



Assessment of several advanced oxidation processes applied in the treatment of environmental concern constituents from a real hair dye wastewater



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ABSTRACT

Currently, little information is available regarding the presence of compounds from raw hair dyeing wastewater. It is known that the most commonly commercial formulations contain components with toxic properties and some by-products may also be mutagenic and carcinogenic. Indeed, virtually no studies can be found in the literature dealing with the treatment of such effluents and identification of environmental concerning substances, such as *p*-phenylenediamine, resorcinol and Bandrowski's base. The present work sought to evaluate the treatment of real hair dyeing effluent through different combinations of advanced oxidation processes including ozonation (O₃), ozone/UV-C (O₃/UV), ozone/photoelectrocatalysis (O₃/PEC), O₃/UV/H₂O₂ and O₃/PEC/H₂O₂. O₃/PEC/H₂O₂ combination provided almost complete mineralization while ozonation promoted less than 50% after 90 min of treatment. HPLC analysis confirmed the presence of *p*-phenylenediamine, resorcinol and Bandrowski's base in the raw effluent, which were completely removed in less than 5 min of treatment through the application of the combined O₃/PEC/H₂O₂ process. A figure of merit, the electric energy per order, was used to compare the different methods, showing that O₃/PEC/H₂O₂ provides lower energy consumption and higher mineralization, and could thus be an efficient option for wastewater treatment.

1. Introduction

People have an inherent desire to improve their appearance, and hair dyes formulations play an important role in improving the quality of life. In the US, 42% of women and 25% of men use hair dyes, while in Brazil 26% of adults use hair dye, most of whom are women [1,2]. Usually, 70% of hair dye formulations used at home and in hair salons are based on permanent dyes, which offer high diversity of coloration, long permanence effect, ease of application and versatility [3,4]. Permanent hair dyes are made from reactions between a 'primary intermediate' (e.g. *p*-phenylenediamine (PPD)) and 'couplers' (or modifiers) (e.g. resorcinol (RSC)) in the presence of an oxidant (e.g. hydrogen peroxide) in alkaline media (e.g. ammonia) [5–8], where dyes are formed after diffusion to the cortex of the strand of hair. These reactions are discussed in detail in the literature [3,5,8]. The main pathways for the PPD and RSC reactions are described in Fig. 1.

Notwithstanding the successful, ample commercialization of this kind of dyes, the prevailing huge concerns with respect to their composition need not be overemphasized [3,5,6,9]. Acute toxicity tests show that all major hair dye ingredients, such as PPD and RSC, have either moderate or low acute toxicity properties [5]. Nearly 99% of hair

color formulations contain at least one potent sensitizer, of which PPD and RSC are present in 78% and 89% respectively [10]. Reports in the literature have also demonstrated that intracellular increase in reactive oxygen species generated through the oxidation of PPD is cytotoxic to HaCaT cells and that this mechanism induces DNA damage [6]. Furthermore, PPD may be oxidized in the presence of air or *via* the oxidant present in the formulation, generating the Bandrowski's base (BB), which is a mutagenic [6,11] sensitizer and a genotoxic by-product [5,12,13]. In addition, due to their chemical structures, these compounds are likely to bioaccumulate and have long-term effects on aquatic organisms [14–16]. In this context, wastewater from hair dyeing has been drawing considerable attention, since a great quantity of these precursors, couplers and dyes (products of reactions), as well as Bandrowski's base (an undesirable sub product) are lost during hair washing after the coloring process and are released in domestic and salon effluents [15,17]. Clearly, the treatment of these effluents is a subject of huge environmental and public health concern.

In most countries, wastewater is treated using biological processes by aerobic microorganisms. When there is knowledge about the formation of biocalcitrant compounds, then anaerobic microorganisms, slow aggregate filtration systems, adsorption, and reverse osmosis make

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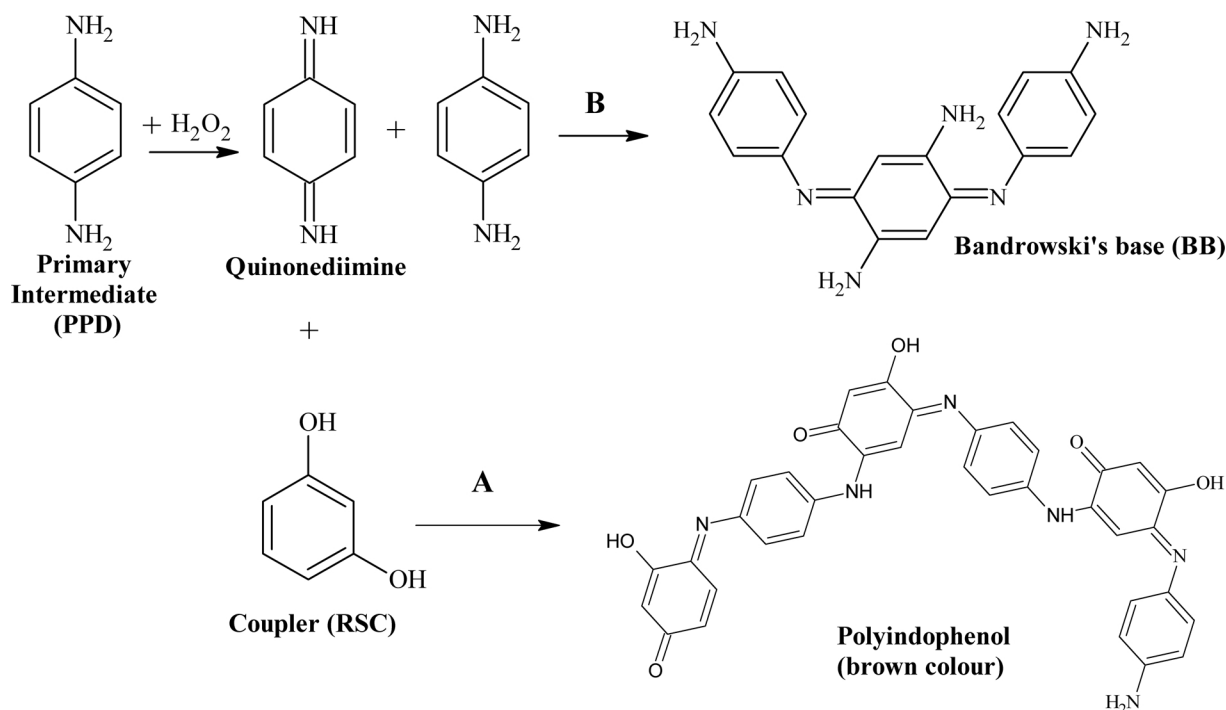


Fig. 1. Chemical pathways for PPD: (A) in the presence of RSC in alkaline media containing H₂O₂ to form the hair dye (polyindophenol); and (B) in the absence of RSC (or other couplers), which leads to the formation of Bandrowski's base. Adapted from Nohynek et al. [38] and Shah et al. [8].

up the other most commonly used processes [18–21]. By virtue of the great diversity of hair salons effluents coupled with the difficulty encountered in treating them, the current treatment mechanisms applied towards addressing wastewater pollution are still far from satisfactory with respect to the established guidelines of the Environmental Protection Agency [22,23]. In general, there is limited knowledge regarding the presence of pollutants and wastewater treatment technologies for small-scale wastewater such as hair salon effluents.

The use of photoelectrocatalytic oxidation (PEC) as a strategy for promoting the degradation of hair dyes has been investigated in the last few years [24–26]. Hydroxyl radical is formed through water oxidation on TiO₂ surface when irradiated by UV light (photocatalysis). The efficiency of this reaction can be enhanced when TiO₂ electrode is under a potential superior to its flat band potential, a process commonly referred to as photoelectrocatalysis [27]. With regard to highly concentrated solutions, the treatment of a hair dye solution (100–1000 mg L⁻¹) via photoelectrocatalysis requires the combination of the process with ozonation [24], which culminates in the formation of greater amount of hydroxyl radicals (\cdot OH), enhancing total organic carbon removal and reducing energy consumption. Ozone is also a powerful oxidant (2.07 V vs 2.8 V for \cdot OH) and can react with organic pollutants via direct attack, which is selective and relatively slow. O₃ cannot mineralize some organic compounds such as inactivated aromatics or saturated carboxylic acids. O₃ can also act via an indirect pathway where \cdot OH radicals are produced by ozone decomposition, which is also an advanced oxidation process (AOP) [28].

To the best of our knowledge, there have been few works reported in the literature dealing with the treatment of hair dyeing effluents [29,30]. Surprisingly, studies on advanced oxidation processes aiming at the treatment of this kind of effluents are lacking in the literature. In addition, neither analytical data regarding the identification of compounds present in the wastewater nor works focusing on detecting the presence of the hazardous BB contaminants in the wastewater are available.

The present work sought to compare the efficiency of some treatment methodologies including ozone alone (O₃); ozone combined with

UV light (O₃/UV) along with the addition of H₂O₂ O₃/UV/H₂O₂; ozone combined with photoelectrocatalysis (O₃/PEC); and ozone in the presence of hydrogen peroxide (O₃/PEC/H₂O₂). For the purpose of conducting the above-mentioned treatment mechanisms, a versatile annular bubble photoelectrocatalytic reactor was used so as to ascertain the best alternative suitable for the treatment of hair dyeing effluent. The presence of target compounds including PPD, RSC and BB, before and after treatment, was analyzed through the development of a liquid chromatography method. The economic aspects of the reactor were evaluated by the figure of merit 'electric energy per order' (E_{EO}) (the electric energy required for degrading a contaminant by an order of magnitude in a unit volume) [31].

2. Experimental

2.1. Hair dyeing wastewater analysis

Wastewater samples were collected in polypropylene bottles of 20 L storage capacity in hair salon sewage following a hair dyeing process. The hair dye formulation (dark brown color) had been applied to the hair according to the label instructions, left to act for 40 min followed by subsequent washing of the hair with tap water until complete removal of the unfixed dye. The wastewater samples were stored at -5 °C when not used within 48 h of collection. The following physicochemical parameters of the collected wastewater were monitored: pH (pHmeter Tecnopon, mPa 210 model), conductivity (multiparameter pHtek® CD-8B), turbidity (portable turbidimeter Quimis® Q279P), color (mg PtCo/L) (colorimeter Hanna Instruments® HI83200), chemical oxygen demand (COD) (Macherey-Nagel® PF-3) and total organic carbon (TOC) (Shimadzu TOC-V_{CPN} model).

The presence of PPD, RSC and BB in the effluent was assessed through the development of a liquid chromatography method using diode array detection (HPLC-DAD (UV-vis)) and taking standard samples of each analyte. The effluent sample that was intended to be used for HPLC-DAD analysis was centrifuged (800 rpm for 2 min) and the supernatant was then removed and vacuum filtered in a 0.47 μm filter.

Subsequently, 95 mL of the sample was eluted in a solid phase extraction cartridge (500 mg, Phenomenex Strata X). The retained content was recovered with 5 mL of methanol and preconcentrated to 0.5 mL by evaporation with N_2 . 0.3 mL of Milli-Q water was then added to the concentrated extract and the volume was adjusted to 1.0 mL by the addition of methanol aiming at obtaining 30% of water content. The sample was then again filtered through a $0.22\ \mu\text{m}$ filter and an aliquot of $20\ \mu\text{L}$ was injected into the HPLC (Shimadzu, LC-10AT model). The separation column employed was an Eclipse[®] ADB C18 ($5\ \mu\text{m}$, $15\ \text{cm} \times 4.6\ \text{mm}$) reverse phase column, preceded by a pre-C18 reverse-phase cartridge (guard column). The mobile phase consisted of acetate buffer of $0.1\ \text{mol L}^{-1}$ (pH 5.6) and methanol. Here, we adopted a gradient of 97%: 3% (acetate buffer: methanol) for 3.7 min, then 90%:10% (acetate buffer:methanol) for 20 min at a flow rate of $0.80\ \text{mL min}^{-1}$. It is worth pointing out that this method was adapted from the work of [32]. RSC and PPD were detected at 279 nm and BB at 413 nm.

The identification of PPD, RSC and BB in the hair dyeing sample was confirmed by comparing the retention times and the UV/Vis spectra with those obtained with a standard solution of PPD, RSC and BB. The standard solution contained $10\ \text{mg L}^{-1}$ of RSC and $10\ \text{mg L}^{-1}$ of PPD (30% water, 70% methanol). This solution was injected into the HPLC following the same elution conditions. In order to obtain the BB intermediate, $1000\ \text{mg L}^{-1}$ of PPD solution in ammonia buffer (pH 8) with 1% of hydrogen peroxide was kept in the presence of oxygen for 40 min as described in previous work [7]. Afterwards, 50 mL of the reaction mixture was then eluted in a solid phase extraction cartridge following the same procedure applied for the preparation of the hair dyeing effluent sample.

2.2. Preparation of the TiO_2NT cylindrical electrode

For the photoelectrocatalytic (PEC) experiments, a cylindrical TiO_2 nanotube array electrode (TiO_2NT) was constructed. The electrode was constituted of $600\ \text{cm}^2$ geometric area and a lateral opening for the flow

of solution (Fig. 2a). The TiO_2NT was prepared in line with reports in the literature [33]. A Ti sheet of $35 \times 17\ \text{cm}$ (0.5 mm thickness) was previously polished and cleaned. The titanium foil was shaped into cylindrical form and TiO_2 nanotubes were grown by electrochemical anodization (30 V for 50 h using Minipa MPL-1303 power supply) in a two-electrode cell using a dimensionally stable anode (De Nora[®]) sheet as a counter electrode. The electrolyte was composed of 0.25% NH_4F in glycerol (90%)/water (10%). The $\text{Ti}/\text{TiO}_2\text{NT}$ electrode was annealed at $450\ ^\circ\text{C}$ for 30 min (heating rate of $2\ ^\circ\text{C min}^{-1}$).

2.3. The reactor for hair salon wastewater treatment

The experiments were performed in an annular bubble reactor (ABR) of 63.5 mm diameter, having a capacity of 1.3 L (Fig. 2b), equipped with sintered glass bubblers at the bottom for injecting O_2/O_3 and operating in batch regime kept under recirculation at a rate of $1060\ \text{mL min}^{-1}$ controlled by a peristaltic pump (Cole-Parmer, model Masterflex L/S 7518-10) with Viton[®] tubing.

For the experiments involving irradiation, an UV-C 36 W lamp (Osram) was inserted at the center of the reactor and a cylindrical electrode of $\text{Ti}/\text{TiO}_2\text{NT}$ was placed around the lamp. Two graphite rods (diameter 1.0 cm) were used as cathodes (Figs. 2b, c). The bias voltage of 2.5 V was controlled using a Minipa PL-1303 power supply. Ozone was produced by an $\text{O}_3\text{R}^{\text{®}}$ ozonator model ID-05 (Brazil) using dry oxygen as the feed gas (99.9% purity). The ozone input rate of $3.85 \times 10^{-4}\ \text{mol min}^{-1}$ was delivered at O_2 flow rate of $1.0\ \text{L min}^{-1}$ monitored with a Cole-Parmer flowmeter ($0.4\text{--}5.0\ \text{L min}^{-1}$). The amount of ozone generated was determined through the use of an ozone analyzer Anseros GM-OEM (254 nm radiation). For all the experiments, aliquots of 15 mL solution were taken out at a pre-determined time and subjected to analysis. All the experiments were performed in an isolated laboratory and inside a fume cupboard with excellent exhaustion.

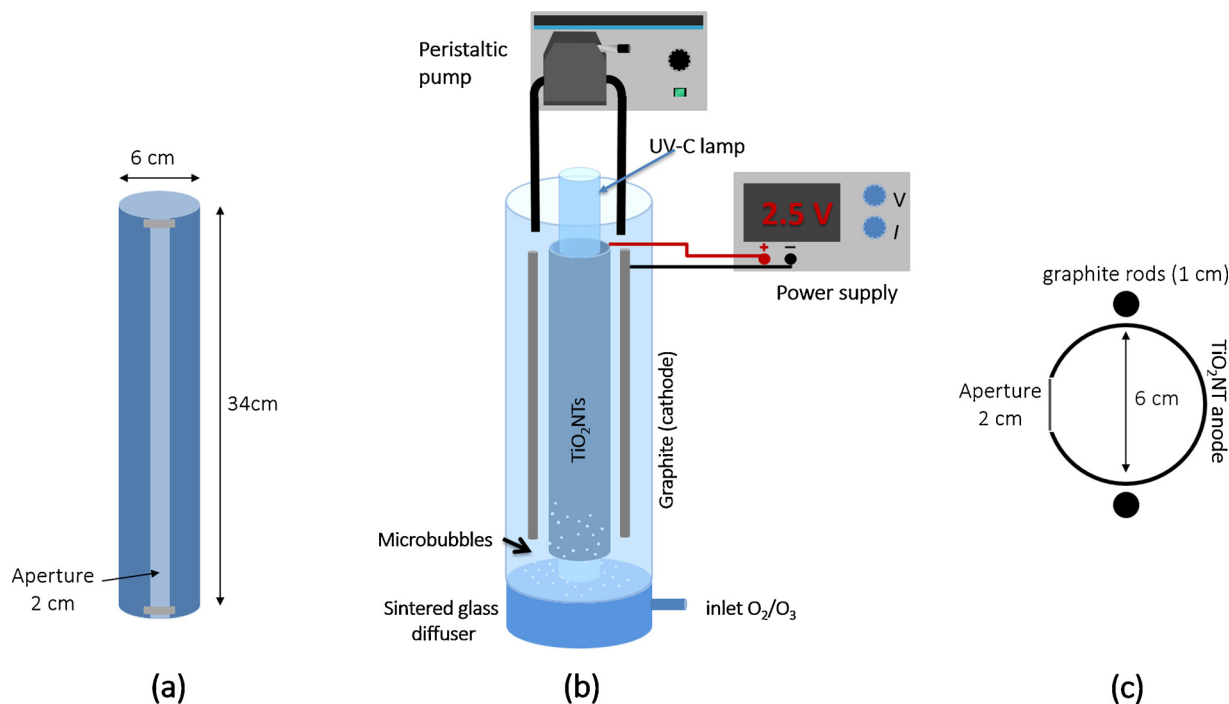


Fig. 2. Schematic representation of (a) the $\text{Ti}/\text{TiO}_2\text{NT}$ s anode with a lateral aperture of 2 cm as a medium for the flowing of solution; and (b) the annular bubble reactor, with injection of microbubbles through a sintered glass diffuser. In the center, one can find a cylindrical electrode of $\text{Ti}/\text{TiO}_2\text{NT}$ s internally irradiated by a 36 W UV-C lamp and polarized under 2.5 V vs two graphite rods using a power supply. The system was kept under recirculation ($1060\ \text{mL min}^{-1}$) using a peristaltic pump; (c) plan view of the electrode arrangement.

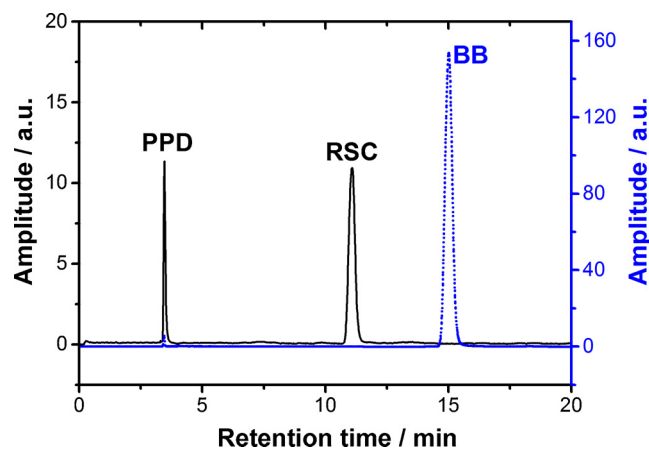


Fig. 3. Chromatogram by HPLC-DAD-UV/vis obtained for 10 mg L^{-1} of standard solution of *p*-phenylenediamine and resorcinol monitored at 279 nm; and Bandrowski's base obtained from a 1000 mg L^{-1} *p*-phenylenediamine solution in ammonia buffer (pH 8) with 1% hydrogen peroxide monitored at 413 nm. Mobile phase acetate buffer of 0.1 mol L^{-1} (pH 5.6) and methanol, at flow rate of 0.80 mL min^{-1} .

2.4. Evaluation of hair dyeing effluent treatment by advanced oxidation processes

A sample of the collected effluent (1.3 L) was transferred to the ABR and subjected to 90 min of treatment based on the aforementioned methodologies including ozonation (O_3), and the combination of oxidation processes namely O_3 and UV-C light (O_3/UV); O_3 , UV-C and H_2O_2 ($\text{O}_3/\text{PEC}/\text{H}_2\text{O}_2$); O_3 and PEC (O_3/PEC); and O_3 , PEC and H_2O_2 ($\text{O}_3/\text{PEC}/\text{H}_2\text{O}_2$). The ozone was supplied at a flow rate of $3.85 \times 10^{-4} \text{ mol min}^{-1}$. All the experiments with addition of hydrogen peroxide started with an initial concentration of 18 mmol L^{-1} , which is equivalent to a $\text{TOC}/\text{H}_2\text{O}_2$ dose ratio of 2.5, in the same range as reported by other work [34]. The concentration of H_2O_2 during the treatment was monitored via the metavanadate method [35]. The aliquots taken during 90 min of degradation were analyzed by HPLC-DAD according to the preparation procedure described previously.

2.5. Calculation of energy consumption: "Electric energy per order"

Bolton et al. [31] have proposed standard figures of merit that allow the comparison of energy consumption irrespective of the nature of the system. While the nature of complexity of real wastewater makes it difficult if not cumbersome to know the exact composition and concentration of a specific compound, the concentration parameter can, nonetheless, be substituted by another parameter such as absorbance or TOC [36,37]. The first criterion for choosing the appropriate equation of energy consumption is the adjustment of the kinetic model. As the degradation kinetics of TOC follows approximately first-order kinetics, it is possible to apply the "electric energy per order" (E_{EO} , $\text{kWh m}^{-3} \text{ order}^{-1}$) (Eq. (1)), which can be defined as the electric energy in kilowatt hours (kWh) required for degrading a contaminant by an order of magnitude in a unit volume (1 m^3):

$$E_{\text{EO}} = \frac{P \times t \times 1000}{V \times \log(\text{TOC}_i/\text{TOC}_f)} \quad (1)$$

where P stands for the rated power (kW) of the oxidation system, t being the treatment time (h), V the treated volume (1.3 L) and TOC_i and TOC_f representing the initial and final total organic carbon measurements (mg L^{-1}). The rated power equals the sum of the energy consumption of the ozonator, the lamp and the power supply. The consumption of each piece of equipment (in Wh) was calculated with the aid of multimeter measurements of current and utility voltage. The lamp, the power supply and the ozonator consume 36 Wh, 8.7 Wh and

58.9 Wh, respectively.

3. Results and discussion

3.1. Physicochemical characteristics of hair dye effluent

The physicochemical parameters evaluated for the collected hair dye effluent presented low conductivity ($164.0 \pm 1.4 \mu\text{S}$), pH close to neutral (7.31 ± 0.12) and high levels of TOC ($169.4 \pm 0.72 \text{ mg L}^{-1}$), COD ($370 \pm 2 \text{ mg L}^{-1}$), color ($347.3 \pm 6.1 \text{ mg PtCo/L}$) and turbidity ($64.83 \pm 2.5 \text{ NTU}$). Another striking feature is the intense foaming observed in the effluent which clearly unfolds new challenges in the quest for a suitable treatment. With the use of ozone-based treatment, for instance, the problem one notices is the gas bubbling that intensifies the foaming while decreasing the volume of liquid, thereby hampering gas/liquid interaction. The use of recirculation was deemed necessary as a result of the huge foaming caused by the solution bubbling, which was minimized by keeping the solution in flow. Similarly, as a result of the huge foaming, it was not possible to treat this effluent only by photo (electro)catalysis. The reason being that while photo(electro)catalysis presents high efficiency when it comes to TOC removal, it, however, exhibits low degradation kinetics which renders it impossible to oxidize surfactants in the first few minutes [24,27]. Hence, the foam formation is found to inhibit the generation of oxidizing species in solution regarded crucial for the degradation of organic compounds.

3.2. Analysis of PPD, RSC and BB in the hair dye wastewater

3.2.1. Determination of the target compounds by HPLC-DAD

The chemical pathways for the formation of Bandrowski's base along with the dye expected as the product of reaction between PPD and RSC in the oxidative medium were illustrated in Fig. 1 [38,8].

Fig. 3 shows a chromatogram obtained for 10 mg L^{-1} of standard solution of PPD and RSC samples at optimized conditions as described in the experimental section. PPD presented a well-defined peak at the retention time (t_r) of 3.45 min and RSC at t_r 11.08 min. Fig. 3 also shows the identification of Bandrowski's base, which is formed during unwanted reaction of PPD under an oxidative medium, such as ammonia buffer (pH 8), with 1% hydrogen peroxide in the presence of oxygen for 40 min [6,7]. The chromatogram obtained for Bandrowski's base presented an intense peak at 15.3 min with high resolution when analyzed by HPLC-DAD using the optimized conditions of acetate buffer 0.1 mol L^{-1} (pH 5.6) and methanol as mobile phase at a flow rate of 0.80 mL min^{-1} and detection at 413 nm.

3.3. Analysis of target compounds in the hair dye effluent

Fig. 4a depicts the chromatograms obtained for hair dye effluent samples analyzed under the same conditions previously defined. The chromatogram obtained at 279 nm illustrates the presence of residues of *p*-phenylenediamine at t_r 3.30 min and those of resorcinol at t_r 11.05 min at concentrations of $0.058 \pm 0.02 \text{ mg L}^{-1}$ and $4.52 \pm 0.17 \text{ mg L}^{-1}$, respectively. The relatively low concentration of PPD is largely as a result of its ease of being oxidized to Bandrowski's base (Fig. 1) [7,39]. In the case of RSC, however, a relatively large concentration of its residue can be seen in the effluent, indicating that an excess of this compound used in the hair dyeing process failed to react in the hair fiber. It is noteworthy that even after three months of storage under refrigeration, the composition of the sample remained stable.

Fig. 4a illustrates the chromatogram of the hair dye effluent obtained at 413 nm which exhibits a high concentration of Bandrowski's base at t_r 15.34 min (the Bandrowski's base was not quantified since there is no standard besides the reaction being non-quantitative). Remarkably, these results raise great concerns to the extent that the literature categorizes BB as strong and potent sensitizers in animal tests

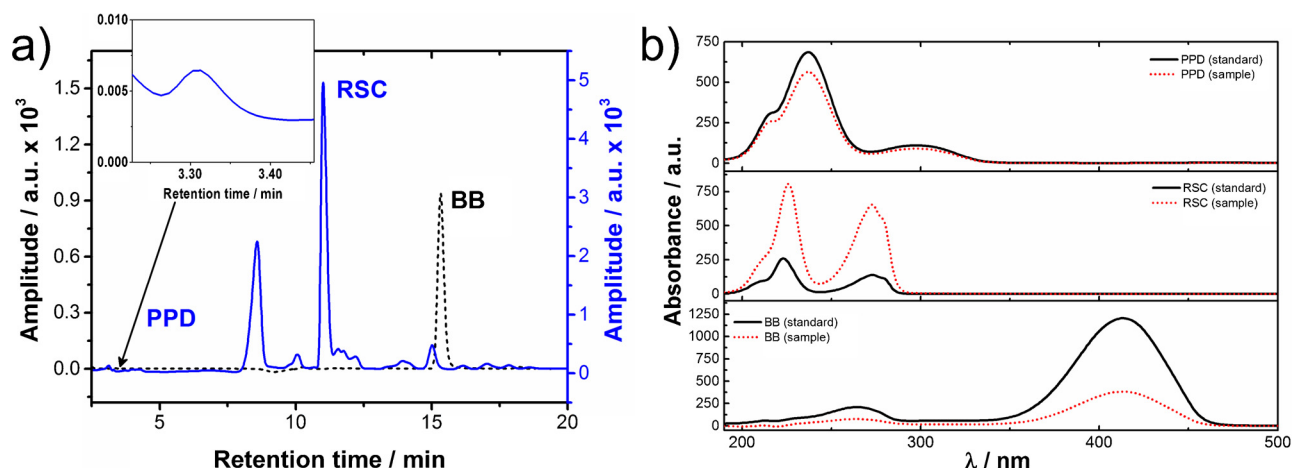


Fig. 4. (a) Chromatograms obtained by HPLC-DAD (UV-vis) for the hair dye effluent sample at 279 nm (for *p*-phenylenediamine and resorcinol) and at 413 nm (for BB). Inset shows the peak related to PPD. Mobile phase acetate buffer 0.1 mol L⁻¹ (pH 5.6) and methanol, flow rate of 0.80 mL min⁻¹. (b) UV-vis spectra of *p*-phenylenediamine and resorcinol and Bandrowski's base in the hydrodynamic mode obtained by HPLC-DAD for both the standard solutions (black line) and the sample (red line).

involving topical exposure in addition to engendering the formation of reactive oxygen species [6,40]. Fig. 4b shows the UV-vis spectra for PPD, RSC and BB in the hydrodynamic mode obtained by HPLC-DAD (UV-vis) for both the standard solutions and the sample. The UV-vis spectra confirm that the substances in the chromatogram refer to the target compounds.

3.4. Treatment of hair dye effluent by several oxidative processes

A sample containing 1.3 L of the wastewater effluent was directly treated by the following processes: ozonation (input rate of 3.85×10^{-4} mol min⁻¹ and O₂ flow rate of 1 L min⁻¹), ozonation combined with UV-C light (O₃/UV, UV-C 36 W lamp), ozonation with PEC (O₃/PEC, voltage of 2.5 V using TiO₂NT electrode irradiated by UV-C 36 W lamp), and ozonation with PEC and UV along with the addition of 18 mmol L⁻¹ H₂O₂ (O₃/UV/H₂O₂ and O₃/PEC/H₂O₂). All the treatment processes were conducted without pH adjustment and recirculation rate of 1060 L min⁻¹. The entire experiments were carried out within 90 min under recirculation and experimental conditions previously reported as ideal for hair dye degradation [24].

Fig. 5a, b show the time evolution of total organic carbon (TOC) and color removal during the treatment by different techniques. Ozonation showed a partial effluent decolorization (62% after 90 min) which is attributed to the oxidizing properties of ozone. Pure ozonation presented the lowest mineralization efficiency compared to the combined methods (48% after 90 min of treatment). This occurred because the selective attack on the double bonds generates by-products that cannot be easily degraded. A further observation worth mentioning has to do with the foaming process which ceased to occur in the first 3 min of treatment, indicating that ozone can attack surfactants compounds efficiently, allowing the treatment of the effluent to continue.

Guided by the aim of improving the results, the other treatment methodologies involving the combination of ozone with UV irradiation, ozone with photoelectrocatalysis, and ozone with hydrogen peroxide were investigated (Fig. 5). The foaming process was found to halt after 1.4 min, 1.0 min, 0.7 and 0.6 min of treatment for O₃/UV, O₃/PEC, O₃/UV/H₂O₂ and O₃/PEC/H₂O₂ treatment mechanisms, respectively.

The results obtained for ozone combined with UV-C irradiation presented a significantly higher efficiency, in as much as ozone can be converted to H₂O₂ and then to ·OH radicals, according to the following sequence of reactions (Eqs. (2)–(9)) [24,41,42].

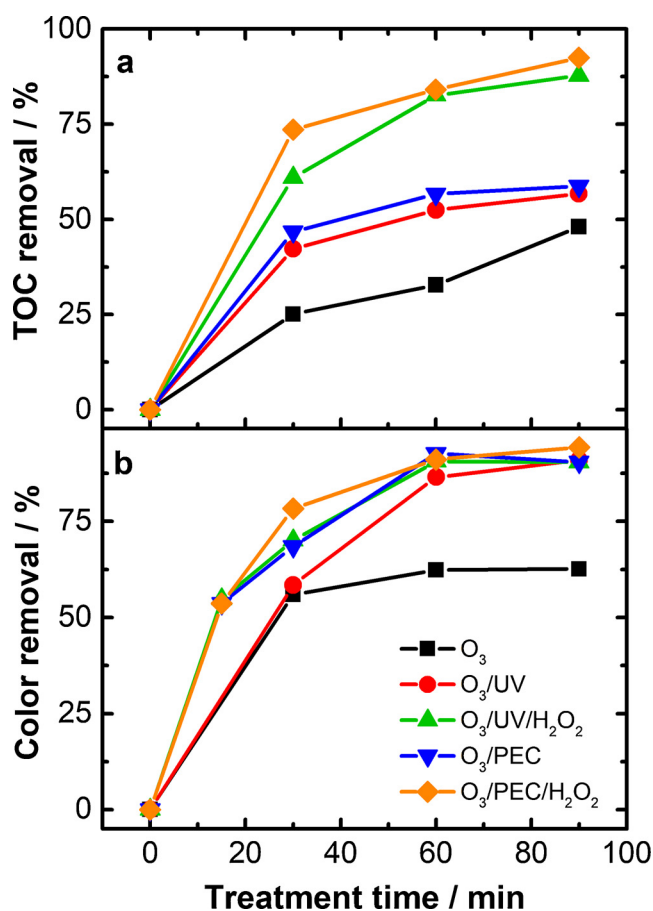


Fig. 5. (a) TOC removal (%) and (b) color removal (%) during the hair dye effluent treatment subjected to different combinations of AOPs. Conditions: ozone input rate of 3.85×10^{-4} mol min⁻¹ and O₂ flow rate of 1 L min⁻¹, voltage of 2.5 V using TiO₂NT electrode, UV-C 36 W lamp, recirculation rate of 1060 mL min⁻¹ and 18 mmol L⁻¹ H₂O₂.



Table 1
Measured parameters for the hair dyeing effluent before and after 90 min of treatment by different techniques.

Oxidation method	Conductivity (μS)	Turbidity (NTU) ^a	pH	COD (mg L^{-1})	[H ₂ O ₂] (mmol L^{-1})
Initial	164.0 \pm 1.4	64.83 \pm 2.5	7.31 \pm 0.12	370 \pm 2	18.3 \pm 0.2 ^b
O ₃	180.7 \pm 1.2	18.4 \pm 0.45	6.64 \pm 0.13	108 \pm 2	–
O ₃ /UV	182.3 \pm 0.94	12.97 \pm 0.64	4.38 \pm 0.10	< 50	–
O ₃ /PEC	171.8 \pm 1.2	5.49 \pm 0.18	4.66 \pm 0.11	< 50	–
O ₃ /UV/H ₂ O ₂	182.3 \pm 1.5	5.45 \pm 0.067	4.38 \pm 0.10	< 50	0.281 \pm 0.1
O ₃ /PEC/H ₂ O ₂	169.8 \pm 0.86	8.97 \pm 0.095	6.96 \pm 0.14	< 50	< L.O.D. ^c

Results of a triplicate.

^a NTU: nephelometric turbidity units.

^b added before starting treatment.

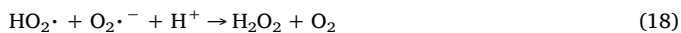
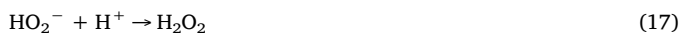
^c L.O.D. = 0.138 mmol L^{-1} .



The combination of ozone with photoelectrocatalysis O₃/PEC showed an improvement in decolorization and TOC removal. By virtue of the high turbidity (64.83 NTU) and color in hair dyeing effluents, a treatment based only on irradiation, such as photo(electro)catalysis, is essentially impracticable because of low penetration of light onto the surface of the photocatalyst. Thus, the use of ozonation in the treatment yields a partial improvement in the effluent decolorization performance as a result of the oxidizing properties of ozone. Furthermore, ozonation also helps the hydrodynamics of the process, ensuring a homogeneous mixture of the reaction medium and simultaneously promoting the breakdown of the main chemical bonds of organic compounds. In this sense, ozonation can provide a favorable environment for photoelectrocatalysis by facilitating the penetration of radiation from the light source to the photocatalyst surface. The combination of O₃/PEC produces larger amounts of ·OH radicals through the photocatalytic conversion of O₃ mediated by TiO₂ (Eqs. (10)–(13)) [24,41]. This can be confirmed by observing the efficiency of decolorization/TOC removal (Fig. 5), where the O₃/PEC combination was the third most efficient technique.



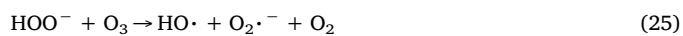
The combinations of O₃/UV and O₃/PEC along with the addition of H₂O₂ presented the highest color and TOC removal percentages. H₂O₂ is a very simple molecule yet with a complex chemical behavior in photocatalysis. It is a known fact that TiO₂ photocatalysis requires a continuous O₂ supply in order to minimize charge recombination, since O₂ acts as a scavenger of photogenerated electrons. In this process, O₂ is reduced by a sequence of reactions aiming at generating H₂O₂ (Eqs. (14)–(18)). In addition, H₂O₂ may be formed through the reaction of two ·OH radicals (Eq. 19) [43]:



Taking into consideration that H₂O₂ can be decomposed into hydroxyl radicals by UV irradiation (Eq. (20)), or that it can be reduced by the photogenerated electrons in TiO₂ (Eq. (21)), H₂O₂ is also likely to be oxidized by photogenerated holes (Eq. (22)) or by ·OH radicals (Eq. (23)) [43].



Apart from the reactions of H₂O₂ with TiO₂, hydrogen peroxide can react with ozone (named peroxide process) to produce additional ·OH radicals (Eqs. (24)–(25)) [44,45].



As such, the high production of ·OH radicals afforded by H₂O₂ (either by photolysis and reaction with ozone, or upon the photocatalytic decomposition of H₂O₂) explains the high percentage of mineralization achieved by O₃/UV/H₂O₂ and O₃/PEC/H₂O₂ combined advanced oxidation processes.

Table 1 compares the influence of each treatment on the turbidity, pH, conductivity, COD removal and H₂O₂ concentration, after 90 min of treatment using the combinations of ozone, ozone with UV, ozone with photoelectrocatalysis, and ozone with hydrogen peroxide. The values of turbidity suffered a considerable decline from 64.83 \pm 2.5 NTU to an acceptable limit of 4.66 \pm 0.11 NTU for wastewater discharge. Microorganisms are typically attached to particulates, as such, the removal of turbidity will contribute towards reducing microbial contamination in treated water [46]. The high turbidity nature of salon wastewater could be largely attributed to the several chemical additives present in hair dye formulation such as surfactants, dyes, moisturizers, etc., which contain extensive carbon chains. Thus, the high decrease in turbidity likewise implies that this water treatment could be applied towards obtaining suitable water for domestic and recreational purposes.

The pH value is found to diminish to that of a slightly acidic solution (pH = 4.66 \pm 0.11). This reduction can be attributed to the generation of both organic acids and H⁺ from water oxidation aiming at the generation of ·OH radicals (TiO₂-h⁺ + H₂O \rightarrow OH· + H⁺). However, conductivity is seen to be almost constant over the treatment duration. A significant difference was obtained for COD removal which decreased from 370 \pm 2 mg L^{-1} to values lower than 50 mg L^{-1} after 90 min of treatment for all the treatment techniques under investigation, with the exception of ozonation by which the decrease in COD removal was found to be less pronounced.

Another observation worth pointing out is the decrease observed in the H₂O₂ concentration to a level below the limit of detection for the

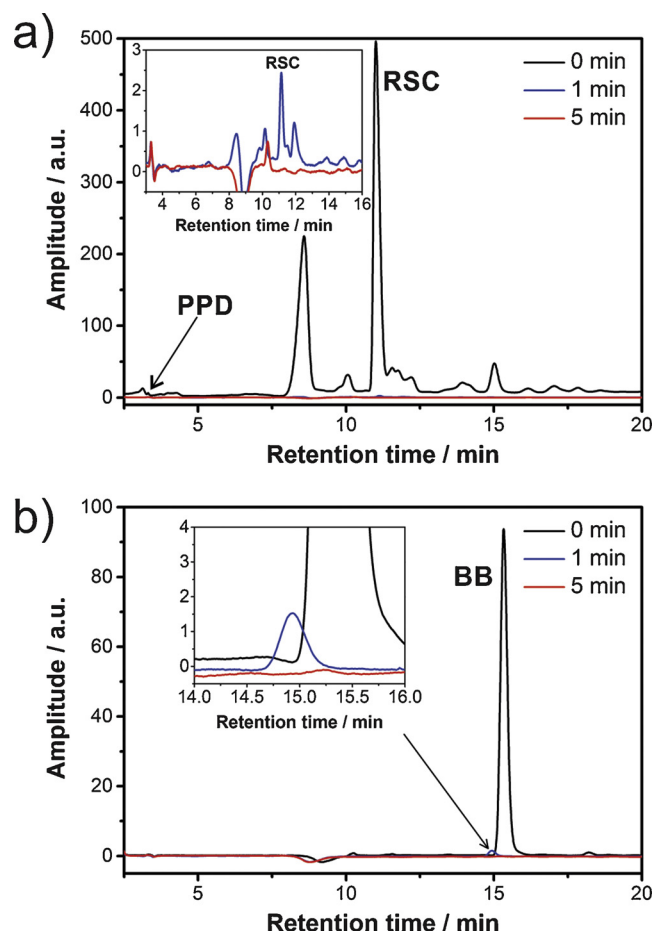


Fig. 6. (a) Chromatograms of hair dye effluent at 279 nm obtained by HPLC-DAD-UV/vis, showing *p*-phenylenediamine (at $t_R = 3.3$ min) and resorcinol (at $t_R = 11.05$ min) before and after $O_3/PEC/H_2O_2$ treatment for 1 and 5 min; and (b) chromatograms of hair dye effluent at 413 nm, showing Bandrowski's base at t_R of 15.34 min, before and after $O_3/PEC/H_2O_2$ treatment for 1 and 5 min. $O_3/PEC/H_2O_2$ conditions: ozone input rate of $3.85 \times 10^{-4} \text{ mol min}^{-1}$ and O_2 flow rate of 1 L min^{-1} , voltage of 2.5 V using TiO_2NT electrode, UV-C 36 W lamp, recirculation at a rate of 1060 mL min^{-1} and $18 \text{ mmol L}^{-1} H_2O_2$.

combined process of $O_3/PEC/H_2O_2$. The monitoring of H_2O_2 is deemed relevant to dose the initial concentration of this reagent without excessive costs besides ensuring that a possible excess does not contribute negatively in the treatment process, since H_2O_2 can act as a scavenger of holes and $\cdot OH$ radicals.

Fig. 6 shows that PPD, RSC and BB occurred in the effluent only after 1 and 5 min of $O_3/PEC/H_2O_2$ treatment. All the chromatographic signals of these harmful compounds were eliminated after 5 min of treatment. Furthermore, the other peaks present in the chromatograms and not identified previously also decreased significantly. There is no formation of new peaks, indicating that there is no formation of undesirable sub-products (that can be detected under these chromatographic conditions), thus it is very unlikely that by-products could be present in longer treatment times. This might suggest the effectiveness of the treatment technique to reduce the possible toxicity of hair dye effluent and to eliminate components with carcinogenic potential that could bioaccumulate and cause harmful effects to the environment.

3.5. Assessment of energy consumption: "Electric energy per order"

Energy consumption represents the largest operation cost of effluents treatment via advanced oxidation processes [31,47]. In this way, we have employed the concept of "electric energy per order" (E_{EO} ,

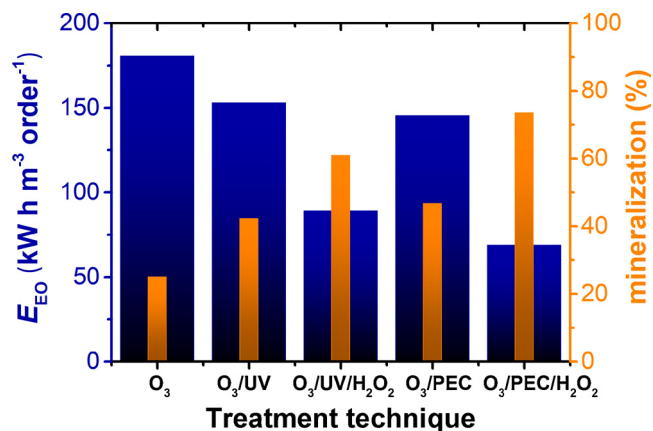


Fig. 7. Figure of merit (electric energy per order, $E_{EO}/\text{kW h m}^{-3} \text{ order}^{-1}$) for the different techniques applied in the advanced treatment (for 30 min) of hair dye effluent in comparison and contrast to mineralization efficiency (%) (Blue wide bars refer to E_{EO} and orange narrow bars refer to % mineralization).

$\text{kW h m}^{-3} \text{ order}^{-1}$) (Eq. (25)) proposed by Bolton et al. [31] (defined in Section 2.5). Taking 30 min as the treatment time for the calculation of E_{EO} , Fig. 7 shows the E_{EO} values for the different oxidation systems. Fig. 7 also shows the amount of mineralization (%) for comparison with E_{EO} , since it is not possible to assess the TOC removal efficiency through isolated E_{EO} values.

Thus, it is noteworthy that the lowest energy consumption values (E_{EO}) are obtained through techniques that make use of H_2O_2 which are also blended with higher effluent mineralization rates. However, for a large-scale design, it is essentially necessary to consider the H_2O_2 costs, since E_{EO} expresses only the energy consumption. The combination $O_3/PEC/H_2O_2$ presented the lowest value of E_{EO} and highest percentage of mineralization as a result of the catalytic decomposition of H_2O_2 to hydroxyl radicals. This decomposition is prompted by the TiO_2 and does not occur in the $O_3/UV/H_2O_2$ system (Eqs. (21), (22)). Among the techniques without H_2O_2 , the combination O_3/PEC presented a slightly lower E_{EO} value and higher percentage of mineralization, thus reinforcing the discussion of the synergistic mechanisms of this combination.

4. Conclusions

Hair dye wastewater is characterized by intense color, high turbidity, in addition to high TOC and COD contents. The chromatographic analysis of this wastewater also demonstrates the presence of large amounts of color precursors (such as PPD and RSC) that remain unreacted, and an undesirable mutagenic by-product – the Bandrowski's base, which can be potentially dangerous once released into surface waters. The results show that hair salon wastewater can fairly be characterized as potential public and environmental health hazard. Techniques based on ozone, photoelectrocatalysis, UV-C and H_2O_2 alone were found to be ineffective when it comes to decreasing the wastewater physicochemical parameters to acceptable limits for the reutilization of the water. Interestingly, the combination of $O_3/PEC/H_2O_2$ presented low electric energy per order and highest mineralization rate, being capable of degrading PPD, RSC and BB completely in less than 5 min. This same combination was also found to eliminate all the unidentified compounds occurring as peaks in the chromatograms, without apparently forming new degradation products. The fact that 42% of women and 25% of men make use of hair dyes raises huge environmental and public health concerns as large amounts of contaminants from the residues of these hair dyes may find their way into surface waters or sewage stations. In this context, our findings are an important step towards the elaboration of an efficient and simple method for the treatment of complex wastewater.

Declarations of interest

None.

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