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Treatment of meat industry wastewater using dissolved air flotation and advanced oxidation processes monitored by GC–MS and LC–MS

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ABSTRACT

The meat processing industry generates a large amount of wastewater which represents a serious problem due to their high levels of organic matter which demands effective and high cost treatments. In the present study the effectiveness of the wastewater treatment by dissolved air flotation (DAF) followed by advanced oxidation processes (AOPs) using photo-peroxidation (H_2O_2/UV) and photo-Fenton reactions were evaluated in laboratory scale. The primary treatment was carried out in a DAF system, using optimal dosages of ferric sulfate and coagulation aids. The efficiency of these processes was evaluated through the following parameters: COD, BOD_5, color, turbidity, total solids, fixed solids and volatile solids, both before and after the DAF and AOP treatments. The elimination efficiency of pollutants was monitored by gas chromatography–mass spectrometry (GC–MS) and liquid chromatography–mass spectrometry (LC–MS) analysis. The results had shown that the DAF treatment efficiently reduced the COD, color, turbidity and total solids contents. In addition, the advanced oxidation process increased the organic matter removal of the treated samples. Among the AOPs, the photo-Fenton reaction reached the best overall results. These results show that the DAF process followed by an AOP process might be efficient for meat wastewater treatment, intended or not to water reuse purposes.

1. Introduction

Food industry is an important industrial sector that represents 8% of all manufacturing industries in Brazil. It is an important consumer of water and a major contribution of loads discharged into the water resources [1].

The treatment of wastewater from the meat processing industry has been one of the greatest concerns of the agro-industrial sector, mainly due to the restrictions that international trade agreements have imposed regarding to its environmental issues. Meat processing plants use approx. 62 Mm^3/year of water worldwide. Nevertheless, only a small amount of this quantity becomes a component of the final product; the remaining part is wastewater of high biological and chemical oxygen demand, high fat content and high concentrations of dry residue, sedimentary and total suspended matter as well as nitrogen and chlorides [2].

The physical nature of these wastewaters has been studied by Sayed et al. [3], who have shown that 40–50% of the screened COD (1 mm mesh) is present as coarse and suspended matter that is insoluble and only slowly biodegradable, and the remainder represented colloidal and soluble matter. However, for meat processing and slaughterhouse effluents, the blood is considered the most problematic component, because of its capacity to inhibit floc formation [4,5]. In fact, even with correct handling during the meat processing, 2.0 and 0.5 l of blood reach the effluent stream from each bovine and swine, respectively [6].

The coagulation/flotation process in meat industry wastewater plants has been used worldwide as an efficient solid separation technique, where the choice of the best process is extremely related to the pollution removal needs [7]. The dissolved air flotation (DAF) process is more efficient and faster than sedimentation techniques, and it produces lower sludge volumes [8]. Previous studies have reported that the organic matter removal of this process can be higher than 98% if the main working parameters were under control, such as the diameter of the bubbles, saturation time and saturation pressure [9].

Advanced oxidation processes (AOPs) are attractive alternatives to biological process and non-destructive physical water treatment

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processes, because they are able to mineralize organic water contaminants [10,11]. AOP treatments use strong oxidizing agents (O_3, H_2O_2) and/or catalysts (Fe, Mn, TiO_2) usually together with high-energy radiation, e.g., UV irradiation. AOPs predominantly involve the generation of a very powerful and non-selective oxidizing specie, the hydroxyl radical ($^\bullet OH$) for the destruction of persistent and hazardous pollutants [12].

When UV radiation is combined with some powerful oxidant, such as H_2O_2, the organic degradation efficiency can be significantly enhanced due the hydroxyl radicals generation caused by the photolysis of H_2O_2 [13]. The degradation of organic pollutants by Fenton type processes could be significantly accelerated in the presence of UV radiation, the so-called photo-Fenton process, that possess high oxidation efficiency [14,15].

In recent years increasing attention has been directed toward the discharge, presence and potential effects of persistent pollutants in the environment. The behavior of the majority of these compounds during wastewater treatment is still mostly unknown; however, previous studies have shown that many pharmaceutical compounds are not completely removed by conventional wastewater treatment technology [16]. Although possible interactions of the major part of these pollutants with living organisms in the environment are not documented, some pharmaceuticals are suspected to affect the endocrine system of fishes and available data on antibiotics indicate that they can exert toxic effects on algae and invertebrates and can favor the development of multiresistant strains of microorganisms [17,18]. While many persistent pollutants break down relatively quickly in the environment many others are highly resistant to degradation [19]. Furthermore, they often have low biodegradability, and can accumulate, reaching detectable and biologically active amounts.

For elimination and degradation purposes, AOP treatments have become more exploited by the food industry for water reuse and pollution control issues. Thus, the aim of this paper is to present a bench-scale treatment of a meat processing industry wastewater using a combined process consisting in DAF as a primary solid separation technique, followed by peroxidation or photo-Fenton as AOPs for the organic load abatement, using GC–MS and LC–MS monitoring in order to evaluate treatment efficiency and elimination of toxic compounds during the organic matter oxidation that can be related to anthropogenic pollution.

2. Materials and methods

2.1. Meat industry wastewater

The wastewater was sampled at the inlet of the physicochemical treatment plant, after the screening process, from a meat processing plant in Santa Catarina State (southern Brazil) whose activities include the slaughter and processing of poultry and swine, which generates around 350 m^3 of wastewater per hour. It was characterized as having a considerable pollutant load, substantial amounts of the following physicochemical parameters: total solids (TS) 2200–2500 mg/l, fixed solids (FS) 1200–2400 mg/l, volatile solids (VS) 1050–1132 mg/l, turbidity (TU) 1000–1200 NTU, initial pH 6.7 ± 0.2, and biochemical and chemical oxygen demands (BOD_5 and COD) of 1400–1600 and 2800–3000 mgO_2/l, respectively. The wastewater was dark brown, with both a strong and putrefied smell.

Data revealed that the end of pipe effluent from the meat industry is characterized by high load of organic matter. The ratio BOD_5/COD of approx. 0.5, indicates that 50% of the COD of this wastewater is easily able to be degraded by biological treatment. Nevertheless, the remainder COD is high, which indicates the necessity of an efficient physicochemical treatment for this wastewater.

Table 1
Mass spectrometric data of selected compounds performed in LC-ESI(+)–MS ($[M+H]^+$) for ion monitoring.

Polar compound	Formula	$m/z_{\text{calculated}}$	m/z_{observed}	Δmmu[a]
Nitrosamine	$C_8H_{18}N_2O$	159.14919	159.14943	0.24
Trimethoprim	$C_{14}H_{18}O_3N_4$	291.14517	291.14572	0.55
Roxitromycin	$C_{41}H_{76}O_{15}N_2$	837.53185	837.53297	1.12

[a] Molar mass unit.

2.2. Materials

The reagent used as coagulant was commercial ferric sulfate (Kemwater, Brazil) kindly provided by Kemwater Brasil. The oxidant H_2O_2 (50%, w/w stock solution) was supplied by Degussa Corporation (Brazil). Necessary pH adjustments were made with diluted HCl and NaOH solutions. Roxitromycin and Trimethoprim were analytical grade compounds purchased from Sigma–Aldrich, Taufkirchen, Germany, while Nitrosamine as an internal standard use was not commercially available, and it was identified using the mass spectrometry library results. The selected ions as enlisted in Table 1 were monitored. All other materials used for the chemical analyses were reagent grade. Standard solutions, quantification procedures and LC–MS identification conditions are fully described in Ref. [20].

2.3. Dissolved air flotation

The first step of physicochemical treatment of the wastewater was carried out using an integrated DAF system containing a 1.5-l volume flotation cell and a pressurized container with 2.6-l volume, designed for batch mode operation. For the DAF assays, the pressure was set at 4.0 bar, and the saturation time of 5 min. Previously, jar test procedures (not reported herein) were also accomplished for the optimal coagulation dosages determination for the coagulant that revealed 80 mg/l Fe^{3+} for the ferric sulfate. The flotation tests were performed in triplicate.

The tests were carried out under optimum reagent solution concentration predetermined. Samples (1.0-l) were then placed in the flotation cell prior to the dissolved air uphold for equalization of the raw wastewater, and the DAF runs were performed with 20% of recirculation, as previously described by many authors [8,9]. Subsequently, the pre-determinate coagulant dose was added into the liquid to initiate the coagulation process in the flotation cell, to provide an increase in floc size and, therefore, their flotation by the microbubbles formed by the dissolved air. The treated wastewater samples were then collected for analysis. Pre-treated wastewater by the DAF process was subsequently treated by AOP.

2.4. Advanced oxidation processes of the pre-treated wastewater

2.4.1. Photochemical reactor

A photoreactor was arranged for the experiments in batch mode operation. Medium pressure mercury lamp (150 W) was used as an UV source of 254 nm. The UV radiation lamp closed in a quartz sleeve was positioned within the center of a cylindrical glass reactor as the light source. A water jacket was installed around the reactor to keep the reactor at a desired temperature (25 °C) by means of a continuous water recirculation controlled by a thermostat. The content of the reactor (400 ml) was continuously mixed using a magnetic stirrer.

2.4.2. AOP procedures

Two AOPs were evaluated, photo-peroxidation (H_2O_2/UV) and photo-Fenton (Fe^{3+}/H_2O_2/UV) processes. To examine the effect of initial H_2O_2 concentrations on the efficiency of the combined process, the reactions were carried out over a period of 120 min in batch mode at different H_2O_2 concentrations (150, 300 and 525 mg/l H_2O_2), adjusted at the beginning of the treatment processes. After 120 min of reaction, the samples were collected and analyzed. The H_2O_2 dosage that presented better results was chosen for photo-Fenton reactions.

In a second step was evaluated the efficiency of photo-Fenton reaction. Coagulant agent (80 mg/l Fe^{3+}) was added to pre-treated (by DAF) wastewater, and the pH was adjusted to 3.0. Hydrogen peroxide (525 mg/l) was added and the reaction was carried out over a period of 120 min in batch mode. After treatment the sample was collected and analyzed.

2.5. *Physicochemical analytical procedures*

Turbidity, BOD_5, COD, total, fixed and volatile solids were measured in accordance with Standard Methods [21]. The remaining H_2O_2 concentration in the reacting solution was determined by the molybdate-catalyzed iodometric method [22]. COD was measured in accordance with the closed reflux dichromate method [21]. The correction for hydrogen peroxide interference in the standard chemical oxygen demand test was performed according to Kang et al. [23].

2.6. *Sampling preparation for the chromatographic analysis*

Commercially available solid phase extraction (SPE) cartridges (1 ml) filled with 100 mg of Isolute ENV+ material from IST (Mid Glamorgan, UK) were used for concentration. Prior to use they were handled as prescribed by the manufacturer. For elution purposes, hexane (for GC–MS) and methanol (for LC–MS) were used for each cartridge, and then evaporated and following concentrated to 1 ml.

2.7. *Gas chromatograph–mass spectrometry (GC–MS) system*

For elimination and/or degradation monitoring by AOP treatments, a GC (Thermo, USA) coupled with a MS (Finnigan, Germany) operating in positive mode of electron impact (EI+) were used for analysis. The separation was performed using a DB-5 column, film thickness 0.25 μm (30 m × 0.25 mm i.d. (J&W Scientific, Folsom, USA). The following conditions were used: carrier gas, helium; linear gas velocity, 25 cm/s; injector temperature, 240 °C; transfer line temperature, 240 °C; injection volume, 2 μl. The GC conditions were: oven temperature 60 °C for 3 min, heating rate of 10 °C/min until 240 °C, keeping constant temperature of 240 °C for 15 min.

2.8. *Liquid chromatograph–mass spectrometry (LC–MS) system*

For elimination and/or degradation monitoring by AOP treatments, LC–MS applying electrospray ionization both in positive and in negative modes (ESI(+) and ESI(−)) were performed, as described by Gebhardt and Schröder [20]. The limits of quantification (LOQs) in LC–MS mode were calculated by a signal-to-noise ratio of 3 (S/N 3:1). All samples were SPE concentrated.

LC-separations were carried out with a Hypersil Gold aQ column (RP5, 5 μm, spherical; 150 mm × 2.1 mm i.d.) from Thermo Fisher Scientific (Langerwehe, Germany) equipped with a Hypersil GOLD aQ pre-column of 10 mm × 2.1 mm i.d., filled with 5 μm, spherical material. Gradient elution by means of (A) methanol/water 90:10 (v:v) in combination with (B) Milli-Q-purified water/methanol 90:10 (v:v) was applied both containing 2 mM ammonium acetate. The gradient was programmed as follows: starting with 20% A/80% B the concentration was increased linearly to 90% A/10% B within 12 min. Up to 20 min the composition was kept constant. The overall flow rate was 0.2 ml/min. An LTQ Orbitrap mass spectrometer (Thermo Electron) was used for research work in negative ESI-MS mode as described by Gebhardt and Schröder [20].

3. Results and discussion

3.1. *Dissolved air flotation and advanced oxidation process assays*

The results show that the wastewater has a high organic load constituted by blood and organic materials that cause the red color and most of the turbidity. Both of these components inhibit the coagulation process due their complexity in relation to their removal from the liquid. The wastewater also has a high concentration of total solids, BOD_5 and COD. Table 2 shows the percent of organic matter removal using DAF and the applied AOPs.

The utilization of coagulants aims to transform the soluble matter into small particles that can be removed by settling or flotation. In the coagulation process, the size and the geometry of the particles vary considerably, which aids the floc formation. The particle removal occurs, according to Gregor et al. [24], through the formation of insoluble complexes favored at lower pH values.

Table 2 shows that the efficiency of organic matter removal for the coagulation assays using DAF is high, especially for COD, BOD, TS and FS removals. In these assays, the reagents were placed into the flotation cell to promote the coagulation process before uphold of the saturated water that generates the microbubbles responsible for the flotation.

According to Lovett and Travers [8], and recently to Rubio et al. [9], the recirculation of part of the pre-treated wastewater is very important to increase the efficiency of DAF systems, especially because of lower volume demands of wastewater for the dissolved air units. From these results, the recirculation rate of 20% seems to be efficient; however, lower recirculation rates should be more investigated.

The results reported herein revealed that the dissolved air flotation process used for the treatment of meat industry wastewater has high efficiency rates in relation to the pollutant reduction. However, even after the physicochemical treatment, the organic load is still high, and an additional treatment is necessary to guarantee

Table 2
Percent of organic matter removal by DAF and the AOPs applied to the meat industry wastewater.

Treatment	AOP reagent (mg/l)		Removal efficiency (%)						B/C[a]
	H_2O_2/UV	Fe^{3+}	VS	FS	TS	TU[b]	BOD_5	COD	
DAF[c]	–	–	89.0	63.1	75.5	88.4	70.3	80.3	0.90
DAF[c] + Perox-1	150	–	85.9	70.6	77.9	92.5	74.3	87.1	0.99
DAF[c] + Perox-2	300	–	78.8	68.3	73.3	92.7	78.6	88.7	0.95
DAF[c] + Perox-3	525	–	77.0	68.3	72.5	93.7	82.9	91.1	0.96
DAF[c] + photo-Fenton	525	80	90.8	34.6	61.5	96.2	95.7	97.6	0.90

[a] Biodegradability measured as BOD_5/COD ratio.

[b] Turbidity.

[c] 80 mg/l Fe^{3+} using ferric sulfate ($Fe_2(SO_4)_3$) as coagulant.

that these effluents achieve lower polluting load before discharge and/or reuse, as previously suggested by many authors [2,4,5,7].

The ratio B/C (BOD_5/COD) showed in Table 2 indicates that the DAF treatment enhanced the wastewater biodegradability; it would justify a posterior biological treatment application. However, considering the nature of the wastewater in study, with high contamination load, it was chosen a process that guaranteed beyond the reduction of the organic load, the oxidation of the effluent and the minimization of sludge formation. Thus, these treated samples by DAF should be submitted to AOP.

Oxidation experiments were carried out in batch mode using the photoreactor under laboratory conditions. The effect of H_2O_2 concentration was investigated by varying hydrogen peroxide (H_2O_2) concentrations between 150 and 525 mg/l. As it is well known, concentration of H_2O_2 plays a more crucial role in deciding the overall efficacy of the advanced oxidation processes. In literature, excessive amounts of hydrogen peroxide create negative effects on removal efficiency, which could be attributed to the formation of much less powerful $^{\bullet}HO_2$ radicals, which are formed by the reaction between hydroxyl radicals and excess hydrogen peroxide [14]. Table 2 shows that in the range of hydrogen peroxide concentration tested, the efficiency of the combined process increased with the hydrogen peroxide dosages increase.

The H_2O_2 and Fe^{3+} dosages used in photo-Fenton process were 525 and 80 mg/l, respectively, which had been determined as optimal from H_2O_2/UV and DAF processes. The photo-Fenton process realized a better efficiency than H_2O_2/UV process in the DAF effluent treatment, and it was justified by the higher formation of hydroxyl radicals (oxidant agent) in the presence of the Fe^{3+} catalyst. High turbidity, COD and solids removals were found for all treatments, especially the photo-Fenton process.

The advanced oxidation processes studied presented an increase in the total solids content, with regard to effluent obtained after DAF treatment, justified by mineralization from compounds of effluent, which must results in CO_2, H_2O and inorganic salts.

The results revealed that dissolved air flotation process followed by advanced oxidation process, in particular photo-Fenton process, can be a good treatment alternative for the purpose of meat wastewater treatment, achieving COD values acceptable to discharge. From experiments with DAF by coagulation followed by photo-Fenton, final COD was 79 mg/l, which represents a percentage of removal of 97.6% with regard the raw wastewater.

3.2. Analytical procedures applying GC–MS and LC–MS techniques

Albeit the utilization of AOP generates treated wastewaters with low pollution loads, the degradation products formed during oxidation processes are mostly unknown. Different classes of organic compounds react differently to each AOP applied. Fig. 1 presents the elimination efficiency of the different AOP tested after the DAF process by GC–MS.

From Fig. 1, GC–MS analyses revealed that phthalates were the main organic compounds presented in the wastewater (Fig. 1(a) – t_R 21.3 min), according to NIST library. Phthalates are chemical substances used as plasticizers, present in pipes, inks and chemical substances used for cleaning purposes. Besides, identification of volatile compounds by NIST library showed that unpolar pollutants in the wastewater (Fig. 1(a)) were predominantly fatty acids, and also phenol-like compounds were detected, as expected, but in lower amounts.

The AOP efficiencies can be compared from Fig. 1(a)–(e). Both the Perox-3 and photo-Fenton as AOP, Fig. 1(d) and (e), respectively, were responsible for the elimination of more than 90% and 99% of the unpolar organic load present in the wastewater, especially for phthalates (hardly eliminable pollutants), decreasing significantly the concentration of organic pollutants that might be responsibly for most of toxicity. Also, no degradation product was either detected or identified by mass spectrometry, what leads to the mineralization of the organic compounds during the AOP treatments.

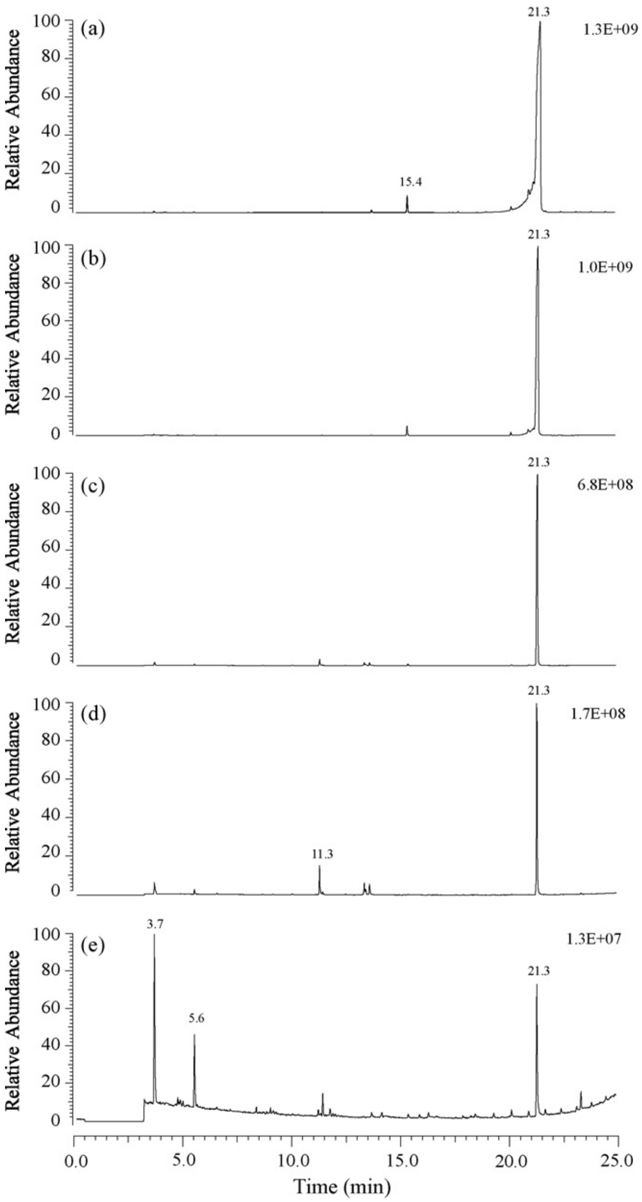

Fig. 1. TIC (total ion current) for the samples of meat industry wastewater analyzed by GC–MS (EI+): samples treated by (a) DAF; (b) DAF + Perox-1; (c) DAF + Perox-2; (d) DAF + Perox-3; (e) DAF + photo-Fenton.

From Fig. 1(d) and (e) is also possible to observe the presence of saturated fatty acids that were not completely degraded by the AOP, since they were detected but clearly covered in Fig. 1(a) due to the higher concentration of phthalates prior to the oxidation processes. These main saturated fatty acids present in all samples corresponded to t_R 3.7, 5.6 and 11.3 min were identified using NIST library as decanoic acid (C10:0), undecanoic acid (C11:0) and pentadecanoic acid (C15:0), respectively.

Additionally, Fig. 2 shows the results of the LC–MS analysis of the samples based on Table 2, in positive "electrospray ionization" (ESI(+)) mode.

The elimination efficiency of the different treatment techniques for polar compounds contained in the wastewater had been examined by LC–MS both in positive and negative modes using methanol

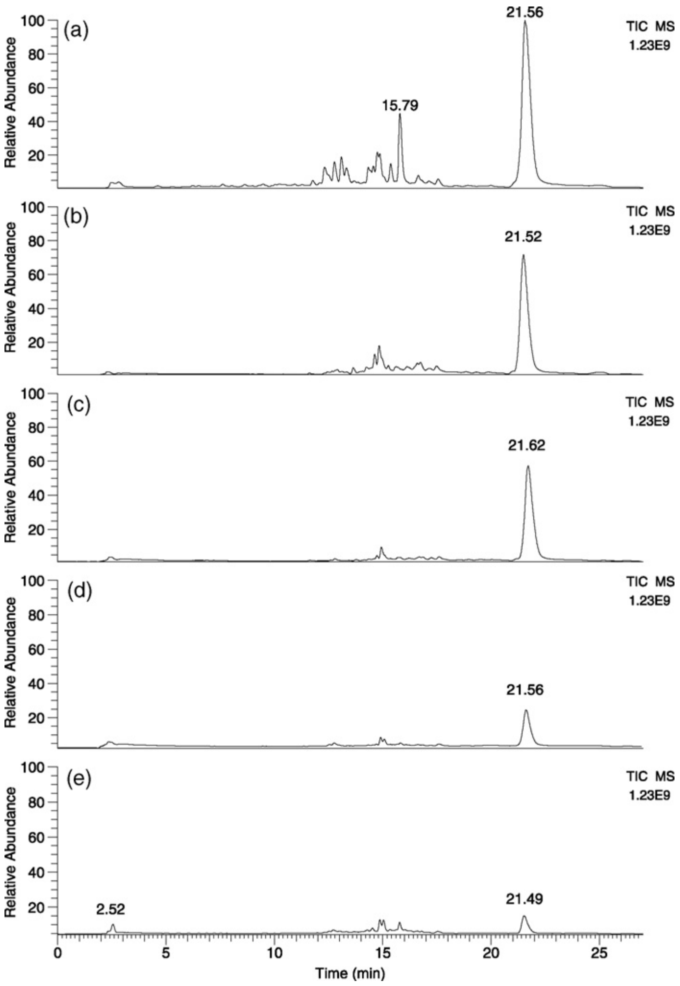

Fig. 2. TIC (total ion current) for the samples of meat industry wastewater analyzed by LC–MS (ESI(+)): samples treated by DAF (a); DAF + Perox-1 (b); DAF + Perox-2 (c); DAF + Perox-3 (d); DAF + photo-Fenton (e).

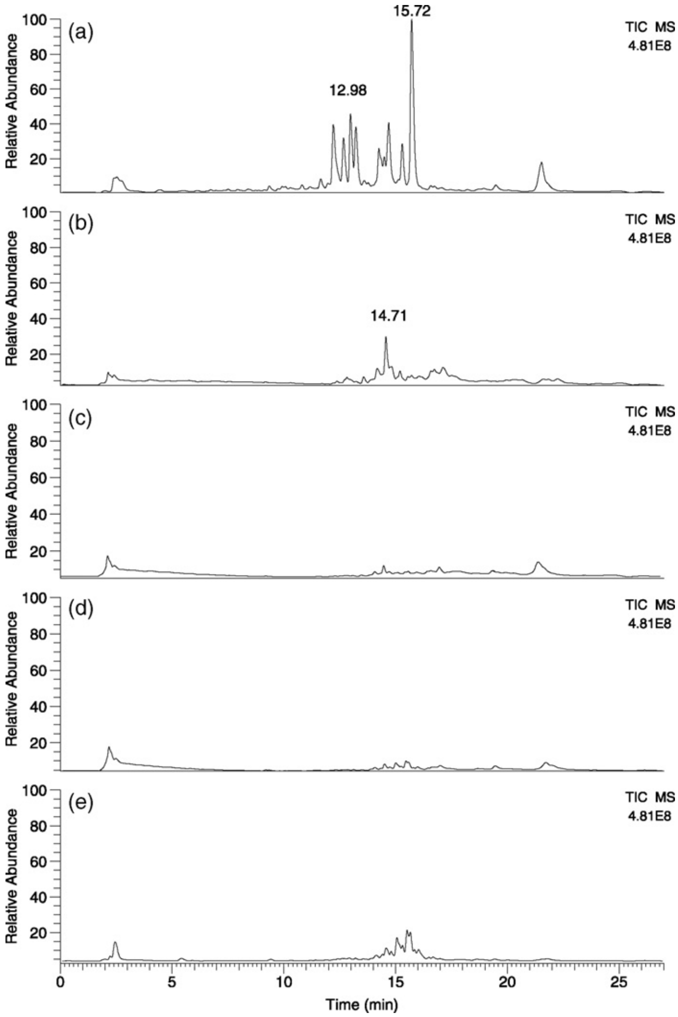

Fig. 3. TIC (total ion current) for the samples of meat industry wastewater analyzed by LC–MS (ESI(−)): samples treated by DAF (a); DAF + Perox-1 (b); DAF + Perox-2 (c); DAF + Perox-3 (d); DAF + photo-Fenton (e).

for the SPE cartridge reconstitution. For the ESI interface, molecular ions could be observed both in positive ($[M+H]^+$) and negative ($[M-H]^-$) ionization modes, as previously described by Li et al. [25]. Fig. 3 shows the results of the LC–MS analysis in negative ionization mode (ESI(−)).

Visual comparison of the TICs (Figs. 2(b)–(e) and 3(b)–(e)) related to the TIC (Figs. 2(a) and 3(a)) permitted a semi-quantitative assessment of the elimination efficiencies of the different AOP treatments. Such visual pattern recognition approach comparing the TICs of LC–MS analyses gave evidence of the high elimination rate for polar compounds with all these different treatment techniques.

As previously reported by the GC–MS analysis (Fig. 1), the LC–MS characterization shows that the application of the AOPs after the DAF process successfully mineralized most of the polar persistent pollutants still presented in these samples, both in positive and negative ionization modes. Best results were achieved by photo-Fenton and photo-peroxidation using 525 mg H_2O_2/l, reaching 88% and 77% of mineralization in positive inonization mode, as well as 78% and 86% in negative ionization mode, respectively.

3.3. Oxidative treatment for the elimination of polar persistent compounds

The identification and monitoring of many polar persistent pollutants by LC–MS techniques has been extensively used, and its effectiveness and efficacy has been previously described in details by Gebhardt and Schröder [20]. In this work, three pollutants that belong to this class of compounds were identified: Roxitromycin and Trimethoprim, two antibiotics used worldwide for both human and veterinary applications, and; Nitrosamine, a product generated during combustion processes in the presence of nitrogen sources, such as tobacco, wood and biofuels, as well as during the smoking process of meat products. These hardly eliminable compounds had been selected as target pollutants for our examination in order to monitor their elimination during AOP treatments. Through the quantification analysis, 0.6 μg/l of Roxitromycin and 0.4 μg/l of Trimethoprim were detected in the effluent treated by DAF. Fig. 4 shows the mass trace chromatograms of the respective compounds.

The detection of these compounds in the wastewater via LC–MS examinations confirmed that high polar pollutants are hardly eliminated by conventional wastewater treatments. Coagulation/flotation techniques are not capable to remove this class of compounds from the water; in fact, the AOPs were also not efficient for the complete elimination of these target compounds. Among the AOPs, the photo-Fenton process achieved the best overall results for the elimination of persistent compounds. The treatments were capable to eliminate Trimethoprim completely, while for Roxitromycin, up to 90% was successfully degraded by photo-peroxidation and photo-Fenton. Nitrosamine was partially degraded by photo-peroxidation, reaching approx. 70% of elimination, while photo-Fenton degraded less than 40% of this polar

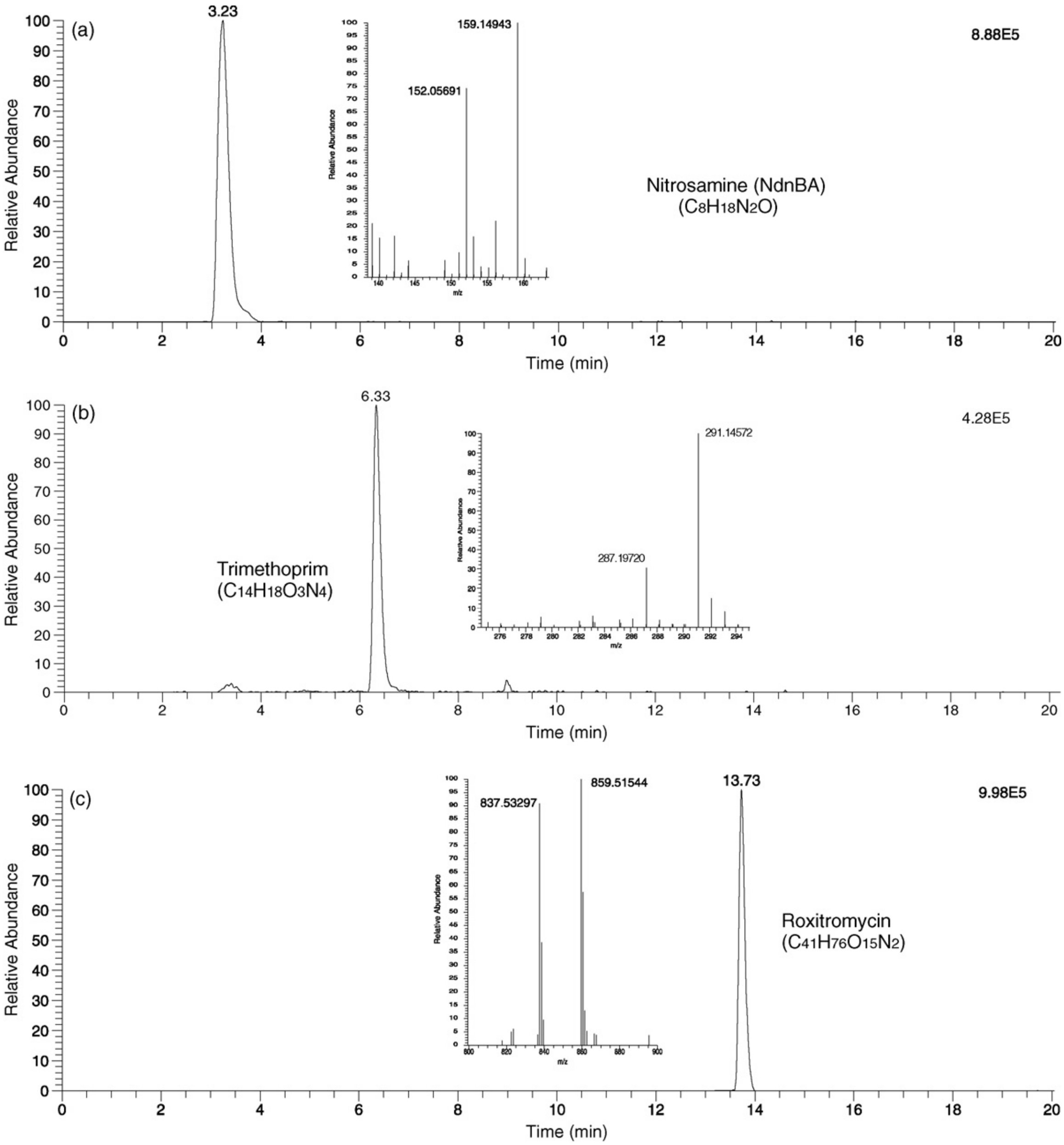

Fig. 4. LC–MS (ESI(+)) mass trace chromatograms of the meat industry wastewater samples after the DAF process, and their respective mass spectra: (a) Nitrosamine, t_R 3.23 min (*m*/*z* 159); (b) Trimethoprim, t_R 6.33 min (*m*/*z* 291); (c) Roxitromycin, t_R 13.73 min (*m*/*z* 837).

pollutant. These elimination results show that the degradation of polar compounds differ significantly both by the type of oxidation applied and by the persistence of each compound in relation to each oxidation condition.

The results show the importance of oxidative treatments after the flotation process, since DAF systems are not capable to remove these target compounds. Nevertheless, the oxidation of these pharmaceuticals or other persistent compounds may generate many degradation products that can be harmful to the environment, and most of these effects are still unknown, as described by many authors [19,26,27]. Besides, the identification of antibiotics in wastewater of meat industry plants confirms that many persistent compounds should be monitored in order to evaluate the effect of these pollutants directly discharged in the environment.

Although the main scope of this work overlies the oxidative treatment of meat industry wastewater, the overall efficiency of the combined treatments may provide some potential applications for different types of industrial wastewater above and beyond meat industry, such as slaughterhouse, dairy, brewery, pharmaceutical, chemical, and paper manufacturing industries, either for reuse purposes or to ensure water discharge parameters below the limits established by environmental laws.

4. Conclusions

The aim of physicochemical treatment is to increase the efficiency of organic load removal from wastewaters. In this study, the results for a dissolved air flotation system showed a high efficiency for this treatment, using the coagulant ferric sulfate to promote the coagulation process before the flotation phenomenon.

High organic load removal from a meat industry wastewater was achieved, as confirmed through the analysis of raw and treated wastewater. Results have shown to be in accordance with previous investigations. The physicochemical results for BOD_5 and COD reduction varied between 54–67% and 74–82%, respectively. For TS and VS, reductions of up to 68% and 84% were achieved, respectively.

The DAF process followed by AOP resulted in effluent with levels of organic load acceptable to discharge, providing the partial disinfection of this wastewater. For COD as an organic load control parameter, the final value achieved after the coupled treatment (DAF followed by AOP-photo-Fenton) was 69 mg/l, representing a percentage of removal of 97.6%.

GC–MS and LC–MS examinations confirmed that unpolar and polar compounds, including phtalates, antibiotics and nitrosamine were present in the meat processing industry wastewater. Their concentrations were low but easily detectable from the microgram to nanogram per liter range. Their elimination using DAF followed by AOP treatments has shown to be efficient, but even in undiminished concentrations; part of those toxic compounds may reach surface waters, with unknown impacts onto the environment. Photo-peroxidation and photo-Fenton processes shown to be successful oxidative treatments for most of the organic pollutants found in the wastewater, which demonstrate that hybrid systems are quite effective. Precise information about the fate of these pollutants and their oxidation products that can be generated during AOP treatments are not yet available.

As a concluding remark, the results herein show the importance of primary treatment to decrease substantially the organic load to be treated in combined systems, and the role of dissolved air flotation in conjunction with advanced oxidation processes for the treatment of meat industry wastewater in achieving low discharge parameters of organic persistent pollutants.

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References

[1] M.I. Badawy, M.E.M. Ali, Fenton's peroxidation and coagulation processes for the treatment of combined industrial and domestic wastewater, Journal of Hazardous Materials B 136 (2006) 961–966.

[2] A. Sroka, W. Kaminski, J. Bohdziewicz, Biological treatment of meat industry wastewater, Desalination 162 (2004) 85–91.

[3] S. Sayed, L. van Ampen, L. Lettinga, Anaerobic treatment of slaughterhouse waste using a granular sludge UASB reactor, Biological Wastes 21 (1987) 11–28.

[4] M.R. Jonhs, Developments in wastewater treatment in the meat processing industry: a review, Bioresource Technology 54 (1995) 203–216.

[5] J. Bohdziewicz, E. Sroka, E. Lobos, Application of the system which combines coagulation, activated sludge and reverse osmosis to the treatment of the wastewater produced by the meat industry, Desalination 144 (2002) 393–398.

[6] W.P. Tritt, F. Schuchardt, Materials flow and possibilities of treating liquid and solid wastes from slaughterhouses in Germany. A review, Bioresource Technology 41 (1992) 235–245.

[7] R.F. de Sena, A. Claudino, K. Moretti, I.C.P. Bonfanti, R.F.P.M. Moreira, H.J. José, Biofuel application of biomass obtained from a meat industry wastewater plant through the flotation process—a case study, Resources Conservation and Recycling 52 (2008) 557–569.

[8] D.A. Lovett, S.M. Travers, Dissolved air flotation for abattoir wastewater, Water Research 20 (1986) 421–426.

[9] J. Rubio, M.L. Souza, R.W. Smith, Overview of flotation as a wastewater treatment technique, Minerals Engineering 15 (2002) 139–155.

[10] I.K. Konstantinou, T.A. Albanis, TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations—a review, Applied Catalysis B: Environmental 49 (2004) 1–14.

[11] N. Daneshvar, M. Rabbani, N. Modirshahla, M.A. Behnajady, Photooxidative degradation of Acid Red 27 in a tubular continuous-flow photoreactor: influence of operational parameters and mineralization products, Journal of Hazardous Materials 118 (2005) 155–160.

[12] I.A. Alaton, I.A. Balcioglu, D.W. Bahnemann, Advanced oxidation of a reactive dye bath effluent: comparison of O_3, H_2O_2/UV-C and TiO_2/UV-A processes, Water Research 36 (2002) 1143–1154.

[13] H. Kusic, N. Koprivanac, L. Srsan, Azo dye degradation using Fenton type processes assisted by UV irradiation: a kinetic study, Journal of Photochemistry and Photobiology A: Chemistry 181 (2006) 195–202.

[14] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment II: hybrid methods, Advances in Environmental Research 8 (2004) 553–597.

[15] V. Kavitha, K. Palanivelu, The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol, Chemosphere 55 (2004) 1235–1243.

[16] T.A. Ternes, Occurrence of drugs in German sewage treatment plants and rivers, Water Research 32 (1998) 3245–3257.

[17] E. Zuccato, D. Calamari, M. Natangelo, R. Fanelli, Presence of therapeutic drugs in the environment, Lancet 322 (9317) (2000) 1789–1790.

[18] I.A. Balcioglu, M. Ötker, Treatment of pharmaceutical wastewater containing antibiotics by O_3 and O_3/H_2O_2 processes, Chemosphere 50 (2003) 85–95.

[19] O.A.H. Jones, N. Voulvoulis, J.N. Lester, The occurrence and removal of selected pharmaceutical compounds in a sewage treatment works utilizing activated sludge treatment, Environmental Pollution 145 (2007) 738–744.

[20] W. Gebhardt, H. Fr. Schröder, Liquid chromatography–(tandem) mass spectrometry for the follow-up of elimination of persistent pharmaceuticals during wastewater treatment applying biological wastewater treatment and advanced oxidation, Journal of Chromatography A 1160 (2007) 43–143.

[21] Apha, Standard Methods for the Examination of Water and Wastewater, 19th ed., Publication office American Public Health Association/American Water Works Association/Water Environment Federation, Washington, 1995.

[22] I.M. Kolthoff, Chemisch Weekblad 17 (1920) 197.

[23] Y.W. Kang, M.J. Cho, K.Y. Hwang, Correction of hydrogen peroxide interference on standard chemical oxygen demand test, Water Research 33 (1999) 1247–1251.

[24] J.E. Gregor, C.J. Nokes, E. Fenton, Optimizing natural organic matter removal from low turbidity waters by controlled pH adjustment of aluminum coagulation, Water Research 3 (1997) 2949–2958.

[25] H.-Q Li, F. Jiku, H. Fr. Schröder, Assessment of the pollutant elimination efficiency by gas chromatography/mass spectrometry, liquid chromatography–mass spectrometry and –tandem mass spectrometry—comparison of conventional and membrane assisted biological wastewater treatment processes, Journal of Chromatography A 889 (2000) 155–176.

[26] K. Ikehata, N.J. Naghashkar, M.G. El-Din, Degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes: a review, Ozone: Science and Technology 28 (2007) 353–414.

[27] M. Bernhard, J. Müller, T.P. Knepper, Biodegradation of persistent polar pollutants in wastewater: comparison of an optimised lab-scale membrane bioreactor and activated sludge treatment, Water Research 40 (2006) 3419–3428.