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Decolorization of the azo dye Reactive Violet 5 by UV-A-Fenton and ultrasound-Fenton processes

Nuno Jorge [1,2]*, Ana R. Teixeira [2], Marco S. Lucas [2] and José A. Peres [2]

[1] Escuela Internacional de Doctorado (EIDO), Campus da Auga, Campus Universitário de Ourense, Universidade de Vigo, As Lagoas, 32004 Ourense, Spain
[2] Centro de Química de Vila Real (CQVR), Departamento de Química, Universidade de Trás-os-Montes e Alto Douro (UTAD), Quinta de Prados, 5001-801 Vila Real, Portugal; ritamourateixeira@gmail.com (A.R.T.); mlucas@utad.pt (M.S.L.); jperes@utad.pt (J.A.P.)
* Correspondence: njorge@uvigo.es

Abstract: The textile dye reactive violet 5 (RV5) is mutagenic, and teratogenic as well as carcinogenic and has to be degraded before the release of textile wastewater into the environment. The aim of this work was to test a UV-A LED and an ultrasound (US) reactor in RV5 degradation. Different AOPs were tested, and only UV-A-Fenton and Fenton processes showed the highest RV5 degradation with 95.5 and 86.6%, respectively. The UV-A-Fenton was optimized by variation of the pH (3.0 – 7.0), H_2O_2 (2.0 – 16.0 mM) and Fe^{2+} (0.05 – 0.20 mM) concentrations. The best operational conditions (pH = 3.0, [RV5] = 0.28 mM, [H_2O_2] = 4.0 mM, [Fe^{2+}] = 0.15 mM) were applied to the US-Fenton process, achieving a RV5 removal of 95.7%. The lowest values of electric energy per order (E_{EO}) = 11 kWh m^{-3} $order^{-1}$ and specific applied energy (E_{SAE}) = 38 kWh mol^{-1} $order^{-1}$ were obtained with the treatment of RV5 aqueous solution by UV-A-Fenton process. This work shows that textile dyes can be treated by UV-A-Fenton and US-Fenton and that UV-A LED reactors can be economic.

Keywords: Electric energy per order; Reactive violet 5; UV-A-Fenton; Ultrasound-Fenton

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1. Introduction

The textile industry is one of the highest water consumption industries, utilizing large amount of dyes, organic and inorganic chemicals and additives in the production process [1]. Among the textile dyes, the azo dye reactive violet 5 (RV5) is a dye used in dyeing and printing of natural, synthetic, man-made and mixed textile materials such as wool, silk, nylon, polyester, acrylic, polyacetate and polyurethane [2]. Due to washing operations, the wastewater produced from textile dyeing mills is not only toxic, but it is also enriched by the presence of mutagenic, and teratogenic as well as carcinogenic chemicals. For instance, the well-known carcinogen, benzidine, is the parent component of most of the azo dyes, which poses a threat to living organisms [3]. In order to treat these types of wastewater advanced oxidation processes (AOPs) can be applied, in which by catalytic and non-catalytic processes generates hydroxyl radicals ($HO^{\bullet}$) with high oxidation potential (2.80 V), which in turn degrades the azo dyes [4]. Among the AOPs, the application of the Fenton process can be an efficient method, in which ferrous iron (Fe^{2+}) reacts with hydrogen peroxide (H_2O_2) to generate $HO^{\bullet}$ radicals (Equation 1). The ferric iron (Fe^{3+}) produced in the reaction also reacts with the H_2O_2 (Equation 2), generating hydroperoxyl radicals ($HO_2^{\bullet}$) with lower oxidation potential (1.65 V) [5].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \quad (2)$$

To enhance the Fenton process, UV radiation with "near-UV to visible region" of light, up to a wavelength of 600 nm can be applied to improve the $HO^{\bullet}$ radical production (Equation 3) and to rapidly reduce the Fe^{3+} back to Fe^{2+} (Equation 4) [6].

$$H_2O_2 + UV \rightarrow 2HO^{\bullet} \quad (3)$$

$$Fe^{3+} + H_2O + UV \rightarrow Fe^{2+} + HO^{\bullet} \quad (4)$$

Another interesting approach is the use of ultrasounds, which promise high reaction rates and short treatment times. In the high temperature and high-pressure region of bubbles, water molecules are prone to react, producing strong oxidizing substances such as $H^{\bullet}$ and $HO^{\bullet}$ radicals (Equation 5) [7]. In addition, the application of ultrasound allows the regeneration of Fe^{3+} to Fe^{2+} (Equation 6), with production of $HO_2^{\bullet}$ radicals [8].

$$H_2O + US \rightarrow HO^{\bullet} + H^{\bullet} \quad (5)$$

$$FeHO_2^{2+} + US \rightarrow Fe^{2+} + HO_2^{\bullet} \quad (6)$$

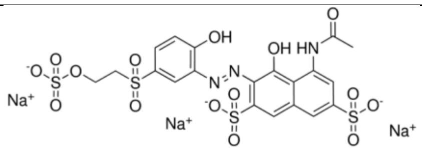
The aim and novelty of this work lies with the application of a self-made UV-A LED reactor for the removal of RV5 from an aqueous solution. It is also aimed the comparison of the efficiency of the UV-A reactor with and ultrasound reactor.

2. Materials and Methods

2.1. Reagents

The reactive dye, reactive violet 5 (RV5, Color Index 18097), was provided by Sigma-Aldrich Co. (St. Louis, Mo, USA) and used as received without further purification. The molecular structure of RV5 in non-hydrolyzed form is illustrated in Table 1. Iron (II) sulfate heptahydrate ($FeSO_4 \bullet 7H_2O$) was acquired by Panreac and hydrogen peroxide (H_2O_2 30% w/w) was acquired by Sigma-Aldrich. NaOH and H_2SO_4 (95%) were both obtained from Analar Normapur. Deionized water was used to prepare the respective solutions.

Table 1. Chemical structure, absorption maxima and molecular weight of reactive violet 5 (RV5) [9].

Name	**Chemical structure**	**λ_{max} (nm)**	**Molecular weight (g/mol)**
Reactive violet 5 (azo dye)		560 and 320 nm	735.59

2.2. Analytic techniques

The maximum absorbance wavelength (λ_{max}) of RV5 was found at 560 nm, and the concentration of the residual dye in solution was calculated by Beer-Lambert's law (Equation 7), using the optical density and molar extinction observed at the characteristic wavelength [10]:

$$A = l\varepsilon C \quad (7)$$

where A is the absorbency, l the path length (cm), ε the molar extinction coefficient (L/mol/cm) and C the dye concentration at time t (mol/L). Dye removal was determined as follows (Equation 8) [11]:

$$\text{Dye degradation (\%)} = \left(\frac{C_{dye,0} - C_{dye,t}}{C_{dye,0}}\right) x100 \quad (8)$$

Where $C_{dye,0}$ and $C_{dye,t}$ are the concentrations of RV5 at reaction time t and 0, respectively.

2.3. Experimental process

The photo-Fenton process was carried out in a lab-scale batch reactor with , which was illuminated with a UV-A LED photo-system. The photo-system consisted by a matrix of 12 InGaN LEDs lamps (Roithner APG2C1-365E LEDS) with a maximum emission wavelength at $\lambda = 365$ nm.

Batch experiments, for ultrasound-Fenton experiments were performed with a VCX 500 Watt Ultrasonic Processor (SONICS Vibra Cell™, Newtown, US), in a cylindrical reactor of 500 mL capacity.

All the experiments were performed in triplicate and the observed standard deviation was always less than 5% of the reported values.

3. Results and discussions

3.1. AOPs application

Considering the difficulty of treatment of wastewaters contaminated by RV5, it were performed several AOPs, to evaluate the efficiency and benefit of each conditions on the dye degradation. Figure 1(a) shows the RV5 removal obtained by different AOPs as a function of time (min) under the operational conditions as follows: pH = 3.0, [RV5] = 0.28 mM, $[H_2O_2] = 4.0$ mM, $[Fe^{2+}] = 0.15$ mM, radiation UV-A (365 nm), $I_{UV} = 32.7$ W m^{-2}, time = 7 min. The results showed the highest removal of 95.5 and 86.6% with application of photo-Fenton and Fenton processes respectively. These results can be explained by the high generation of $HO^{\bullet}$ radicals by these processes, leading to the removal of RV5 from aqueous solution. The remaining AOPs were observed to have low capacity for $HO^{\bullet}$ radical production, thus explaining the low efficiency in RV5 degradation. These results are supported by the findings of Teixeira *et al.*, [11] who observed a high acid red 88 removal with application of Fenton and photo-Fenton process. It was also observed that other AOPs showed low efficiency in textile dye removal.

The selection of the optimum pH of the solution is important to achieve high efficiency in RV5 degradation. The pH of the wastewater was varied from 3.0 to 7.0 and results showed a RV5 removal of 95.5, 90.2, 84.4 and 80.6%, respectively, for pH 3.0, 4.0, 6.0 and 7.0 (Figure 1(b). Clearly as the pH increased above 3.0, the degradation efficiency decreases due to (1) iron precipitation as hydroxide derivate, reducing the Fe^{2+} availability, (2) to the dissociation and auto-decomposition of H_2O_2 [12].

The next step in photo-Fenton optimization is the variation of the H_2O_2 concentration (2.0 – 16.0 mM). The results showed the highest RV5 removal with application of 4.0 mM H_2O_2 (95.5%). The application of 2.0 mM H_2O_2 was insufficient to generate $HO^{\bullet}$ radicals in sufficient amounts to degrade the RV5 (Figure 1(c)). Above 4.0 mM H_2O_2 it was observed radical scavenging by the excess of H_2O_2 present in solution (Equation 9), thus explaining the decrease in RV5 removal [13].

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \quad (9)$$

Finally, the optimization of the concentration of Fe^{2+} catalyst in the range of 0.05 – 0.20 mM was performed using the conditions obtained previously. The results in Figure 1(d) shows a RV5 removal of 87.2, 90.4, 95.5 and 90.3%, respectively, for 0.05, 0.10, 0.15 and 0.20 mM Fe^{2+}. As the Fe^{2+} concentration increases to 0.15 mM a higher generation of $HO^{\bullet}$ radicals occurs and simultaneously a higher concentration of RV5 is degraded. However, increasing the Fe^{2+} above 0.15 mM, leads to scavenging reactions, thus decreasing the RV5 removal (Equation 10) [13].

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + HO^{-} \quad (10)$$

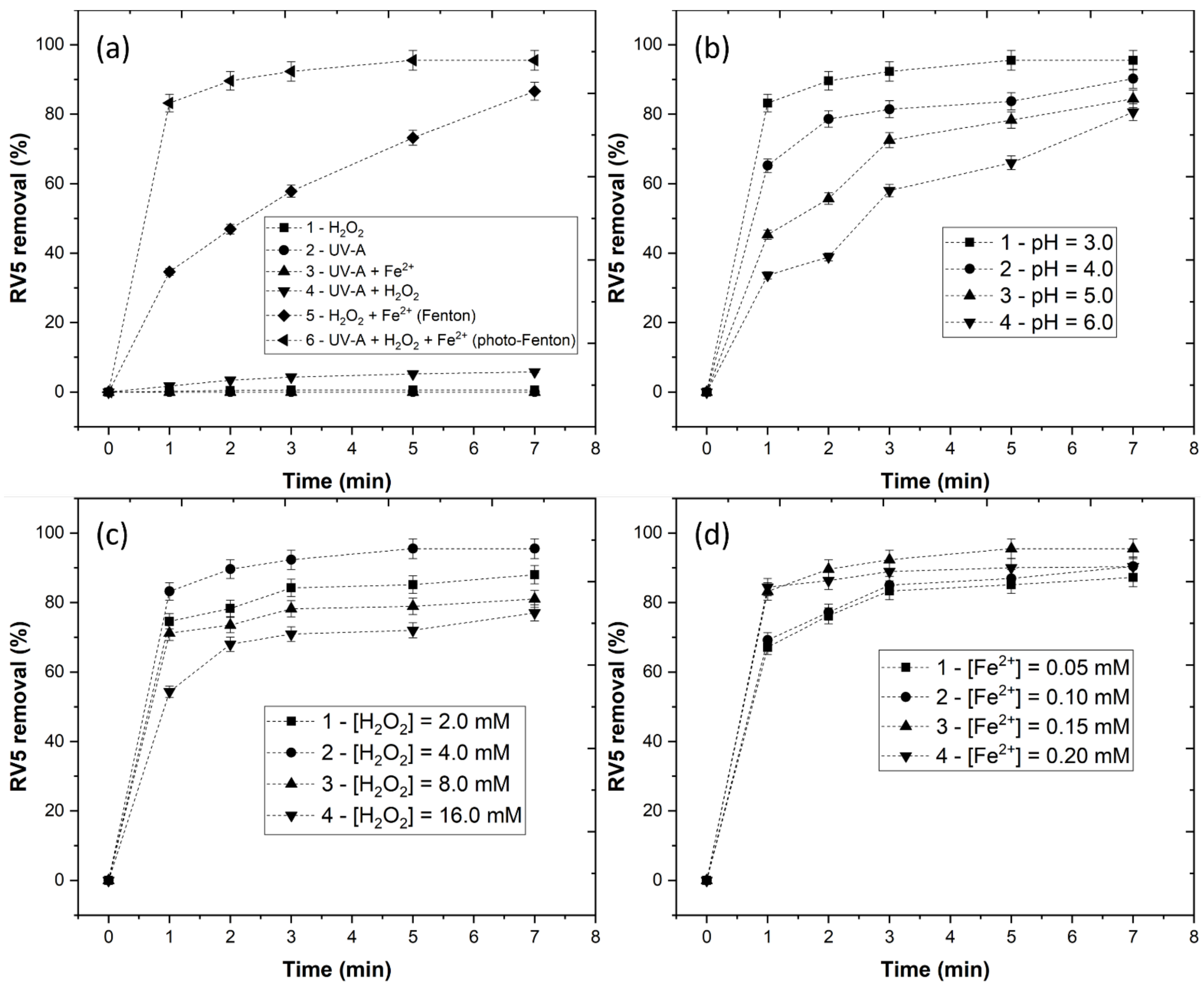


Figure 1. RV5 removal with variation of (a) AOPs, (b) pH (3.0 – 7.0), (c) H_2O_2 concentration (2.0 – 16.0 mM) and (d) Fe^{2+} concentration (0.05 – 0.20 mM).

The US-Fenton process was applied under the operational conditions: pH = 3.0, [RV5] = 0.28 mM, $[H_2O_2]$ = 4.0 mM, $[Fe^{2+}]$ = 0.15 mM, P = 500 W, A = 40%, cavitation time ON 5 s, cavitation time OFF 3s, time = 7 min (Figure 2).

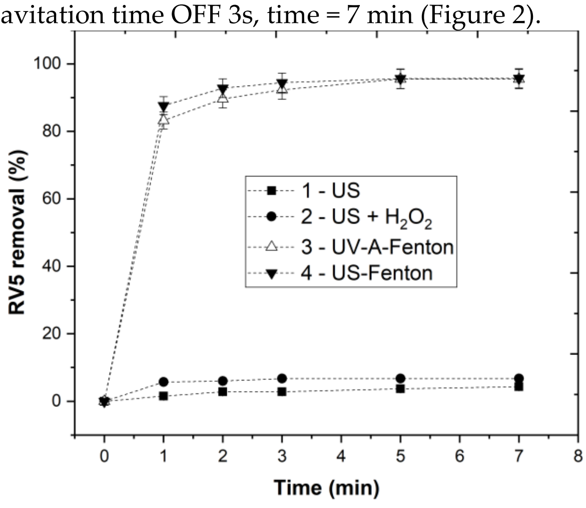


Figure 2. RV5 removal by application of US, US + H_2O_2, UV-A-Fenton and US-Fenton.

The results shows that application of US and US + H_2O_2 were insufficient to generate a high amount of $HO^{\bullet}$ radicals, thus explaining the low removal efficiency. The application of US-Fenton reached 95.7% RV5 removal, similar to the UV-A-Fenton. These results are in agreement to the work of Thanekar and Gogate [14] who observed low COD removal with application of US and US + H_2O_2 in industrial wastewater treatment and to Rahmani *et al.*, [8] who observed a high COD removal with application of US-Fenton in the treatment of activated sludge. The results obtained by Fenton, UV-A-Fenton and US-Fenton were fitted into a pseudo first-order kinetic rate ($\ln([RV5]_t = -kt + \ln[RV5]_0)$). The results showed that application of UV-A and US radiation increased significantly the kinetic rate of RV5 removal (Table 2). Having an effective process is not sufficient, it must also be cost effective, therefore the electric energy per order (Equation 11) and the specific applied energy (Equation 12) were evaluated [11].

$$E_{\mathrm{EO}}=\frac{38.4\mathrm{x}10^{-3}\mathrm{xP}}{\mathrm{Vxk}} \tag{11}$$

$$E_{\mathrm{SAE}}=\frac{E_{\mathrm{EO}}}{\mathrm{C_0x}10^{3}} \tag{12}$$

where P is the rated power of the system (kW), V is the reactor volume (m^3) and C_0 is the initial dye concentration (mol L^{-1}). The results showed that although US-Fenton has the highest kinetic rate, the energy consumption is higher, mainly, due to the power of the reactor which is higher than the UV-A reactor. By applying the cost of electricity in Portugal (0.08 € kWh^{-1}) [15] it was observed that US-Fenton is more expensive than UV-A-Fenton.

Table 2. Effect of AOPs in pseudo first-order kinetic rate (k), electric energy per order (E_{EO}), specific applied energy (E_{SAE}) and cost. Means in the same column with different letters represent significant differences ($p < 0.05$) within each parameter by comparing the treatment processes. n.q. – not quantified.

Process	**k (min^{-1})**	**E_{EO} (kWh m^{-3} order^{-1})**	**E_{SAE} (kWh mol^{-1} order^{-1})**	**Cost (€ m^{-3})**
Fenton	0.270 ± 0.01 a	n.q.	n.q.	n.q.
UV-A-Fenton	0.477 ± 0.01 b	11 ± 0.32 a	38 ± 1.13 a	0.84 ± 0.03 a
US-Fenton	0.483 ± 0.01 b	159 ± 4.77 b	568 ± 17.04 b	12.72 ± 0.38 b

4. Conclusions

This research work addresses the treatment of a non-biodegradable textile dye (RV5). Different feasible and efficient technological alternatives are shown and compared, by means of a preliminary economical assessment, to find out the lower-cost process in terms of operation. An initial assessment shows that RV5 is very hard to degrade and only Fenton and UV-A-Fenton shows the highest efficiency with 95.5 and 86.6%, respectively. The US-Fenton is concluded to be an efficient system with 95.7% RV5 removal. Finally, it is concluded that although US-Fenton achieves higher kinetic rate in RV5 degradation, it is more expensive that UV-A-Fenton.

Author Contributions: For research articles with several authors, a short paragraph specifying their individual contributions must be provided. The following statements should be used "Conceptualization, N.J. and A.R.T.; methodology, N.J.; software, N.J.; validation, N.J., M.S.L. and J.A.P.; formal analysis, N.J.; investigation, N.J.; resources, M.S.L. and J.A.P.; data curation, N.J.; writing—original draft preparation, N.J.; writing—review and editing, M.S.L. and J.A.P.; visualization, J.A.P.; supervision, M.S.L. and J.A.P.; project administration, J.A.P.; funding acquisition, J.A.P. All authors have read and agreed to the published version of the manuscript."

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