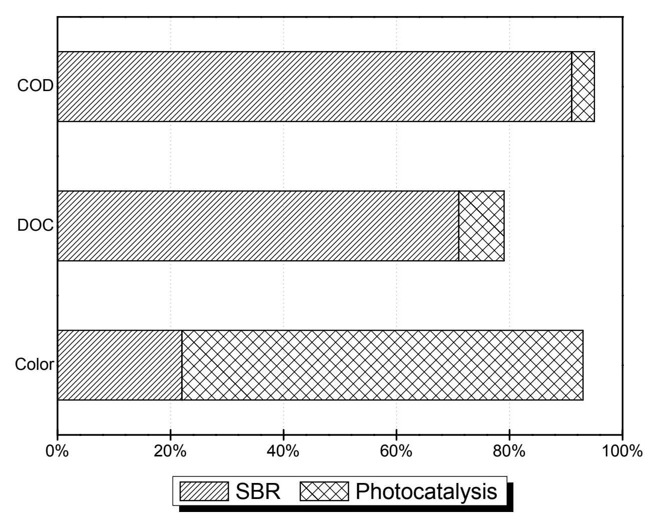


Figure 7: Coupling performance regarding COD, DOC, and color removals: SBR (3 h) + Photocatalysis (1 h).

Ecotoxicity

After 60 min of photocatalysis, the wastewater was non-toxic to the test-organism. This is an important and promising result, since it suggests that it is probably safe to dispose of the photocatalytically treated wastewater.

CONCLUSIONS

The SBR alone was capable of removing 90% of COD, 75% of DOC, and only 22% of color in 3 hours. When it was combined with one hour of heterogeneous photocatalysis (TiO_2/UV), COD, DOC, and color removals improved to 95%, 80%, and 93%, respectively. Therefore, the wastewater quality was substantially improved, making it probably safe to be discharged.

The best photocatalytic conditions (factorial design) were: pH 7.0, T = 25 °C (which are, approximately, the wastewater natural conditions after biological treatment) and 2.0 g TiO_2 L^{-1}. Those are promising conditions, as costs would be significantly reduced. Color removal followed a pseudo-first order model: $k = (5.4 \pm 0.92) \times 10^{-2}$ min^{-1}, $R^2 = 0.991$. On the other hand, photolysis removed only 20% of color in 1 h.

By the end of the treatment process, the wastewater was non-toxic to the test-organism (seedlings of lettuce, *Lactuca sativa*). This is an important and promising result, since it also suggests that it is probably safe to dispose of the photocatalytically treated wastewater.

ACKNOWLEDGEMENTS

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NOMENCLATURE

AOP	Advanced Oxidation Process	
ASP	Activated Sludge Process	
SBR	Sequencing Batch Reactor	
COD	Chemical Oxygen Demand	mg L^{-1}
DOC	Dissolved Organic Carbon	mg L^{-1}
EC_{50}	Effective Concentration	%
HRT	Hydraulic Residence Time	h
MOC	Mean Oxidation Number of Carbon	dimensionless
SSV	Settle Sludge Volume	mg L^{-1}
SVI	Sludge Volume Index	mL g^{-1}
VS	Volatile Solids	mg L^{-1}
TS	Total Solids	mg L^{-1}

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