

Single and combined electrochemical oxidation driven processes for the treatment of slaughterhouse wastewater

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ABSTRACT

Electrochemical oxidation (EO) and EO related processes, either alone or in combination with pre-ozonation, were investigated as a polishing step for slaughterhouse wastewater treatment. The wastewater had previously been subjected to grit removal, degreasing, biological treatment and settling, but failed to comply with European emission limits for treated urban wastewaters in regards to organic compounds, suspended solids and colour. Besides EO alone, the following processes were applied: EO with hydrogen peroxide (EO/H₂O₂), EO with ultraviolet C light (EO/UVC) and EO with ultraviolet C light and hydrogen peroxide (EO/UVC/H₂O₂). Without pre-ozonation, electrochemical processes could be arranged in the following order according to their ability to mineralisation and colour removal: EO < EO/H₂O₂ < EO/UVC < EO/UVC/H₂O₂. To reach a colour of 25 mg Pt-Co/L, it took more than 480 min for EO, ~400 min for EO/H₂O₂, ~260 min for EO/UVC and ~120 min for EO/UVC/H₂O₂. At this treatment time, chemical oxygen demand and suspended solids were below the European emission limit values. The pre-ozonation step improved organics removal by EO and all related processes by converting the original organic compounds into easily oxidisable compounds. Beyond that, ozonation itself led to suspended solids and colour abatement to values in agreement with the legislated/permmissible discharge limits.

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1. Introduction

One of the most hazardous wastewaters is the one coming from slaughterhouses, as stated by the United States Environmental Protection Agency (Bustillo-Lecompte et al., 2014; USEPA, 2004). This type of wastewater presents a variable composition and it is characterised not only by the presence of animal residues, but also by persistent chemicals, mainly floor cleaning products and disinfectants (Alfonso-Muniozguren et al., 2018). This makes slaughterhouse wastewater a potential source of hazardous organic matter. It is necessary to develop novel, clean and efficient technologies that allow a proper treatment of slaughterhouse wastewaters since this kind of wastewater is not completely treated by

conventional physical-chemical processes (Amuda and Alade, 2006; Bustillo-Lecompte and Mehrvar, 2016; Massé and Masse, 2000; Satyanarayan et al., 2005).

In this context, electrochemical advanced oxidation processes (EAOPs) can be considered as a good alternative for slaughterhouse wastewater final treatment due to their ability to remove recalcitrant compounds. Specifically, electrochemical oxidation (EO) with non-active anodes, such as the boron-doped diamond (BDD) anode, favours the production of large amounts of free hydroxyl radicals ($\bullet\text{OH}$) (Marselli et al., 2003). These radicals present a high oxidation potential (2.8 V), promoting the complete mineralisation of the organic matter present in the effluents (Ameta et al., 2012). EO performance can be improved by coupling it with hydrogen peroxide (H₂O₂) and UVC light since these combined technologies can produce synergistic effects for the removal of organic matter (Martínez-Huitle et al., 2015; Montanaro et al., 2017; Moreira et al., 2017).

To the best of the authors' knowledge, just few articles have

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been published on the use of EAOPs as a polishing technology for the treatment of slaughterhouse wastewater. Awang et al. (2011) obtained 85% chemical oxygen demand (COD) removal ($COD_0 = 220 \text{ mg O}_2/\text{L}$) with 55 min of EO treatment at $30 \text{ mA}/\text{cm}^2$ using aluminium electrodes. Davarnejad and Nasiri (2017) achieved 92% COD reduction ($COD_0 = 2932 \text{ mg O}_2/\text{L}$) after 55 min of electro-Fenton treatment using iron electrodes. In turn, Vidal et al. (2019) reported up to 88% COD removal ($COD_0 = 195$ or $867 \text{ mg O}_2/\text{L}$) by a solar photoelectro-Fenton process after an anaerobic digestion of synthetic slaughterhouse wastewater. All these studies showed the potential of EAOPs for the treatment of slaughterhouse wastewater.

The present study was focused on the application of EO using a BDD anode and EO related processes, alone or in combination with a pre-ozonation, as a polishing step for the removal of recalcitrant organics, suspended solids and colour from a real slaughterhouse wastewater previously subjected to grit removal, degreasing, biological treatment and settling. The ultimate aim was to produce a wastewater dischargeable into water bodies. The EO related processes included EO with external addition of H_2O_2 (EO/ H_2O_2), EO assisted by UVC light (EO/UVC) and EO in the presence of UVC radiation and H_2O_2 (EO/UVC/ H_2O_2). An annular channel photoreactor with tangential inlet/outlet pipes was used (Moreira et al., 2019), enhancing the dynamics of macromixing, the contact time between fluid particles and light, and the homogenisation of radiation distribution. To the best of the authors' knowledge, this is the first report on the application of EO with a BDD anode, EO/ H_2O_2 , EO/UVC and EO/UVC/ H_2O_2 processes to the remediation of a slaughterhouse wastewater.

2. Materials and methods

2.1. Slaughterhouse wastewater

The wastewater was collected from a pig slaughterhouse located in the north of Portugal. Before collection, the wastewater was treated on site by the following treatment train: (i) grit removal, (ii) degreasing, (iii) biological process in an activated sludge biological reactor, and (iv) settling. The main physicochemical characteristics of the wastewater are summarised in Table 1.

2.2. Chemicals

H_2O_2 used as external oxidant was of 30% w/v purity from

Labbox. Pure and dry oxygen used to generate ozone was supplied by Linde (HiQ® Oxygen 4.5, Purity $\geq 99.995\%$). All the other chemicals were supplied by Merck, Probalab, Alfa Aesar and VWR Chemicals. Ultrapure water used in experimental determinations was obtained from a Millipore® Direct-Q system ($18.2 \text{ M}\Omega \text{ cm}$ resistivity at 25°C).

2.3. Analytical methods

A Shimadzu TOC-V_{CSN} analyser was used to determine dissolved total carbon (DTC) and dissolved inorganic carbon (DIC). Dissolved organic carbon (DOC) was calculated subtracting DIC to DTC (accuracy of $\pm 2\%$, detection limit of $2 \text{ mg}/\text{L}$). A pseudo-first-order kinetic model was fitted to the DOC data as a simple mathematical model to quantitatively compare the processes efficiency. The kinetic model was adjusted by a nonlinear regression method using Fig. P software for Windows from Biosoft. The pseudo-first-order kinetic constants for DOC removal (k_{DOC}), in min^{-1} , were calculated via Eq. (1):

$$[\text{DOC}]_t = [\text{DOC}]_0 \times e^{-k_{\text{DOC}} \times t} \quad (1)$$

where $[\text{DOC}]_t$ is the DOC content after time t and $[\text{DOC}]_0$ is the DOC content just before the reaction beginning.

The fitting was performed by minimising the sum of the squared deviations between experimental and predicted values. The goodness of fitting was assessed by calculating the relative standard deviations, the coefficient of determination (R^2) and the residual variance (S^2_R).

Colour in the Pt-Co scale was determined by measuring the absorbance at 400 nm in a VWR UV-6300PC double beam spectrophotometer (accuracy of $\pm 0.6\%$, detection limit of $3 \text{ mg Pt-Co}/\text{L}$). This spectrophotometer was employed in all ultraviolet–visible measurements. The concentration of H_2O_2 was determined by the colorimetric metavanadate method, measuring the absorbance at 450 nm , as detailed described by Nogueira et al. (2005) (detection limit of $0.5 \text{ mg}/\text{L}$). COD (accuracy of $\pm 8\%$, detection limit of $12 \text{ mg O}_2/\text{L}$), total suspended solids (TSS) (detection limit of $2.0 \text{ mg}/\text{L}$) and turbidity (accuracy of $\pm 2\%$, detection limit of 0.1 NTU) were determined according to Standard Methods for the Examination of Water and Wastewater (Clesceri et al., 2005). A HI 9829 Multiparameter equipment from Hanna Instruments was used to measure temperature (accuracy of $\pm 0.1\%$), conductivity (accuracy of $\pm 1\%$)

Table 1
Physicochemical characteristics of the collected slaughterhouse wastewater.

Parameter (units)	Collected slaughterhouse wastewater	Ozonated slaughterhouse wastewater	Emission limit value (Directive no. 91/271/CEE)
pH	7.5	7.9	6.0–9.0
DOC (mg/L)	31	31	–
COD (mg O_2/L)	241	177	125
TSS (mg/L)	39	21	35
Turbidity (NTU)	16	n.d.	–
Colour (visual aspect)	Dark brown	Transparent	–
Colour (mg Pt-Co/L)	230	37	–
Conductivity ($\mu\text{S}/\text{cm}$)	5451	5424	–
Cl^- (mg/L)	968	943	–
NO_3^- (mg/L)	200	58	–
NO_2^- (mg/L)	79	<0.01	–
NH_4^+ (mg/L)	96	199	–
PO_4^{3-} (mg/L)	82	67	–
SO_4^{2-} (mg/L)	50	53	–
Na^+ (mg/L)	767	780	–
K^+ (mg/L)	84	83	–
Ca^{2+} (mg/L)	28	28	–
Mg^{2+} (mg/L)	11	11	–

n.d. – not determined.

and pH (accuracy of ± 0.02 pH). The concentration of inorganic ions was measured according to the procedure given by Cotillas et al. (2018a). Oxidants were determined iodometrically taking into account the procedure reported by Kolthoff and Carr (1953). The procedure to follow was: (i) 10 mL sample were taken from the recirculation vessel and mixed with 4 mL sulphuric acid (H_2SO_4 , 20% v/v), (ii) 0.5 g potassium iodide (KI) were added to the mixture, (iii) 0.5 mL starch (20% v/v) were dropped into the mixture, darkening the colour of the mixture, and (iv) 0.1 M sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) were added drop by drop to the mixture until a change in colour into transparent-white was observed. The volume of sodium thiosulfate was annotated to compute the amount of free oxidants (Cañizares et al., 2009).

For samples containing H_2O_2 , sodium sulphite (Na_2SO_3) in a Na_2SO_3 -to- H_2O_2 molar ratio of 1:1 (Liu et al., 2003) was added immediately after samples collection to quench the H_2O_2 and cease the oxidation process. Before determination of DTC, DIC, colour and inorganic ions, samples were filtered through 0.45 μm Nylon filters from Whatman.

2.4. Experimental setup

Fig. 1 shows the scheme of the two experimental units used in the current study. The ozonation system (Fig. 1a) was composed by: (i) a BMT bubble column containing an air stone diffuser at the bottom for ozone supply, made of glass and cylindrical in shape (internal diameter of 73 mm, maximum fluid column height of 370 mm, volume capacity of around 1.5 L), (ii) a BMT 802N ozone generator fed by pure and dry oxygen at a constant flow rate regulated by a digital mass flow controller, able to produce up to 4 g O_3/h , (iii) a BMT DH3b de-humidifier, (iv) a BMT 964 ozone analyser, and (v) a BMT heated catalyst ozone destroyer unit. All the system was maintained within a fume cupboard to avoid ozone exposure.

The electrochemical system (Fig. 1b), used for EO, EO/UVC, EO/ H_2O_2 and EO/UVC/ H_2O_2 experiments, was mainly composed of: (i) a glass annular channel photoreactor, called FluHelik reactor, fully described by Moreira et al. (2019), characterised by tangential inlet/outlet pipes that promote the generation of a helical motion of fluid, and a concentric quartz tube filled by a low pressure 11 W UVC lamp (HNS 11W G5 Osram Puritec), (ii) a continuous flow electrochemical filter-press cell, MicroFlowCell from ElectroCell

(Tarm, Denmark), detailed described elsewhere (Moreira et al., 2014), equipped with a 10 cm^2 BDD anode and a 10 cm^2 platinum (Pt) cathode (inter-electrode gap of ~ 3.7 mm), and coupled to a MLINK DPS3005 power supply (0–5 A, 0–30 V) to provide constant current density (galvanostatic mode), (iii) a 1.5 L recirculation cylindrical glass vessel thermostatically controlled and magnetically stirred at 400 rpm to provide solution homogenisation, and (iv) a gear pump (Ismatec, model BVP-Z) to flow the solution throughout the system at 50 L/h. The BDD electrode comprised a conductive niobium sheet with 2 mm thickness coated with a BDD thin film of around 5 μm thickness. The system units were connected by polytetrafluoroethylene (PTFE) tubing.

2.5. Experimental procedure

The ozonation pre-treatment was carried out by filling the bubble column with 1.4 L of the collected slaughterhouse wastewater and injecting a constant inlet ozone dose of 100 $\text{mg O}_3/\text{L}_{\text{gas}}$ at a gas flow rate of 0.3 L/min for 10 min. Injected and exhausted ozone were continuously monitored, as well as temperature and pH.

To carry out EAOPs, a volume of 1.4 L of slaughterhouse wastewater (as collected or pre-treated by ozonation) was placed into the recirculation vessel and the gear pump was switched on to pump the solution through the system. Then, the thermostatic bath was switched on and set at a temperature that allowed solution to reach 25 ± 1 °C. In EO/ H_2O_2 and EO/ H_2O_2 /UVC processes, a content of 850 $\text{mg H}_2\text{O}_2/\text{L}$ was initially added and after proper homogenisation (10 min) an initial control sample was collected. For EO and EO/ H_2O_2 processes, the reaction was started by switching on the power supply at a constant current density of 100 mA/cm^2 . For EO/UVC and EO/ H_2O_2 /UVC processes, the UVC lamp was also switched on. Samples were taken at different time intervals. During reaction, the temperature of the thermostatic bath was regulated to keep the inner solution at 25 ± 1 °C. pH was not adjusted during reaction.

3. Results and discussion

3.1. Characteristics of the real slaughterhouse wastewater

From Table 1, one can highlight the following main characteristics of the collected slaughterhouse wastewater: (i) organics

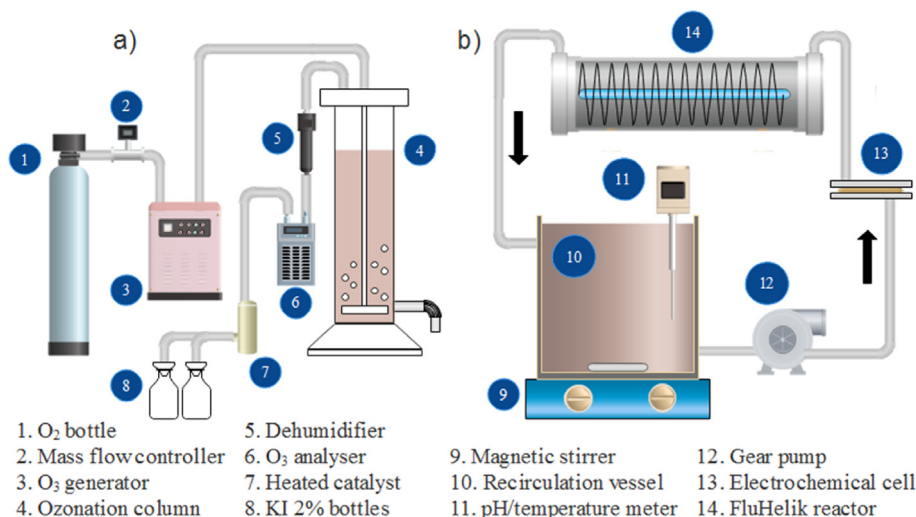


Fig. 1. Scheme of the experimental setup: (a) ozonation system and (b) electrochemical system.

content exceeding the emission limit value imposed by the European legislation (Directive no. 91/271/CEE) for discharge from urban wastewater treatment plants (WWTPs) in terms of COD (241 versus 125 mg O₂/L), (ii) solids content slightly above the European emission limits (Directive no. 91/271/CEE) in regards to the TSS content (39 versus 35 mg/L), and (iii) visible dark brown colour, corresponding to 230 mg Pt-Co/L, which is above the typical acceptable colour limit values for treated wastewaters leaving WWTPs, i.e. 25–75 mg Pt-Co/L (Anjaneyulu et al., 2005; USEPA, 1986), depending on the nature of the receiving water body (river, sea, lake, etc.).

3.2. Application of EAOPs alone

Fig. 2a shows DOC removal as a function of the specific charge (Q) during the treatment of the pre-treated slaughterhouse wastewater by EO, EO/H₂O₂, EO/UVC and EO/UVC/H₂O₂ processes at a current density of 100 mA/cm². Table 2 displays the pseudo-first order kinetic constants for the DOC removal for all the experiments included in this study.

The EO process was able to remove DOC, although poorly. This indicates the occurrence in low extent of organics oxidation by direct electron transfer to the anode surface, and the production of low amounts of the following agents and/or a small participation of

these agents on the organics oxidation: (i) physisorbed $\bullet\text{OH}$ at the BDD anode surface, denoted BDD($\bullet\text{OH}$), generated by water oxidation via reaction (2), and (ii) active chlorine species, such as hypochlorous acid (HClO), hypochlorite (ClO⁻) and chlorine (Cl₂), generated from the oxidation of chloride (Cl⁻) ions (Cl⁻ content of the effluent of 968 mg/L) at the anode via reactions (3–4) (Panizza and Cerisola, 2009). At the pH registered during reactions (pH 7 to 8), the dominant active chlorine species is HClO, and ClO⁻ is also present. HClO can be electrochemically converted into chlorate ion (ClO₃⁻) via reaction (5). ClO₃⁻ and Cl⁻ can be oxidised to perchlorate (ClO₄⁻) via reactions (6)–(9). ClO₃⁻ and ClO₄⁻ are very poor oxidants and hazardous for human health (Brown and Gu, 2006; Sánchez-Carretero et al., 2011).

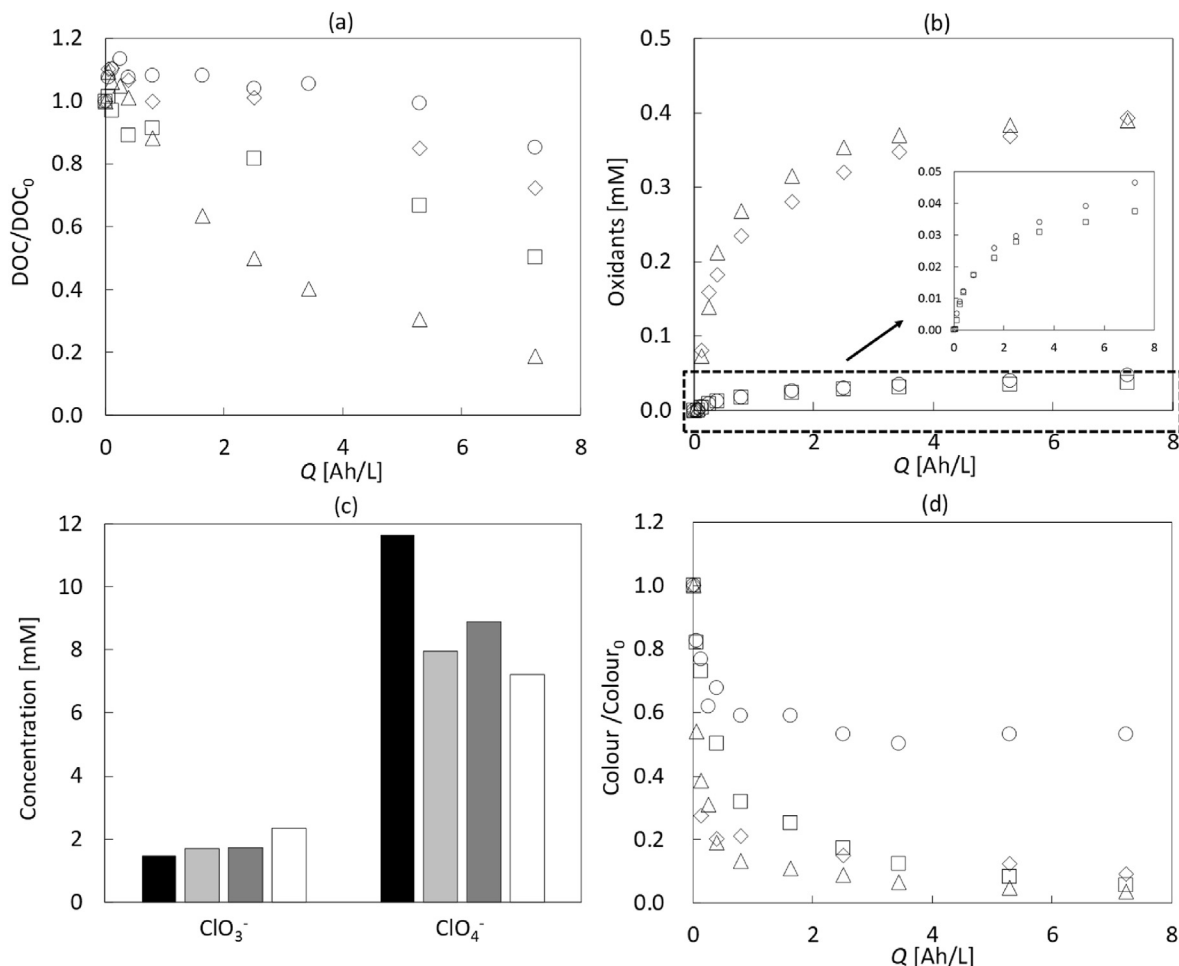
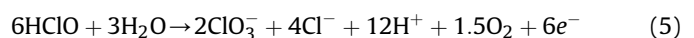
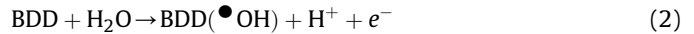


Fig. 2. (a) Normalised DOC decay as a function of Q, (b) concentration of free oxidants as a function of Q, (c) concentration of ClO₃⁻ and ClO₄⁻ at the reaction end, and (d) colour decay as a function of Q for the treatment of the slaughterhouse wastewater without pre-ozonation by the following EAOPs: (○, ■) EO, (◇, ▣) EO/H₂O₂, (□, ▢) EO/UVC and (△, ▤) EO/UVC/H₂O₂. Operating conditions: constant current density of 100 mA/cm², solution temperature of 25 °C, initial solution pH of 7.5, initial volume of 1.4 L, initial H₂O₂ addition of 850 mg/L and 11 W UVC lamp.

Table 2

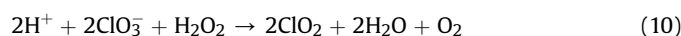
k_{DOC} values for all the applied processes along with the corresponding interval of adjustment, residual variance (S^2_{R}) and coefficient of determination (R^2).

Process	DOC			
	Time interval (min)	k_{DOC} (10^{-3} min^{-1})	S^2_{R} (mg^2/L^2)	R^2
H ₂ O ₂	Null DOC removal			
UVC	Null DOC removal			
UVC/H ₂ O ₂	No fitting of a pseudo-first-order kinetic model to experimental data			
EO	No fitting of a pseudo-first-order kinetic model to experimental data			
EO/H ₂ O ₂	0, 30-180-480	0.78 ± 0.06	3.3	0.959
EO/UVC	0, 60-480	1.27 ± 0.08	3.2	0.979
EO/UVC/H ₂ O ₂	0-480	3.5 ± 0.2	19	0.972
10' O ₃ +EO	0-480	1.13 ± 0.04	1.9	0.988
10' O ₃ +EO/UVC	0-480	2.3 ± 0.2	13	0.970
10' O ₃ +EO/UVC/H ₂ O ₂	0-480	3.5 ± 0.1	3.0	0.994



The generation of low amounts of HClO and ClO⁻ was confirmed by the low amount of oxidants determined by iodometric titration during the EO process (Fig. 2b). Note that the iodometric titration method was able to detect oxidants such as HClO, ClO⁻, Cl₂, chlorine dioxide (ClO₂), persulphate and H₂O₂ and unable to determine ClO₃⁻ and ClO₄⁻ since the pH of the method was not sufficiently acidic (Girenko et al., 2019; Greenwood and Earnshaw, 1997). Fig. 2c shows the contents of ClO₃⁻ and ClO₄⁻ determined by ion chromatography. ClO₄⁻ was present in high amount, much higher than ClO₃⁻, since ClO₄⁻ is a final product of Cl⁻ oxidation and ClO₃⁻ follows a typical trend of intermediate compound during the electrochemical processes.

The addition of H₂O₂ to EO slightly improved the DOC removal (Fig. 2a and Table 2). This can be ascribed to the oxidising potential of H₂O₂ (Cañizares et al., 2007). This oxidant may have degraded some by-products formed during the EO process and/or may have reacted with electrogenerated ClO₃⁻, favouring its decomposition to ClO₂ (reaction (10)), a powerful disinfectant which can contribute to the mineralisation process (Cotillas et al., 2015). Fig. 2b confirms the presence of higher amounts of oxidants in the EO/H₂O₂ process compared to the EO process. Note that H₂O₂ was unable to oxidise the original organics of the slaughterhouse wastewater since a null DOC decay was achieved when adding H₂O₂ alone to the slaughterhouse wastewater (data not shown). The lower amount of ClO₄⁻ in the EO/H₂O₂ process compared to that of the EO process (Fig. 2c) can be attributed to the reaction of H₂O₂ with HClO, which may have prevented a portion of HClO to be electrochemically oxidised to ClO₃⁻ via reaction (5), thereby avoiding ClO₄⁻ production via reaction (9).



The supply of UVC light during EO was more beneficial than the addition of H₂O₂ in regards to the mineralisation extent (Fig. 2a and Table 2). This can be attributed to the homolysis of the generated HClO according to reaction (11), with consequent production of extra $\bullet\text{OH}$ and chlorine radicals (Cl \bullet) (Feng et al., 2007). Additionally, UVC light may have been able to degrade some organic by-products. Note that a blank experiment revealed that UVC light alone was unable to degrade the organics available in the

slaughterhouse effluent matrix. The occurrence of HClO homolysis may have led to the accumulation of lower amounts of ClO₄⁻ in the EO/UVC process compared to the EO process (Fig. 2c) since less HClO was available to be converted into ClO₃⁻ and ClO₄⁻. The amount of total oxidants in the EO/UVC and EO processes was quite similar (Fig. 2b). HClO is an intermediate and so the occurrence of HClO homolysis may have not affected expressively the total amount of oxidants in the EO/UVC process.



The coupling of EO, UVC radiation and H₂O₂ oxidant led to the highest organic matter removal (Fig. 2a and Table 2). This can be ascribed to the homolysis of H₂O₂ under UVC irradiation via reaction (12) (Moreira et al., 2017), resulting in the generation of high amounts of $\bullet\text{OH}$. It is important to mention that the coupling of the EO process with the UVC/H₂O₂ process had some synergetic effects considering that the EO + UVC/H₂O₂ process provided around half of the DOC decay compared to the EO/UVC/H₂O₂ process after 180 min of reaction (data not shown). The total amount of oxidants was quite similar for EO/UVC/H₂O₂ and EO/H₂O₂ processes (Fig. 2b) and can be attributed mainly to H₂O₂ and ClO₂ oxidants. The H₂O₂ was more rapidly degraded in the EO/UVC/H₂O₂ process (data not shown) due to the homolysis of H₂O₂ under UVC light. Fig. 2c reveals a lower accumulation of ClO₄⁻ in the EO/UVC/H₂O₂ process compared to those observed in the other EAOPs, likely mainly due to reaction of active chlorine species with H₂O₂. These results show that the coupling of EO, UVC radiation and H₂O₂ oxidant not only increased the process efficiency in terms of organics degradation but also decreased the concentration of undesirable oxidation by-products.



After the application of a specific charge of 7.3 Ah/L (480 min of reaction), COD values were reduced from 241 mg O₂/L to <125 mg O₂/L, i.e. the emission limit value imposed in the European Union (Directive no. 91/271/CEE). For the EO/UVC and EO/UVC/H₂O₂ processes, COD values as low as 40 and < 10 mg O₂/L were found.

There was a perceptible increase in DOC to values above the initial one during the first instants of EO process (Fig. 2a), which can be attributed to the dissolution of some suspended organic matter. Organic solids dissolution also occurred for the other EAOPs, although without a noticeable DOC increase. The amount of suspended solids visibly decreased during EAOPs, mainly during the first ca. 30 min of reaction. To reduce the TSS content from 39 to 35 mg/L, it should not have taken longer than 10 min. TSS contents below 15 mg/L were achieved after applying a specific charge of 7.3 Ah/L for all tested EAOPs.

Regarding colour (Fig. 2d), it was achieved an abrupt colour

decay during the first instants of reaction for all the processes. This decay corresponded to ~ 60 mg Pt-Co/L for EO and EO/UVC processes and to ~ 150 mg Pt-Co/L for EO/H₂O₂ and EO/UVC/H₂O₂ processes, after 10 min of reaction. These results indicate the presence of readily oxidisable coloured organic and/or inorganic compounds in the effluent matrix, part of them susceptible to oxidation by H₂O₂ (either directly or by the action of ClO₂ produced from ClO₃⁻ in the presence of H₂O₂). The coloured organic compounds were converted into non-coloured organic by-products as pointed by the absence of remarkable DOC decays simultaneously with these dramatic colour removals. For longer reaction times, processes could be arranged in the following sequence according to their ability to remove colour: EO < EO/H₂O₂ < EO/UVC < EO/UVC/H₂O₂. This behaviour was similar to that found in terms of mineralisation. To reach a colour of 25 mg Pt-Co/L, it took more than 480 min for the EO process, ~ 400 min for the EO/H₂O₂ process, ~ 260 min for the EO/UVC process and ~ 120 min for the EO/UVC/H₂O₂ process.

3.3. Application of EAOPs in combination with a pre-ozonation step

As a second approach, an ozonation pre-treatment was carried out before the application of EAOPs. The main aim was to reduce colour and TSS and assess the influence of these changes on the efficiency of EAOPs. Preliminary results (data not shown) indicated maximum colour and TSS removals for an ozonation time of 10 min using an inlet ozone dose of 100 mg O₃/L_{gas} at a flow rate of 0.3 L/min. Then, an ozonation pre-treatment under the same conditions was applied to the slaughterhouse wastewater before the application of EAOPs. Under these conditions, a transferred ozone dose (OD_T) of ~ 120 mg O₃/L_{effluent} was estimated after the 10 min reaction via Eq. (13). At 10 min reaction, the off-gas concentration was ~ 68 mg O₃/L_{gas}.

$$OD_T = \frac{Q_g}{V_L} \int_0^t (C_{O_3, I-g} - C_{O_3, O-g}) dt \quad (13)$$

with C_{O₃, I-g} being the constant inlet ozone concentration (100 mg O₃/L_{gas}) and C_{O₃, O-g} being the outlet/off-gas concentration (mg O₃/L_{gas}), Q_g being the applied gas flow rate (L/min) and V_L being the volume of slaughterhouse wastewater in the reactor (L).

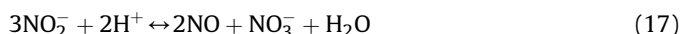
Characteristics of the slaughterhouse wastewater after ozonation are displayed in Table 1. Colour was reduced from 230 to 37 mg Pt-Co/L (dark brown to transparent colour), indicating a high ability of ozonation to convert coloured organic and/or inorganic compounds into non-coloured ones. TSS were reduced from 39 to 21 mg/L, pointing to the dissolution of organics and/or inorganics. Both colour and TSS were in agreement with legislated/permissible limits for final wastewater discharge into water bodies. DOC content remained constant, whereas COD, which takes into account dissolved and suspended organic matter, decreased from 241 to 177 mg O₂/L, remaining above the European discharge limit into waterbodies (Directive no. 91/271/CEE), i.e. 125 mg O₂/L. That indicates the ability of ozonation not only to dissolve suspended organics but also to degrade them.

Fig. 3a compares DOC decay profiles as a function of specific charge achieved for EO, EO/UVC and EO/UVC/H₂O₂ processes using the collected slaughterhouse wastewater with and without pre-ozonation. The ozonation pre-treatment improved the DOC removal in EO and EO/UVC processes. For the EO/UVC process, the k_{DOC} was 1.8 times higher when using the pre-ozonated wastewater. These results can be mainly attributed to the presence of readily oxidisable organic compounds in the ozonated effluent. The improvement of light transmissibility in the ozonated effluent may have not contributed to a large enhancement of HClO homolysis via

reaction (11) in the EO/UVC process since the superiority of the EO/UVC over the EO process in regards to DOC removal was even slightly higher for the non-ozonated wastewater (35% versus 27% after 480 min of reaction). For the EO/UVC/H₂O₂ process, the DOC decay was similar using both wastewaters, and, in addition, the superiority of the EO/UVC/H₂O₂ process over the EO/UVC one was much less pronounced for the pre-ozonated wastewater. That suggests a higher susceptibility of organic compounds in the pre-ozonated effluent for oxidation, with oxidants produced in the EO/UVC process being almost enough to maximise the DOC decay.

Fig. 3b reveals the accumulation of much lower contents of ClO₄⁻ for EAOPs carried out with the ozonated wastewater. This means that ozone used as a pre-treatment for slaughterhouse wastewater can limit the formation of undesirable by-products during the electrochemical processes. The amount of total oxidants along the various EAOPs for the pre-ozonated wastewater (Fig. 4) was quite similar to that of the wastewater without pre-ozonation (Fig. 2b), indicating no influence of the wastewater matrix on these oxidants generation.

Nitrate (NO₃⁻) and ammonium (NH₄⁺) ions were monitored during EAOPs carried out with the slaughterhouse wastewater with and without pre-ozonation (Fig. 5). NO₃⁻ concentration decreased at the beginning of all the processes. This behaviour can be explained by the electrochemical reduction of NO₃⁻ to NH₄⁺ over the cathode surface (reactions (14)–(15)) (Lacasa et al., 2012). Afterwards, a linear increase was registered in the concentration of NO₃⁻, which can be related to the release of nitrogen to the wastewater from the oxidation of the organic matter (reactions (16)–(18)) (Cotillas et al., 2018b). The maximum NO₃⁻ concentration achieved was dependent on the employed configuration, being lower during EO using the wastewater as collected and higher during EO/UVC/H₂O₂ using pre-ozonated wastewater. These results are directly related to the mineralisation efficiency during the treatment of the slaughterhouse wastewater.



On the other hand, the trend observed for NH₄⁺ concentration showed an initial increase due to the electroreduction of NO₃⁻, as previously explained, followed by a decrease. To explain this decrease, it is important to highlight the influence of chlorine species on nitrogen speciation. Specifically, the electrogenerated ClO⁻ can react with NH₄⁺, favouring the production of chloramines (reactions (19)–(21)) (Cotillas et al., 2018a; Perez et al., 2012). These species present an oxidant capacity that can also contribute to the mineralisation of the organic matter present in effluents.



It is worth mentioning that the total amount of nitrogen was higher than the European discharge limit into waterbodies, i.e.

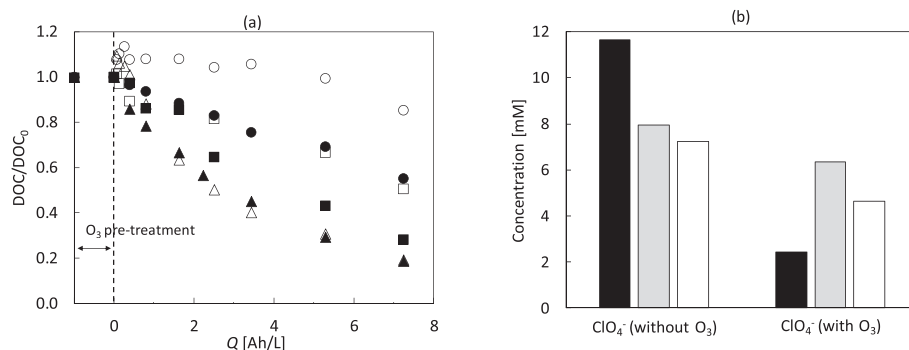


Fig. 3. Comparison between EAOPs for the treatment of the slaughterhouse wastewater with and without pre-ozonation in terms of (a) normalised DOC decay as a function of Q and (b) concentration of ClO_4^- at the reaction end. Processes: (○, ■) EO, (●, ■) $10^1\text{O}_3+\text{EO}$, (□, ■) EO/UVC, (■, ■) $10^1\text{O}_3+\text{EO/UVC}$, (△, □) EO/UVC/ H_2O_2 and (▲, □) $10^1\text{O}_3+\text{EO/UVC/H}_2\text{O}_2$. Operating conditions: constant current density of 100 mA/cm^2 , solution temperature of 25°C , initial solution pH of 7.5, initial volume of 1.4 L, initial H_2O_2 addition of 850 mg/L and 11 W UVC lamp.

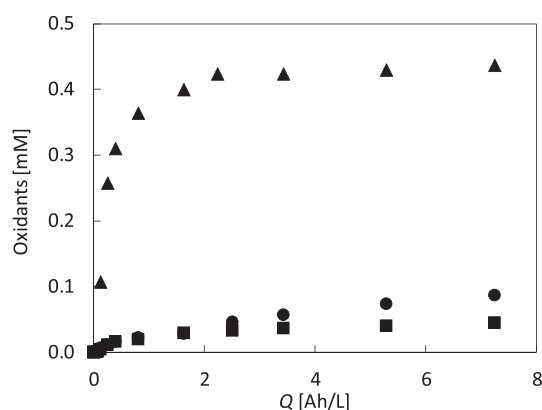


Fig. 4. Concentration of free oxidants as a function of Q for the treatment of the slaughterhouse wastewater with pre-ozonation by the following EAOPs: (●) $10^1\text{O}_3+\text{EO}$, (■) $10^1\text{O}_3+\text{EO/UVC}$ and (▲) $10^1\text{O}_3+\text{EO/UVC/H}_2\text{O}_2$. Operating conditions: constant current density of 100 mA/cm^2 , solution temperature of 25°C , initial solution pH of 7.5, initial volume of 1.4 L, initial H_2O_2 addition of 850 mg/L and 11 W UVC lamp.

10 mg/L (Directive no. 91/271/CEE), for the slaughterhouse wastewater with and without pre-ozonation (Table 1). NH_4^+ , NO_2^- and NO_3^- species contributed to around 160 mg/L of nitrogen for both wastewaters (ozonated and non-ozonated) and additional nitrogen can come from organic matter and undissolved compounds. This problem can be solved by enhancing the biological stage.

4. Conclusions

The applied EAOPs were able to remove recalcitrant organics, suspended solids and colour from the pre-treated slaughterhouse wastewater. EAOPs could be arranged in the following sequence in regards to their efficiency for mineralisation: $\text{EO} < \text{EO/H}_2\text{O}_2 < \text{EO/UVC} < \text{EO/UVC/H}_2\text{O}_2$. After 480 min of reaction (7.3 Ah/L of specific charge), COD values below the emission limit value imposed in the European Union, i.e. $125 \text{ mg O}_2/\text{L}$, were found for all EAOPs. Suspended solids dissolution occurred during EAOPs. A TSS value below 35 mg/L , i.e. the European TSS emission limit, was achieved after no longer than 10 min of all the EAOPs. A portion of the coloured compounds was easily removed at the first reaction instants for all EAOPs, but some coloured matter was more persistent. For long reaction times, EAOPs could be ordered in the same sequence in terms of their ability for colour removal as for mineralisation. To reach a colour of 25 mg Pt-Co/L , it took more than 480 min for the EO process, $\sim 400 \text{ min}$ for the EO/ H_2O_2 process, $\sim 260 \text{ min}$ for the EO/UVC process and $\sim 120 \text{ min}$ for the EO/UVC/ H_2O_2 process.

The addition of an ozonation stage prior to EAOPs converted the original organic compounds into easily oxidisable compounds, which enhanced the ability of all EAOPs for organic compounds removal. As a result, the superiority of the EO/UVC/ H_2O_2 process over the EO/UVC one was not as evident for the pre-ozonated slaughterhouse wastewater as for the non-ozonated wastewater. Beyond that, ozonation itself was able to reduce suspended solids and colour to below the legislated/permissible limits for treated wastewaters leaving WWTPs. Respecting the production of

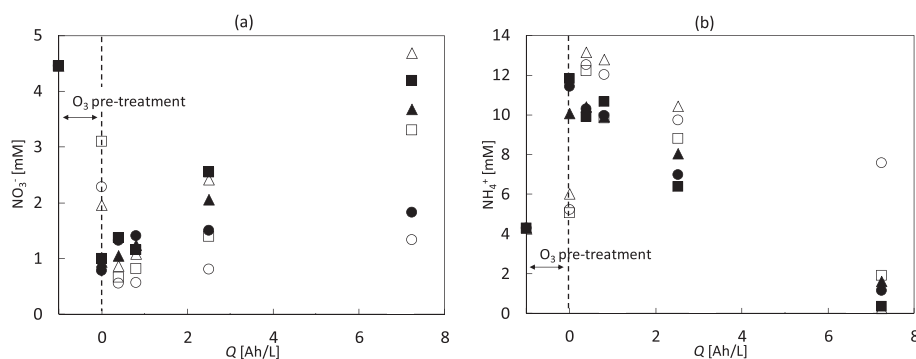


Fig. 5. (a) NO_3^- and (b) NH_4^+ concentration as a function of Q for the treatment of the slaughterhouse wastewater by the following EAOPs: (○) EO, (●) $10^1\text{O}_3+\text{EO}$, (□) EO/UVC, (■) $10^1\text{O}_3+\text{EO/UVC}$, (△) EO/UVC/ H_2O_2 and (▲) $10^1\text{O}_3+\text{EO/UVC/H}_2\text{O}_2$. Operating conditions of Fig. 3.

hazardous compounds such as ClO_4^- , the pre-ozonation step was beneficial.

Future research on the enhancement of the biological treatment stage should be carried out in order to provide effluent nitrification/denitrification, thereby allowing to comply with the total nitrogen discharge limit.

CRedit authorship contribution statement

Pello Alfonso-Muniozguren: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing. **Salvador Cotillas:** Conceptualization, Data curation, Methodology, Writing - review & editing. **Rui A.R. Boaventura:** Resources, Writing - review & editing. **Francisca C. Moreira:** Resources, Writing - review & editing. **Judy Lee:** Conceptualization, Methodology, Writing - review & editing. **Vitor J.P. Vilar:** Conceptualization, Methodology, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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