CHEMICAL ENGINEERING TRANSACTIONS

VOL. 95, 2022

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Selena Sironi, Laura Capelli

ISBN 978-88-95608-94-5; **ISSN** 2283-9216

DOI: 10.3303/CET2295040

Advanced Oxidation Processes with Uv-H_2O_2 For Nitrification and Decolorization of Dyehouse Wastewater

Néstor A. Urbina-Suarez [a,b,*], Andrés F. Barajas-Solano[a], Antonio Zuorro[c], Fiderman Machuca[d]

[a] Universidad Francisco de Paula Santander, Facultad de Ciencias del Medio Ambiente, Grupo Ambiente y Vida, Avenida Gran Colombia No. 12E-96, Cúcuta, Norte de Santander, Colombia.
[b] Universidad del Valle, School of Natural Resources and Environment, Ciudad Universitaria Meléndez, Calle 13 # 100-00 760015 Cali, Colombia.
[c] Dept.of Chemical Engineering, Materials and Environment, Sapienza University, Via Eudossiana 18, 00184 Roma, Italy
[d] Universidad del Valle, School of Natural Resources and Environment, Centro de Excelencia en Nuevos Materiales–CENM Ciudad Universitaria Meléndez, Calle 13 # 100-00 760015 Cali, Colombia
nestorandresus@ufps.edu.co

In this work, a UV/H_2O_2 system was evaluated using an experimental design 2 level I-optimal response surface design to analyze the effect of temperature, pH, UV lamp power (W), and H_2O_2 concentration on dye load removal and nitrification from industrial cleaning wastewater. Results showed that the optimum conditions were 80 °C, pH 4, PW-UV 60 W, and H_2O_2 3.1 Mol*L^{-1}. Removal percentages of 45% for COD, 47.5% color, 87% Fe, 82% Cr and 91% ammonium oxidation to nitrate were achieved. It can be concluded that the effluents treated by this process could be promising for reuse and exploitation in biotechnological tools through microalgae and cyanobacteria.

1. Introduction

Dry cleaners wastewater is a type of effluent generated by a wide variety of industrial sectors that require the use of synthetic dyes with recalcitrant compounds (Urbina et al., 2021); worldwide, the emission of this type of wastewater is led by the textile industry with 54% followed by the dyeing industry 21%, paper, and pulp 10%; tanneries and paints with 8% (Samsami et al., 2020). Fabric dyeing and its treatment generate 20% of wastewater worldwide. It has been reported that it requires up to 200 L of water to produce 1 kg of fabric (Bilińska et al., 2017), and the size of this industry will increase between 20% and 30% in 2025 (Garcia et al., 2020). Wastewater from dry cleaners is highly pollutant since dyeing requires recalcitrant compounds made of benzidine substances (Direct Black 38, Direct Blue 6, and Direct Brown 95) that are highly toxic and non-biodegradable (Katheresan et al., 2018). Azo dyes are the most common pigment found in textile wastewater (Reza Samarghandi et al., 2020). Other substances are polyvinyl alcohol (PVA), carboxymethylcellulose, surfactants, organic processing acids, sulfides, formaldehyde, detergents, oil, dispersants, $NaNO_3$, NaCl, and Na_2SO_4 that assist dye fixation (Sarker et al., 2019). These recalcitrant compounds generate a highly harmful, toxic effluent that is highly dangerous to ecosystems and human health (Jia et al., 2020). Dry cleaners' wastewater is hard to treat using biological processes due to their recalcitrant pollutants (Mani and Hameed, 2019). Some bacteria can effectively degrade dyes and other compounds using oxidative-reducing enzymes such as azoreductase, and laccase peroxidase, which catalyzes the mineralization and degradation of many pigments. However, the scaling of this type of process is complex (Mishra and Maiti, 2018).

Microalgae and cyanobacteria have emerged as a promising technology in treating these effluents; these organisms can degrade different compounds present in these effluents while generating biomass with value-added metabolites such as lipids, carbohydrates, pigments, and others (Oyebamiji et al., 2019). The main drawback is the presence of metal ions which can reduce their growth rate (Urbina et al., 2022), and lower the biomass quality, which will reduce the applicability of that biomass (Gita et al., 2021). Advanced oxidation processes (AOPs) can be a better alternative for the degradation of non-biodegradable organic compounds, the

Paper Received: 15 March 2022; Revised: 10 May 2022; Accepted: 3 September 2022
Please cite this article as: Urbina-Suarez N.A., Barajas-Solano A.F., Zuorro A., Machuca F., 2022, Advanced Oxidation Processes with Uv-h2o2 for Nitrification and Decolorization of Dyehouse Wastewater, Chemical Engineering Transactions, 95, 235-240 DOI:10.3303/CET2295040

mineralization of pollutants, and the removal of recalcitrant organic materials present in these effluents (Atalay and Ersöz, 2020). Different AOPs such as ozone photo-Fenton, ultrasonic, and photocatalysis has been reported for degrading azo dyes (Maroudas et al., 2021). AOPs coupled with UV have gained relevance in recent years. The use of photo-Fenton in the treatment of textile effluents has reported high color removals up to 70%, but with low COD removal (<10%) (Kumar Shivappa Masalvad and Kumar Sakare, 2020). A study on advanced oxidation of peroxydisulfate (PDS) and peroxymonosulfate (PMS) activated by UV showed that a pH of 6-8 had positive effects on water treatment (Sbardella et al., 2019); on the other hand, it has been reported that degradation by direct photolysis with UV under acidic pH can degrade parabens (Álvarez et al., 2020). The effect of temperature and UV lamp power are still a relevant topic of research. Therefore, the present work evaluates the implementation of a UV/H_2O_2 system in real dyeing wastewater and the effect of temperature, pH, UV lamp power (W), and H_2O_2 concentration on the removal of the dye load and the generation of nitrates as a potential use in the cultivation of microalgae and cyanobacteria.

2. Materials and methods

2.1 Dry cleaners wastewater

The wastewater was obtained from a textile dry-cleaner company in the city of Cúcuta (Norte de Santander, Colombia). The sample was taken every 30 min (in duplicate) through a 24 h interval; the final sample volume was 500 mL. The sample was kept cold at 4°C and then transferred to the laboratory for further analysis.

2.2 Physicochemical characterization of the dyeing effluents.

The dyeing wastewater was physicochemically characterized according to standard methods 23 ed (Table 1).

Table 1: Physicochemical characterization

PARAMETER	METHOD	PARAMETER	METHOD
COD (mg*L^{-1})	Standard Methods 5220C	pH	Standard Methods 4500B
BOD (mg*L^{-1})	Standard Methods 5210B-4500-OG	Conductivity (μS*cm^{-1})	Standard Methods 2510B
Nitrates (mg*L^{-1})	Colorimetric	Total Suspended Solids (mg*L^{-1})	Standard Methods 2540D
Nitrites (mg*L^{-1})	Colorimetric	Heavy Metals (Fe, Ni, Cd, Cr, Cu y Zn) (mg*L^{-1})	Standard Methods 3111D
Ammonia nitrogen (mg*L^{-1})	Colorimetric	Sulfides (mg*L^{-1})	Standard Methods 4500-
Phosphates (mg*L^{-1})	Colorimetric	Chlorides (mg*L^{-1})	Standard Methods 4500-ClB

2.3 Experimental Analysis

An I-optimal response surface design (Table 2) was created on Design Expert 13 software®. The design had 4 variables (temperature, initial pH, UV lamp power, and H_2O_2 concentration) with two levels. The response variables were COD, NO_3, and color. The design resulted in 40 experiments conducted in triplicate for a total of 120 experiments. The stipulated conditions were obtained from the review of the little existing literature and the experience of the working team. The results were analyzed using a two-way ANOVA on Design Expert 13 software®.

Table 2: Experimental design

PARAMETER	FACTOR		
	-1	0	1
H_2O_2 (mg*L^{-1})	0.3	0.5	0.7
Lamp power (W)	30	45	60
pH (mg/L)	4	5	6
Temperature (°C)	50	65	80

Prior to experimentation, the solids from wastewater were removed by sedimentation (30 min, 27°C). A 250 mL volume reactor with an operating volume of 200 mL was used for the photocatalytic experiments. Each experiment was mixed at 550 rpm and the pH was adjusted using either HCl and NaOH (0.1 M). a solution of

H_2O_2 (35% v/v) was used for the calculation of the different concentrations in the design. Finally, 15W UV-C (254 nm) lamps were used. Each lamp emitted light intensity of 44 µW * cm^{-2}.

2.4 Analytical methods

Total organic carbon (TOC) was determined using a TOC analyzer (Thermo Fisher Scientific). The operating conditions were a sample volume of 0.5 mL, water chase volume 1.0 mL, injection line rinse on, injection line rinse volume 0.5 mL, acid volume 0.5 mL, ICS parge flow 200 mL*min^{-1}, carrier gas delay time 0.40 min, ICS parge time 50 min, detector sweep flow 500 mL*min^{-1}, furnace sweep time 1.0 min, and system flow 200 mL* min^{-1}. For the determination of color removal, a spectrophotometric scan was performed on a THERMO GENESYS10 brand spectrophotometer in a range of 220 to 750 nm at 25 °C. The measurement separation interval was calibrated at 1 nm. Deionized water was used to measure the baseline.

3. Results and discussions

3.1 Physicochemical characterization

The physicochemical characterization of dry cleaning wastewater is shown in Table 3.

Table 3: Physicochemical characterization of dry cleaning wastewater

PARAMETER	VALUE	PARAMETER	VALUE
COD (mg*L^{-1})	622 ± 2.01	Fe (mg*L^{-1})	7.5 ± 0.02
BOD (mg*L^{-1})	214.2 ± 3.2	Ni (mg*L^{-1})	0.05 ± 0.0
Nitrates (mg*L^{-1})	24.3 ± 0.46	Cr (mg*L^{-1})	0.1 ± 0.001
Nitrites (mg*L^{-1})	3.23 ± 0.003	Cd (mg*L^{-1})	0.002 ± 0.0
Ammonia nitrogen (mg*L^{-1})	15.6 ± 1.06	Zn (mg*L^{-1})	0.67 ± 0.02
Phosphates (mg*L^{-1})	0.96 ± 0.023	Cu (mg*L^{-1})	0.12 ± 0.003
Total Suspended Solids (mg*L^{-1})	602.4 ± 5.67	Sulfides (mg*L^{-1})	0.5 ± 0.001
Conductivity (µS*cm^{-1})	1302 ± 0.56	Chlorides (mg*L^{-1})	893.88 ± 4.76
pH	5.98 ± 0.1		

It has been reported that industrial textile effluents have a strong color product of the chemicals used in the dyeing process, a large number of suspended solids (SS), a fluctuating pH (4-9), and a high concentration of COD (Assémian et al., 2018). The composition and concentration of these compounds in dry cleaning effluents are highly variable and depend on the manufacturing processes, the type of fibers, the amount of water used in the process, and the chemicals (Silva et al., 2020). The results obtained (Table 3) show that the pollutant load with had a low biological degradability due to the COD/BOD ratio. The samples showed an acid pH (5.98 ± 0.1) and a high content of iron (7.5 ± 0.02 mg*L^{-1}), which is above the levels allowed by current Colombian regulations. the concentrations of the remaining metals were below the regulations.

3.2 Color removal

The results for the ANOVA analysis for the color removal (table 4) using hydrogen peroxide show that the Model F-value of 5.82 implies the model is significant. There is only a 0.05% chance that a large F-value could occur due to noise. In this case, Temperature and pH are the most significant variable. Finally, the Lack of Fit F-value of 0.94 implies the Lack of Fit is not significant relative to the pure error.

Table 4: ANOVA analysis of 2 level I-optimal Response Surface design for color removal.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	8.05	5	1.61	5.82	0.0005	significant
A-Temperature	1.78	1	1.78	6.44	0.0159	
B-pH	6.28	1	6.28	22.70	< 0.0001	
C-Hydrogen peroxide	0.0768	1	0.0768	0.2775	0.6018	
D-pW	0.4623	2	0.2312	0.8354	0.4424	
Residual	9.41	34	0.2767			
Lack of Fit	4.57	17	0.2687	0.9440	0.5466	not significant
Pure Error	4.84	17	0.2847			
Cor Total	17.46	39				

The effluents of dry cleaners contain dyes and dye impurities, mainly azo-type dyes, which hinder the degradation of the pollutant load. As observed in this study, color removal is linked to the amount of OH^- available for oxidation, and this process is affected by the pH. Acidic pH favors the generation of OH^- and oxidation of dyes, while alkaline pH decreases the removal of color. Korpe and Rao (2021) found that under alkaline pH, the dissociated form of H_2O_2 can remove OH^-, which will decrease the efficiency of color removal.

3.3 Nitrification

The results for the ANOVA analysis on the nitrification (Table 5) using hydrogen peroxide show that the Model F-value of 3.18 implies the model is significant. There is only a 0.6% chance that an F-value this large could occur due to noise. In this case, A^2 (Temperature) and the interactions Temperature-pH, pH-Hydrogen peroxide, and Hydrogen peroxide-pW are the most significant. Finally, the Lack of Fit F-value of 1.14 implies the Lack of Fit is not significant relative to the pure error.

Table 5: ANOVA analysis of 2 level I-optimal Response Surface design for Nitrification.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	4.74	17	0.2787	3.18	0.0060	significant
A-Temperature	0.3067	1	0.3067	3.49	0.0749	
B-pH	0.0271	1	0.0271	0.3090	0.5839	
C-Hydrogen peroxide	0.0003	1	0.0003	0.0032	0.9554	
D-pW	0.1308	2	0.0654	0.7452	0.4863	
AB	0.3957	1	0.3957	4.51	0.0452	
AC	0.1312	1	0.1312	1.50	0.2343	
AD	0.4778	2	0.2389	2.72	0.0878	
BC	1.08	1	1.08	12.30	0.0020	
BD	0.1652	2	0.0826	0.9414	0.4052	
CD	1.07	2	0.5360	6.11	0.0078	
A^2	0.7329	1	0.7329	8.35	0.0085	
B^2	0.0139	1	0.0139	0.1582	0.6947	
C^2	0.1303	1	0.1303	1.49	0.2359	
Residual	1.93	22	0.0878			
Lack of Fit	0.4859	5	0.0972	1.14	0.3759	not significant
Pure Error	1.44	17	0.0850			
Cor Total	6.67	39				

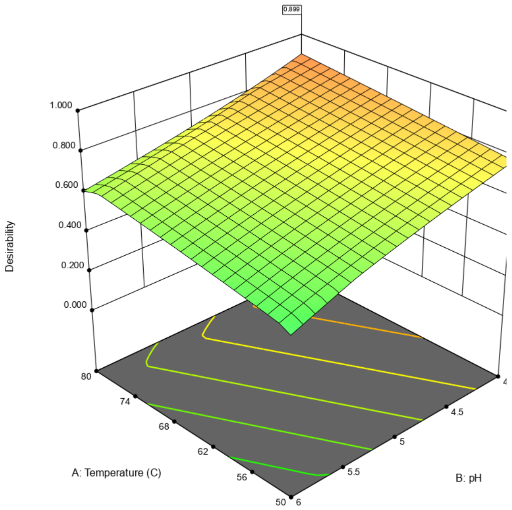

Figure 1: Surface response of the interaction between pH and temperature

The surface response of the interaction between temperature and pH, (Figure 1) shows that lower pH and higher temperatures will increase the nitrification and the removal of color. Using the solution obtained for color removal and nitrification (Table 4) was corroborated by performing eight new experiments (one original, plus seven replicates) The results were analyzed using one-way ANOVA. Nitrification is a process that demonstrates the effectiveness of AOPs in the oxidation of organic matter and azo groups of dyes in simpler forms. This process occurs due to the release of oxygen radicals that oxidize $N\text{-}NH_3$ into $N\text{-}NO_3$. Studies have revealed that acidic pH promote the oxidation of the azo dyes; also it has been reported that at room temperature the consumption of peroxide by the pollutants is lower; therefore a temperature increase is required to maintain OH^- generation and improve the reactivity of these radicals (Korpe and Rao, 2021).

The results obtained from the experimental design and the response surface in this work allowed us to determine the variables to corroborate the process conditions for its optimization: (80°C, pH 4, 0.31 M of H_2O_2, and pW 60 W). Figure 2a. shows the results obtained. For the case of nitrate, the value obtained was higher than expected, while for the color removal rate, there were no significant differences between the expected and the obtained results.

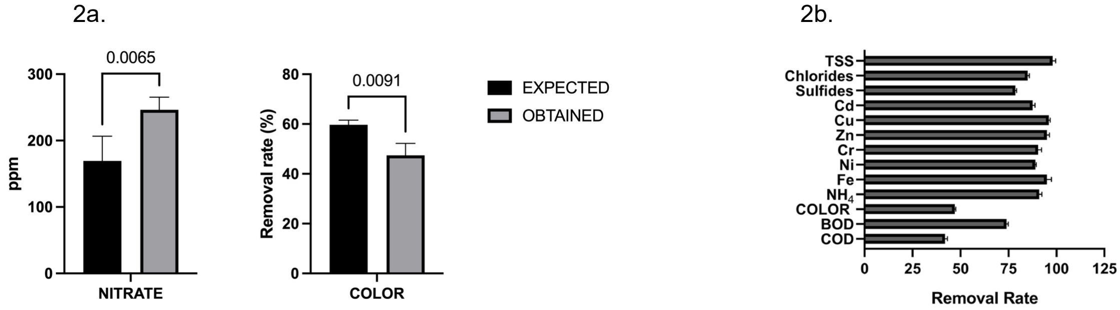

Figure 2. (a) color removal and nitrification. (b) Removal of contaminants

Figure 2b presents that for some metals, it was possible to remove up to 90% of their initial content; on the other hand, the ammonium oxidation process reached 86%, while the BOD, COD, and color removal were lower (70, 45, and 45%, respectively). The chemical composition of the effluent after the UV/H_2O_2 treatment shows promising potential as an alternative culture media to produce algal biomass. In recent years, advanced oxidation processes and biological processes with algae and cyanobacteria have gained popularity (Urbina-suarez et al., 2021); however, more studies are required to identify the optimal conditions for their operation and promote the combined use of AOPs and microalgae biotechnology.

4. Conclusions

It can be concluded that the AOPs $UV\text{-}H_2O_2$ method proved to be efficient in degrading the pollutant load of the dyeing. It was found that the OH^- radical plays a critical role in the pollutant's removal; also, it was found that pH affects the degradation process of organic matter and the nitrification process. Acidic pH favors the generation of OH^- radicals and their interaction with the different pollutants. On the contrary, alkaline pH tends to increase COD because the dissociated form of H_2O_2 tends to capture OH^- radicals, affecting the process. Finally, parameters were determined to optimize the oxidative process of these effluents, finding that 48% of color is removed and nitrification is stimulated, allowing potential reuse and utilization.

Acknowledgments

The authors would like to thank Universidad Francisco de Paula Santander (Colombia) and Universidad del Valle (Colombia) for funding this project.

References

Álvarez, M.A., Ruidíaz-Martínez, M., Cruz-Quesada, G., López-Ramón, M.V., Rivera-Utrilla, J., Sánchez-Polo, M., Mota, A.J., 2020. Removal of parabens from water by UV-driven advanced oxidation processes. Chem. Eng. J. 379, 122334. https://doi.org/10.1016/j.cej.2019.122334

Assémian, A.S., Kouassi, K.E., Zogbé, A.E., Adouby, K., Drogui, P., 2018. In-situ generation of effective coagulant to treat textile bio-refractory wastewater: Optimization through response surface methodology. J. Environ. Chem. Eng. 6, 5587–5594. https://doi.org/10.1016/j.jece.2018.08.050

Atalay, S., Ersöz, G., 2020. Hybrid application of advanced oxidation processes to dyes' removal. Green Chem. Water Remediat. Res. Appl. 209–238. https://doi.org/10.1016/B978-0-12-817742-6.00007-4

Bilińska, L., Gmurek, M., Ledakowicz, S., 2017. Textile wastewater treatment by AOPs for brine reuse. Process Saf. Environ. Prot. 109, 420–428. https://doi.org/10.1016/j.psep.2017.04.019

Garcia, V.S.G., Rosa, J.M., Borrely, S.I., 2020. Toxicity and color reduction of a textile effluent containing reactive red 239 dye by electron beam irradiation. Radiat. Phys. Chem. 172, 108765. https://doi.org/10.1016/j.radphyschem.2020.108765

Gita, S., Shukla, S.P., Deshmukhe, G., Choudhury, T.G., Saharan, N., Singh, A.K., 2021. Toxicity Evaluation of Six Textile Dyes on Growth, Metabolism and Elemental Composition (C, H, N, S) of Microalgae Spirulina platensis: The Environmental Consequences. Bull. Environ. Contam. Toxicol. 106, 302–309. https://doi.org/10.1007/s00128-020-03074-7

Jia, F., Yin, S., Chen, L., Chen, X., 2020. The circular economy in the textile and apparel industry: A systematic literature review. J. Clean. Prod. 259, 120728. https://doi.org/10.1016/j.jclepro.2020.120728

Katheresan, V., Kansedo, J., Lau, S.Y., 2018. Efficiency of various recent wastewater dye removal methods: A review. J. Environ. Chem. Eng. 6, 4676–4697. https://doi.org/10.1016/j.jece.2018.06.060

Korpe, S., Rao, P.V., 2021. Application of advanced oxidation processes and cavitation techniques for treatment of tannery wastewater - A review. J. Environ. Chem. Eng. 9, 105234. https://doi.org/10.1016/j.jece.2021.105234

Kumar Shivappa Masalvad, S., Kumar Sakare, P., 2020. Application of photo Fenton process for treatment of textile Congo-red dye solution. Mater. Today Proc. 46, 5291–5297. https://doi.org/10.1016/j.matpr.2020.08.650

Mani, A., Hameed, S.A., 2019. Improved bacterial-fungal consortium as an alternative approach for enhanced decolourisation and degradation of azo dyes: A review. Nat. Environ. Pollut. Technol. 18,49–64.

Maroudas, A., Pandis, P.K., Chatzopoulou, A., Davellas, L.R., Sourkouni, G., Argirusis, C., 2021. Synergetic decolorization of azo dyes using ultrasounds, photocatalysis and photo-fenton reaction. Ultrason. Sonochem. 71, 105367. https://doi.org/10.1016/J.ULTSONCH.2020.105367

Mishra, S., Maiti, A., 2018. The efficacy of bacterial species to decolourise reactive azo, anthroquinone and triphenylmethane dyes from wastewater: a review. Environ. Sci. Pollut. Res. 25, 8286–8314. https://doi.org/10.1007/s11356-018-1273-2

Oyebamiji, O.O., Boeing, W.J., Holguin, F.O., Ilori, O., Amund, O., 2019. Green microalgae cultured in textile wastewater for biomass generation and biodetoxification of heavy metals and chromogenic substances. Bioresour. Technol. Reports 7, 100247. https://doi.org/10.1016/j.biteb.2019.100247

Reza Samarghandi, M., Tari, K., Shabanloo, A., Salari, M., Zolghadr Nasab, H., 2020. Synergistic degradation of acid blue 113 dye in a thermally activated persulfate (TAP)/ZnO-GAC oxidation system: Degradation pathway and application for real textile wastewater. Sep. Purif. Technol. 247, 116931. https://doi.org/10.1016/j.seppur.2020.116931

Samsami, S., Mohamadi, M., Sarrafzadeh, M.H., Rene, E.R., Firoozbahr, M., 2020. Recent advances in the treatment of dye-containing wastewater from textile industries: Overview and perspectives. Process Saf. Environ. Prot. 143, 138–163. https://doi.org/10.1016/J.PSEP.2020.05.034

Sarker, M.R., Chowdhury, M., Deb, A., 2019. Reduction of Color Intensity from Textile Dye Wastewater Using Microorganisms: A Review. Int. J. Curr. Microbiol. Appl. Sci. 8, 3407–3415. https://doi.org/10.20546/ijcmas.2019.802.397

Sbardella, L., Velo-Gala, I., Comas, J., Rodríguez-Roda Layret, I., Fenu, A., Gernjak, W., 2019. The impact of wastewater matrix on the degradation of pharmaceutically active compounds by oxidation processes including ultraviolet radiation and sulfate radicals. J. Hazard. Mater. 380, 120869. https://doi.org/10.1016/j.jhazmat.2019.120869

Silva, L.G.M., Moreira, F.C., Cechinel, M.A.P., Mazur, L.P., de Souza, A.A.U., Souza, S.M.A.G.U., Boaventura, R.A.R., Vilar, V.J.P., 2020. Integration of Fenton's reaction based processes and cation exchange processes in textile wastewater treatment as a strategy for water reuse. J. Environ. Manage. 272. https://doi.org/10.1016/j.jenvman.2020.111082

Urbina-Suarez, N.A., Ayala-González, D.D., Rivera-Amaya, J.D., Barajas-Solano, A.F., Machuca-Martínez, F., 2022. Evaluation of the Light/Dark Cycle and Concentration of Tannery Wastewater in the Production of Biomass and Metabolites of Industrial Interest from Microalgae and Cyanobacteria. Water (Switzerland) 14. https://doi.org/10.3390/w14030346

Urbina-suarez, N.A., Machuca-martínez, F., Barajas-solano, A.F., 2021. Advanced oxidation processes and biotechnological alternatives for the treatment of tannery wastewater. Molecules 26, 1–25. https://doi.org/10.3390/molecules26113222