



Granular activated carbon promoted ozonation of a food-processing secondary effluent

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ABSTRACT

This paper reports on the application of a simultaneous combination of ozone and a granular activated carbon (O₃/GAC) as a tertiary treatment of a wastewater generated from the activity of various food-processing industries. Prior to the O₃/GAC treatment, the wastewater was subjected to conventional primary and secondary treatments in a full-scale wastewater treatment plant (WWTP). The effluent from the WWTP presented high organic load (COD > 500 mg/l and TOC > 150 mg/l), which could be much reduced by the O₃/GAC treatment. Results from the O₃/GAC experiments were compared with those obtained in single ozonation, single adsorption onto GAC and sequential O₃-GAC adsorption experiments. While single processes and the sequential one showed limited capacity to remove organic matter for the food-processing effluent (COD removal <40%), the simultaneous O₃/GAC process led to decreases of COD up to 82% at the conditions here applied. The combined process also improved the ozone consumption, which decreased from about 19 g O₃/g TOC (single ozonation process) to 8.2–10.7 g O₃/g TOC (O₃/GAC process). The reusability of the GAC throughout a series of consecutive O₃/GAC experiments was studied with no apparent loss of activity for a neutral GAC (PZC = 6.7) but for a basic GAC (PZC = 9.1).

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1. Introduction

The food-processing industry requires great amounts of water, since this latter is used throughout most of plant operations such as production, cleaning, sanitizing, cooling and materials transport, among others. As a result, food-processing industries generate large amounts of wastewater. Generally speaking, food-processing wastewaters can be considered as “friendly” as they rarely contain toxic pollutants though they usually present high organic load (i.e., high BOD and COD) as well as variable amounts of suspended and dissolved solids, nutrients and pathogen microorganisms. In addition, some types of food-processing wastewaters (e.g., distillery and olive-oil production wastewater) contain some low-biodegradable compounds that cannot be easily removed by the conventional biological treatment methods applied in wastewater treatment plants (WWTPs) [1,2]. Wastewater reclamation is recently gaining great interest as a water management option to deal with food-processing wastewaters [3]. In this area, wastewater reclamation is intended for purposes such as recovery of valuable products, saving of fresh water, reduction of wastewater discharge and disposal costs and/or improvement of effluent quality.

Primary and secondary biological treatment methods, aimed to remove suspended solids, BOD and nutrients to some extent, are the preferred treatment choice to deal with food-processing wastewaters [4,5]. However, to guarantee a safe reuse of the treated effluent, tertiary and disinfection treatments are also necessary. In this sense, ozonation may be a recommended technology to be used as an advanced treatment at WWTPs treating various types of food-processing wastewaters as ozone reacts with a wide variety of organic pollutants present in these wastewaters (e.g., phenolic compounds) and it is a clean disinfecting agent leaving no residue after its use [6,7]. Moreover, Esplugas et al. [8] found ozonation as an economically advantageous technology for the removal of phenol from water by comparison with other classical advanced oxidation methods (O₃/H₂O₂, UV/H₂O₂, UV/O₃, UV/H₂O₂, O₃/UV/H₂O₂, Fe²⁺/H₂O₂ and TiO₂ photocatalysis). Consequently, ozonation must be considered as a primary candidate technology for the tertiary treatment of food-processing wastewaters of phenolic nature. However, the direct ozonation of organic compounds in wastewater may lead to the formation of some recalcitrant by-products, which further require huge doses of ozone to be fully mineralized (i.e., converted into CO₂). In order to enhance the mineralization of such recalcitrant compounds with ozone, the literature reports on the simultaneous use of ozone and granular activated carbon (GAC) [9–13]. The O₃/GAC method is a relatively new process in which the GAC performs a dual role: adsorption of organic pollutants from the wastewater and decomposition of the aqueous ozone over its sur-

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face to yield free radical oxidizing species, which in turn, are able to quickly mineralize recalcitrant compounds, both, adsorbed and in solution. This treatment method has been proven useful, either as standalone or as part of an integrated process, for the degradation of aqueous solutions of some compounds typically present in some food-processing wastewaters such as polyphenols and carboxylic acids [11–13]. However, to our knowledge, no empirical studies have been published so far on the treatment of real food-processing effluents but one preliminary study [14].

In our previous work, we briefly reported on the treatment of an actual food-processing secondary effluent by means of ozonation in the presence of a GAC, with promising results [14]. As part of our continuing work, in this paper we report on the effects of some operating variables such as aqueous pH, the ozone dose, the GAC amount, the concentration of phenolic compounds in the effluent to be treated, the GAC particle size and the liquid recirculation flow rate. A kinetic approach is presented and the stability of the GAC throughout some semi-batch ozonation cycles and continuous experiments is checked. The results of this study should contribute to provide an empirical basis for the assessment of the O_3 /GAC as an effective tertiary treatment for food-processing wastewater reclamation.

2. Experimental

The food-processing secondary effluent was collected from a full-scale WWTP located in Almendralejo (Extremadura, Spain). Extremadura is a region with a large number of small and medium-size food-processing industries, whose activities have a great social and economic impact on the area. The WWTP of Almendralejo treats a mixture of wastewaters coming from various food-processing local facilities including wineries, distilleries and olive industries. The scheme of the treatment at the WWTP consists of a sequence of screening, primary sedimentation and activated sludge processes. The samples used in this study were collected at the exit of the activated sludge settler. Immediately after their collection, the samples were shipped to the laboratory, analyzed and kept frozen in PET bottles until their use. A characterization of this food-processing effluent was reported earlier [14] and it is reproduced in the second column of Table 1. The methods followed and/or equipments used for the analyses are also listed in Table 1 [15,16]. From the high values of suspended solids, BOD, COD and TOC, it is apparent that the effluent quality was not appropriate for reuse but needed polishing. The treatment level achieved at the WWTP was far from good likely because of the large organic load of the incoming wastewater (COD > 5000 mg/l) and the presence of inhibitory compounds such as polyphenols. For that reason, a new 18,000 m³/day WWTP is projected and under construction.

A commercial GAC from Chemviron Carbon (Belgium), namely Darco 12-20 mesh, was primarily used in this study. Prior to be used, the GAC samples were boiled in ultrapure water (Millipore Milli-Q system) for 1 h, washed repeatedly and then dried at 110 °C for 12 h to be, afterwards, stored in a desiccator at room temperature. Textural characterization of GAC samples was accomplished as reported previously [14]. Some main texture characteristics of this GAC are moderate surface area ($S_{BET} = 710 \text{ m}^2/\text{g}$) and micropore volume (0.16 cm³/g) but well-developed macro- and mesoporosity (macropore and mesopore volume = 0.51 g/cm³). From the chemical point of view this GAC presents a high concentration of surface oxygen groups (0.99 mequiv./g), 16.2% ash content and an almost neutral point of zero charge (PZC = 6.3). These properties made this GAC an *a priori* suitable material for adsorbing large organic molecules usually present in food-processing effluents. In addition to Darco 12-20 mesh, a GAC of basic character (Hydraffin P110 from

Lurgi; $S_{BET} = 950 \text{ m}^2/\text{g}$; micropore volume = 0.45 cm³/g; PZC = 9.1) was also used for the sake of comparison.

Most of the GAC promoted ozonation experiments were carried out in semi-batch mode as reported previously [14]. The length of each experiment was 2 h, unless otherwise specified. The reactor consisted of two separated compartments: a glass bubble-column (i.d. 5 cm; length = 20 cm) used as a gas–liquid contactor and a chamber (i.d. 2 cm) where the GAC was packed as a fixed bed. In a typical experiment, 250 ml of the food-processing secondary effluent were loaded onto the gas–liquid column and continuously recirculated through the GAC bed by means of a peristaltic pump (Masterflex, Cole-Parmer Instrument). At the same time a 25 NI/h flow rate of an oxygen–ozone stream was supplied to the gas–liquid contactor through a porous plate located at its bottom. A 301.7 model Sander ozone generator was used to produce an applied ozone dosage between 2 and 6 g/lh. The concentrations of ozone in the gases entering and leaving the bubble column were continuously monitored with Anseros Ozonat GM-6000 analyzers. During the course of the experiments, liquid samples were withdrawn from the gas–liquid column at intervals by means of a syringe and analyzed for aqueous ozone concentration [17], COD and TOC. In addition, other parameters such as suspended solids, BOD₅, polyphenols concentration (PC) and UV_{254nm} absorbance were analyzed in the effluent after experiment completion. Continuous experiments were carried out as described above but with a continuous 0.5 l/h flow rate of the food-processing secondary effluent provided by a peristaltic pump (Masterflex, Cole-Parmer Instrument). For comparative purposes, single ozonation experiments (without GAC) and single adsorption experiments (without ozone) were also conducted.

3. Results and discussion

3.1. Comparison between single ozonation, single adsorption onto GAC and GAC-promoted ozonation (O_3 /GAC) experiments

Fig. 1 shows temporal COD (left graph) and TOC (right graph) profiles during the course of single ozonation, single adsorption, sequential O_3 –GAC adsorption and O_3 /GAC experiments. It is clearly seen that not the sequential but the simultaneous use of ozone and GAC enhanced the degradation of the food-processing effluent. Thus, for example, the percentage of COD removed after 2 h of treatment was about 35% by single ozonation, 40% by single adsorption and only 25% by a sequential O_3 –GAC process comprising single ozonation for 20 min followed by single adsorption onto GAC for 100 min. The low COD and TOC removal efficiencies of this sequential process are likely due to the fact that partial ozonation of the effluent leads to the formation of polar by-products which are hardly adsorbable onto the GAC. A similar behavior was previously observed when using the GAC Darco 12-20 for the adsorption of a pre-ozonated solution of the pharmaceutical compound sulfamethoxazole [18]. In contrast, about 65% COD removal was achieved by the O_3 /GAC process.

The single ozonation experiment proceeded with relatively fast removal of COD and TOC during the first 20 min, henceforth COD and TOC removal rates were drastically slowed down. This suggests that ozone was able to quickly react with some organic compounds present in the food-processing effluent. In fact, polyphenols and other UV_{254nm} absorbing compounds, which are known to readily react with ozone, were almost fully removed from the effluent by single ozonation (removal >95%). However, some other effluent constituents and reaction by-products were quite refractory to ozone.

Regarding the single adsorption onto the GAC, the COD and TOC temporal profiles in Fig. 1 are very much alike to each other, show-

Table 1
Characterization parameters of the food-processing effluent used in this work before and after O₃/GAC treatment.

Parameter	Before treatment	After treatment ^a	Analytical method and/or equipment
pH	6.1 ± 0.5	6.3 ± 0.3 (6–9) ^b	pH-meter (Radiometer Copenhagen HPM82)
χ, mS/cm	1.4 ± 0.8	1.5 ± 0.7	Conductivity-meter (Hanna HI9033)
TSS, mg/l	321 ± 36	30 ± 10	Gravimetric method [15]
VSS, mg/l	220 ± 21	18 ± 8	Gravimetric method [15]
COD, mg/l	522 ± 55	97 ± 14 (<125)	Photometric method (Dr Lange cuvette tests) [15]
BOD ₅ , mg/l	150 ± 100	15 ± 10 (<25)	Respirometric method (Oxitop® WTW system)
TOC, mg/l	171 ± 12	39 ± 13	TOC analyzer (TOC-V _{CSH} Shimadzu)
TIC, mg/l	27 ± 6	57 ± 9	TOC analyzer (TOC-V _{CSH} Shimadzu)
PC, mg/l ^c	26 ± 5	2 ± 2	Folin-Ciocalteu method [16]
P-PO ₄ ³⁻ , mg/l	3.0 ± 0.2	2.0 ± 0.4 (0, 4–5)	Photometric method (Spectroquant test)
TN, mg/l	16.8 ± 1.1	9.7 ± 0.9 (<10)	Photometric method (Spectroquant test)
N-NH ₄ ⁺ , mg/l	14.0 ± 0.8	8.8 ± 0.7	Photometric method (Spectroquant test)
UV _{254nm} ^d	0.40 ± 0.03 ^e	0.05 ± 0.01 ^e	Spectrophotometer (ThermoSpectronic Helios α)

Nomenclature: χ = conductivity; TSS = total suspended solids; VSS = volatile suspended solids; COD = chemical oxygen demand; BOD₅ = biological oxygen demand; TOC = total organic carbon; TIC = total inorganic carbon; PC = polyphenols concentration; P-PO₄³⁻ = phosphate concentration expressed as phosphorous; TN = total nitrogen; N-NH₄⁺ = ammonium concentration, expressed as nitrogen; UV₂₅₄ = absorbance at 254 nm.

^a The treatment consisted of rapid sand filtration followed by O₃/GAC treatment at the conditions indicated in Fig. 1.

^b Values in brackets are those typically required for treated wastewater according to the BREF on the food, drink and milk industries (EU IPPC Directive).

^c Polyphenol concentration is expressed as equivalent gallic acid.

^d A quartz cell of 1 cm path length was used to measure UV absorbance.

^e The sample was diluted five times with ultrapure water before UV-analysis.

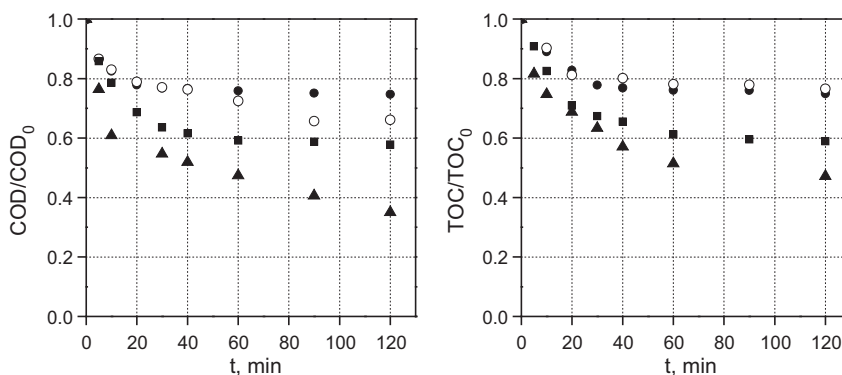


Fig. 1. Evolution of dimensionless residual COD and TOC with time during the course of single ozonation (○), single adsorption onto the GAC (■), sequential O₃ (20 min)–GAC adsorption (100 min) (●) and O₃/GAC (▲) experiments. Process conditions: *T* = 20 °C; pH = 6; recirculation flow rate = 2 l/h; GAC amount (if used) = 5 g; GAC particle size (if used) = 1.0–1.25 mm; ozone dosage (if applied) = 4 g/l h.

ing two different stages: a first period of about 1 h where COD and TOC were partially removed and a second stage at which steady-state COD and TOC values were achieved. Accordingly, the graphs in Fig. 1 suggest the presence of such a fraction of non-adsorbable organic compounds in the food-processing effluent. Much longer adsorption experiments than that shown in Fig. 1 were also carried out revealing that only small additional fractions (<8%) of COD and TOC were removed when extending the adsorption time from 2

24 h. The observed fast adsorption kinetics can be explained by the porous nature of the GAC with a high content of large pores which would ease the diffusion of adsorbates towards the adsorption centers. In order to assess the sorption capacity of the GAC used in this work at different experimental conditions, a series of single adsorption experiments were carried out varying the amount of GAC and the effluent pH. Fig. 2 shows the COD temporal profiles during the course of these experiments. It can be seen that, at any of the con-

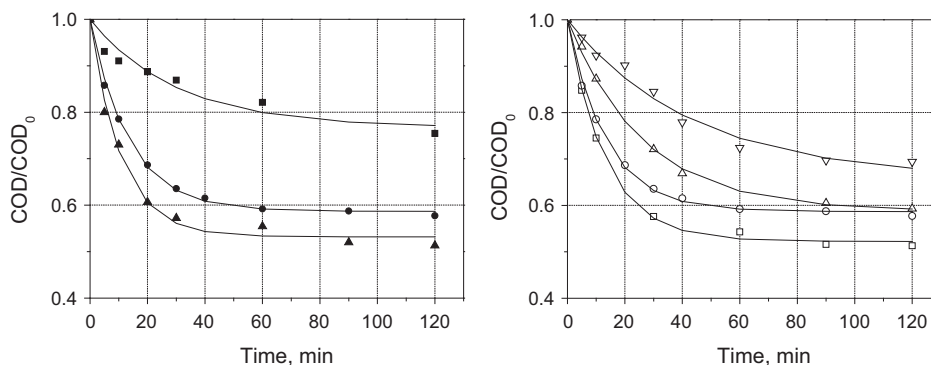


Fig. 2. Evolution of dimensionless residual COD with time during the course of experiments of adsorption onto the GAC. Effects of the amount of GAC (■) 2 g; (●) 5 g; (▲) 20 g and pH (□) 4; (○) 6; (△) 7; (▽) 9. Process conditions (unless otherwise specified): *T* = 20 °C; pH = 6; recirculation flow rate = 2 l/h; GAC amount = 5 g; GAC particle size = 1.0–1.25 mm.

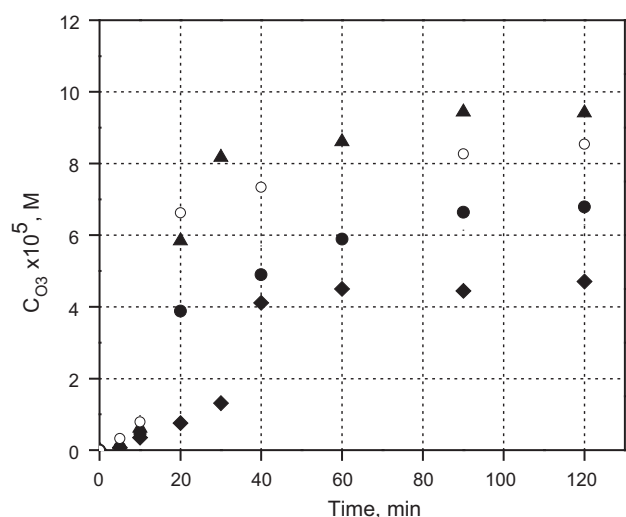


Fig. 3. Evolution of the dissolved ozone concentration with time during the course of a single ozonation experiment ((○) pH 6) and various O_3 /GAC experiments at different pHs ((▲) pH 4; (●) pH 6; (◆) pH 9). Process conditions: $T = 20^\circ C$; recirculation flow rate = 2 l/h; GAC amount (if used) = 5 g; GAC particle size (if used) = 1.0–1.25 mm; ozone dosage = 4 g/l h.

ditions applied, the GAC showed limited capacity to remove COD from the effluent, with residual COD above 50% (i.e., >250 mg/l) after 2 h. The kinetic behavior of COD sorption onto the GAC was modeled using the pseudo-first order approach given by Eq. (1):

$$\frac{dq_t}{dt} = k(q_e - q_t) \quad (1)$$

where q_e and q_t are the adsorption capacities of the GAC at equilibrium and at a time t , respectively, and k stands for the pseudo-first order rate constant. Table 2 summarizes the kinetic parameters obtained from a non-linear regression analysis of data in Fig. 2. It can be seen that the equilibrium adsorption capacity drastically decreased with the amount of GAC, which means that the GAC could not be efficiently used to remove organic compounds from the secondary effluent by adsorption to a great extent. On the other hand, increasing pH did not favour the adsorption of organic compounds of the food-processing effluent onto the GAC, as both the adsorption capacity and the pseudo-first order rate constant decreased with pH.

From Fig. 1 it can also be seen that the rates of COD and TOC degradation in the O_3 /GAC experiment were, at any reaction time, greater than those for the single ozonation and the single adsorption experiments. During the first minutes of the O_3 /GAC experiment, ozone reacted in a fast kinetic-regime with the ozone-reacting substances present in the food-processing effluent as no dissolved ozone was found in solution (see Fig. 3). At the same time, the readily adsorbable compounds reached the surface of the GAC and become adsorbed. As can be seen in Fig. 3, after the first 10–20 min of reaction, ozone started to accumulate in solution, being able to reach the surface of the GAC where it could be chemisorbed and decompose through a series of complex reactions to yield secondary oxidants, including surface free radicals and hydrogen peroxide [19]. In addition, it has been postulated that aqueous hydroxyl radicals are eventually generated as well, either through direct ozone–GAC reactions or through the indirect O_3 – H_2O_2 reaction [19–21]. To assess whether or not aqueous hydroxyl radicals were generated in the case-study, an O_3 /GAC experiment was carried out in the presence of 1 mM tert-butanol, which is frequently used in research studies to scavenge aqueous hydroxyl radicals formed from ozone decomposition. It was found that the rate of TOC degradation was lowered

down to a noticeable extent when tert-butanol was added to the effluent. Thus, TOC conversion after 2 h of the O_3 /GAC treatment decreased from 53% (in the absence of tert-butanol) to 39%, which confirmed the presence of aqueous hydroxyl radicals. These highly oxidizing species would react in a non-selective manner with organic compounds, thus improving COD and TOC degradations. The fact that ozone decomposed over the GAC can also be inferred from Fig. 3, where it can be seen that, in the experiments carried out at pH 6, the concentration of dissolved ozone was lower in the O_3 /GAC experiment than in the single ozonation experiment.

Table 1 shows a complete characterization of the food-processing effluent before and after a treatment comprising rapid sand filtration and O_3 /GAC treatment. As can be seen not only COD and TOC but also other quality parameters such as BOD, polyphenols, suspended solids, UV-absorbance and nutrients were reduced to some extent. In brackets in the third column of Table 1 are also typical quality parameters of food-processing wastewater after treatment according to the Best Practice Reference Document (BREF) on the food, drink and milk industries produced in response to the EU Directive on Integrated Pollution Prevention and Control (IPPC Directive). It can be seen that the treatment performance was high enough to obtain an effluent complying with the required discharge limits. Another important aspect of ozonation technologies is the amount of ozone consumed to achieve the required treatment objective as it is the most important factor in determining the treatment cost. Thus, in an ozonation process aimed to mineralize organic compounds, the ozone consumption can be defined as the average amount of ozone consumed per unit mass of TOC removed in the whole reaction time (i.e., $t_f = 2$ h). It can be calculated by means of Eq. (2):

$$\eta_{O_3} = \frac{F_g \int_0^{t_f} (C_{O_3,i} - C_{O_3,o}) dt}{V(\text{TOC}_0 - \text{TOC}_{t_f})} \quad (2)$$

where F_g is the gas flow rate; $C_{O_3,i}$ and $C_{O_3,o}$ are the concentrations of ozone at the reactor inlet and outlet gas streams, respectively; and V stands for the volume of food-processing effluent. By applying Eq. (2) to data of single ozonation and O_3 /GAC experiments it was found that η_{O_3} decreased from 18.8 to 8.2, which means that the O_3 /GAC process made a much more efficient use of ozone than the single ozonation process.

3.2. The O_3 /GAC process: influence of variables

A few series of O_3 /GAC experiments were carried out under different process conditions to study the effect of some variables such as pH, the ozone dose applied, the amount of GAC, the concentration of polyphenols in the food-processing effluent, the recirculation flow rate and the GAC particle size. Table 3 provides a summary list of the variables studied and the results obtained in terms of average degradation of COD, TOC, PC and BOD_5 and ozone consumption.

3.2.1. Effect of pH

The effect of pH on the O_3 /GAC process performance was studied in the range 4–9. Despite the fact that pH is usually a key variable in wastewater ozonation processes [22], in our O_3 /GAC experiments this variable did not exert noticeable influence on the degradation level of the food-processing effluent, though minor improvements in COD and TOC conversions were noticed at pH 9, as can be seen in Table 2. At this point it should be kept in mind that the removal of organic matter from the food-processing secondary effluent by the O_3 /GAC process was due to the contribution of three processes: (i) direct ozonation in the gas–liquid column; (ii) adsorption onto the GAC; and (iii) free-radical oxidation promoted by GAC. The overall effect of pH on the process performance must consider the indi-

Table 2
Pseudo-first order kinetic parameters for the COD adsorption of the food-processing secondary effluent onto the GAC.

GAC amount (g)	pH	q_e (mg/g)	$k \times 10^2$ (min ⁻¹)	R^2
2		15.2 ± 1.6	3.31 ± 0.86	0.927
5	6	10.8 ± 0.1	7.35 ± 0.28	0.998
20		3.0 ± 0.1	9.27 ± 0.76	0.990
5	4	12.5 ± 0.1	7.52 ± 0.33	0.998
	7	10.8 ± 0.2	3.77 ± 0.17	0.998
	9	8.9 ± 0.6	2.29 ± 0.32	0.982

Process conditions (unless otherwise specified): COD₀ = 522 mg/l; TOC₀ = 171 mg/l; PC₀ = 25 mg/l; T = 20 °C; pH = 6; R = 2 l/h; w = 5 g; D_p = 1–1.25 mm.

vidual effects over each of these contributions. On one hand, high pH would accelerate single ozonation in the gas–liquid column as ozone reacts with the hydroxide ion to decompose into hydroxyl radicals [23]. On the other hand, as shown in Fig. 2, high pH did not favour the adsorption of organic compounds of the food-processing effluent onto the GAC used in this work. Finally, the effect of pH on the transformation of ozone into secondary oxidants over the GAC surface is controversial, with the literature reporting on different mechanisms depending on the aqueous pH and the surface acidity/basicity of the GAC [19]. As can be seen in Fig. 3, in our experiments the concentration of dissolved ozone at the entrance of the GAC bed decreased with the pH. Therefore, at low pH there was more dissolved ozone available to be transformed into secondary oxidants than at high pH. Accordingly, in the case studied, it is most likely that low pH also favoured the degradation of organic compounds on the GAC bed. Regarding the amount of ozone consumed, a little less amount of ozone was consumed (per unit of TOC removed) at pH 4 and 6 than at pH 7 and 9 (see Table 3). This is likely due to the fact that at low pH the contribution of single adsorption to TOC removal is favoured.

3.2.2. Effect of the ozone dose

The effect of the ozone dose applied was investigated by varying the ozone concentration in the inlet gas so that the ozone dose was in the range 4–12 g O₃ per litre of food-processing effluent treated. As it is apparent from Table 3, the increasing ozone dose led to higher COD and TOC removals, with minor effect on PC and BOD₅ removals. On the other hand, the increase in the ozone dose led to a less-efficient use of ozone as the ozone consumption rose with the ozone dose. Therefore, very high ozone doses cannot be recommended from a practical point of view.

Table 3
Summary results of average process performance of the O₃/GAC treatment of the food-processing effluent for 2 h.

Variable	COD removal (%)	TOC removal (%)	PC removal (%)	BOD ₅ removal (%)	η_{O_3} (g O ₃ /g TOC)
pH = 4	62	64	93	62	8.6
pH = 6	64	53	94	76	8.2
pH = 7	56	61	98	67	10.0
pH = 9	69	73	97	57	10.1
O ₃ dose = 4 g/l	50	55	95	76	7.5
O ₃ dose = 8 g/l	64	53	94	76	8.2
O ₃ dose = 12 g/l	72	70	97	80	10.7
w = 2 g	50	34	93	71	9.6
w = 5 g	64	53	94	76	8.2
w = 20 g	82	77	94	76	8.6
PC ₀ = 25 mg/l	72	70	97	80	8.2
PC ₀ = 40 mg/l	64	52	94	76	9.7
PC ₀ = 60 mg/l	65	60	98	76	10.0
R = 1 l/h	62	50	95	NM	8.5
R = 2 l/h	64	53	94	76	8.2
R = 5 l/h	72	64	94	NM	9.6
D _p = 0.8–1.0 mm	69	70	91	NM	8.7
D _p = 1.0–1.25 mm	64	53	94	76	8.2
D _p = 1.6–2.0 mm	58	56	94	NM	9.1

Nomenclature: PC₀ = polyphenol concentration; R = recirculation liquid flow rate; w = amount of GAC; D_p = GAC particle size; NM = not measured.

Process conditions (unless otherwise specified): COD₀ = 522 mg/l; TOC₀ = 171 mg/l; PC₀ = 25 mg/l; T = 20 °C; applied O₃ dose = 8 g/l; pH = 6; R = 2 l/h; w = 5 g; D_p = 1–1.25 mm.

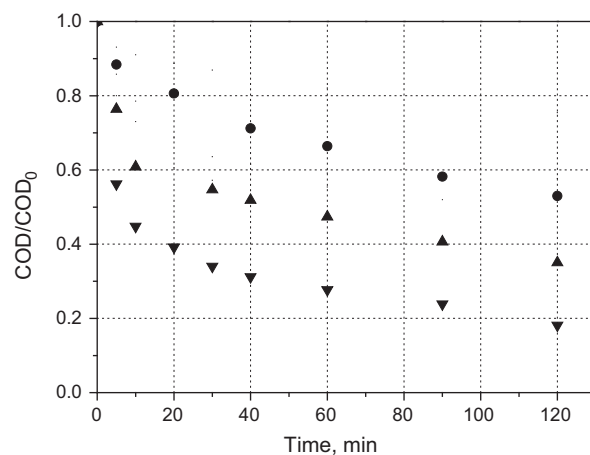


Fig. 4. Evolution of dimensionless residual COD with time during the course of O₃/GAC experiments. Effect of the amount of GAC ((●) 2 g; (▲) 5 g; (▼) 20 g). Process conditions: T = 20 °C; pH = 6; recirculation flow rate = 2 l/h; GAC particle size = 1.0–1.25 mm; ozone dosage = 4 g/l h.

3.2.3. Effect of the amount of GAC

In order to study the effect of the amount of activated carbon, a series of O₃/GAC experiments were carried out using different amounts of GAC in the bed from 2 to 20 g. As can be seen in Table 3 this variable exerted a strong influence on the removal of COD and TOC achieved within the process. Obviously, at least part of this improvement must be due to the increase of the organic matter uptake by GAC (i.e., adsorption) when rising the GAC amount. In addition, a higher GAC amount is also expected to lead to faster ozone decomposition over the GAC surface. Fig. 4 shows the influ-

ence of the GAC amount on the kinetics of COD removal by the O_3 /GAC process. If compared with Fig. 2, it can be concluded that the GAC amount played an important role in the oxidation of organic matter. Thus, in Fig. 2 it can be seen that increasing the GAC amount from 2 g to 5 g resulted in a significant improvement of the COD uptake by GAC but this did not further increase noticeably when increasing the GAC amount up to 20 g. In the O_3 /GAC process, however, the GAC amount exerted a strong positive influence on the COD removal over the whole range studied, as shown in Fig. 4.

3.2.4. Effect of the concentration of polyphenols in the effluent

The removal of polyphenols from food-processing effluents is an important issue as, in general, they show low biodegradation level while ozone has a great potential for removing them from wastewater [6,7,13]. In this work, the influence of polyphenols concentration was studied by carrying out various experiments in which the effluent was enriched with gallic acid. No appreciable effect of this variable, in the range here studied, was observed as deduced from results depicted in Table 3. Thus, COD, PC and BOD removals after 2 h of treatment were almost the same for all the experiments with different initial PCs. Minor variations in the TOC removal were also noticed.

3.2.5. Effects of the GAC particle size and the recirculation liquid flow rate

As described above, the O_3 /GAC process, as applied in this work, comprised two heterogeneous processes: a gas–liquid process in the bubble column and a liquid–solid adsorption–reaction process on the GAC bed. In order to assess whether mass-transfer effects controlled the process kinetics, two series of experiments were carried out at different GAC particle size and recirculation liquid flow rate. As can be seen in Table 3, the decreasing particle size led to higher organic matter removal rates, which suggests that the solid–liquid process was controlled by mass transfer. Also, the concentration of dissolved ozone was the lowest when using GAC particles in the 0.8–1.0 mm size range, also indicating that the diffusion of ozone through the GAC pore network towards the active sites was favoured, that is, internal diffusion resistance developed for ozone transport. The recirculation liquid flow rate also affected the degradation rate. Thus, as shown in Table 3, the increasing liquid flow rate led to higher COD and TOC removals, which is a consequence of the heterogeneous-nature and hydrodynamics of the process: a higher liquid flow rate decreased the external diffusion resistances and allowed a larger amount of ozone to reach the GAC bed, thus enhancing the solid–liquid reaction. Neither the GAC particle size nor the recirculation liquid flow rate had significant impact on the ozone consumption as can be seen in Table 3.

3.3. Kinetic approach

As can be appreciated in Figs. 1 and 4 the O_3 /GAC process comprised two kinetic stages following apparent first-order kinetics: an initial stage of rapid disappearance of COD and TOC followed by a slower kinetic stage. Accordingly, Eq. (3) was proposed for COD depletion:

$$-r_{\text{COD}} = k_{\text{COD}_1} \text{COD}_1 + k_{\text{COD}_2} \text{COD}_2 \quad (3)$$

Fig. 5 shows the pseudo-first order kinetics plots where it can be seen that experimental data fitted well the proposed kinetic model. Table 4 shows the values of the apparent rate constants computed for various pHs. The values of k_{COD_1} were noticeably higher than those calculated from data of single ozonation experiments ($k_{\text{COD}_1} = 4.0 \times 10^{-4} \text{ s}^{-1}$ at pH = 6), suggesting a strong contribution of adsorption onto GAC to the overall COD removal in the first stage of the O_3 /GAC process. The lower value computed for k_{COD_1} at pH 9 than at pH 4 or 6 can be explained by the negative effect of pH on

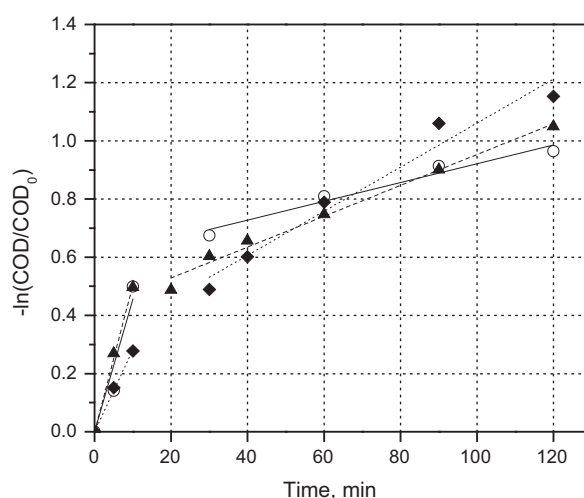


Fig. 5. Determination of the apparent pseudo-first order rate constants for the ozonation of the food-processing secondary effluent in the presence of the GAC at different pHs ((○) pH 4; (▲) pH 6; (◆) pH 9). Process conditions: $T = 20^\circ\text{C}$; recirculation flow rate = 2 l/h; GAC amount = 5 g; GAC particle size = 1.0–1.25 mm; ozone dosage = 4 g/l/h.

COD adsorption onto the GAC used in this work. Regarding the second stage, k_{COD_2} for the O_3 /GAC process was great by comparison with that for the single ozonation process ($k_{\text{COD}_2} = 3.3 \times 10^{-5} \text{ s}^{-1}$ at pH = 6), specially at high pH, at which the decomposition of ozone over the GAC was favoured.

3.4. Activated carbon reusability

In order to assess the reusability of the GAC, a series of experiments was conducted using several times the same sample of GAC in various repetitive O_3 /GAC experiments. The experiments were conducted with two GAC of different PZC: Darco 12-20 mesh (PZC = 6.7) and Hydriffin P110 (PZC = 9.1). Fig. 6 shows the TOC conversions achieved in four consecutive 1-h semi-batch experiments. No loss of activity was observed for Darco 12-10 mesh, as TOC conversion was almost identical for all the experiments with this GAC. Contrary, TOC conversion decreased from 56.7% (first run) up to 47.6% (fourth run) when using Hydriffin P110. The literature reports that the GAC acts as a promoter of ozone decomposition rather than a catalyst itself [19]. Thus, the GAC surface can be modified as a result of the reaction, thus decreasing its ability to

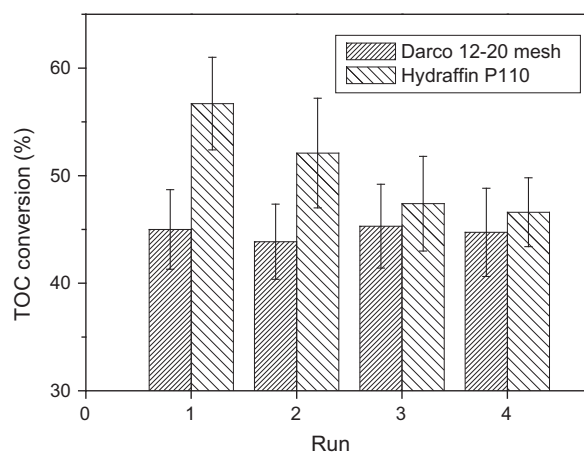


Fig. 6. TOC conversion achieved in repetitive O_3 /GAC experiments reusing the GAC process conditions: $T = 20^\circ\text{C}$; pH = 6; recirculation flow rate = 2 l/h; GAC amount = 5 g; GAC particle size = 1.0–1.25 mm; ozone dosage = 4 g/l/h.

Table 4

Apparent pseudo-first order rate constants for the ozonation of the food-processing secondary effluent in the presence of the GAC.

pH 4		pH 6		pH 9	
$k_{\text{COD}_1} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{COD}_2} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{COD}_1} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{COD}_2} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{COD}_1} \times 10^4 \text{ (s}^{-1}\text{)}$	$k_{\text{COD}_2} \times 10^4 \text{ (s}^{-1}\text{)}$
7.5 ± 0.5	0.5 ± 0.1	8.0 ± 0.2	0.8 ± 0.1	5.0 ± 0.1	1.3 ± 0.6

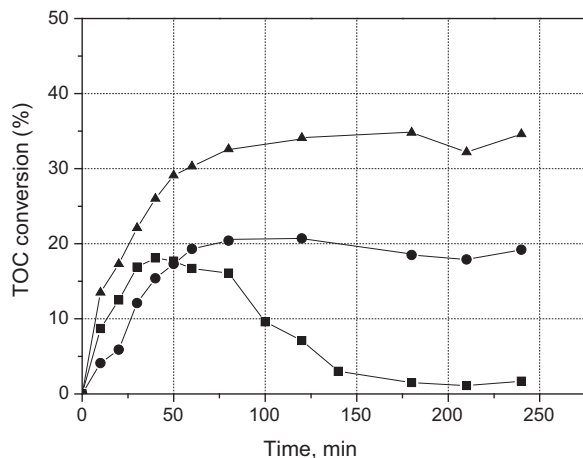
Process conditions (unless otherwise specified): $\text{COD}_0 = 522 \text{ mg/l}$; $\text{TOC}_0 = 171 \text{ mg/l}$; $\text{PC}_0 = 25 \text{ mg/l}$; $T = 20^\circ\text{C}$; O_3 dosage = 2 g/l h ; $\text{pH} = 6$; $R = 2 \text{ l/h}$; $w = 5 \text{ g}$; $D_p = 1\text{--}1.25 \text{ mm}$.

Fig. 7. TOC conversion achieved in continuous single ozonation (●), single adsorption (■) and O_3/GAC experiments (▲). Process conditions: $T = 20^\circ\text{C}$; $\text{pH} = 6$; recirculation flow rate = 21 l/h ; GAC amount (if used) = 5 g ; GAC particle size (if used) = $1.0\text{--}1.25 \text{ mm}$; ozone mass flow rate (if applied) = 1 g/h ; wastewater residence time = 30 min .

decompose ozone. Results in Fig. 6 demonstrate that the basic GAC Hydrarffin P110 is more prone to deactivation than the slightly acidic Darco 12-20 mesh.

3.5. Continuous experiments

Finally, continuous-mode single ozonation, single adsorption and O_3/GAC experiments were conducted for 4 h with a wastewater residence time of 30 min. Fig. 7 compares the TOC conversion throughout these experiments. It can be seen that steady-state TOC conversions were achieved in single ozonation (about 20%) and O_3/GAC (about 35%) experiments, while in the adsorption experiment TOC conversion reached a maximum value (about 18%) from which it decreased dramatically up to almost zero as a result of GAC saturation. In the O_3/GAC experiment the GAC saturation was prevented because of the oxidation of adsorbed products by surface free radicals generated from the decomposition of ozone over the GAC.

4. Conclusions

This work shows that the O_3/GAC process is a promising advanced oxidation method for the treatment of secondary food-processing effluents in order to reduce their organic load to a minimum, making them suitable for reuse. The method combines the benefits of ozone, a strong oxidizing chemical, and the adsorption capacity of activated carbon. In addition, ozone decomposes over the GAC surface to yield free radical species like the hydroxyl radical, which are able to quickly mineralize organic compounds present in the effluent. The advantages of the O_3/GAC over direct ozonation are both higher organic matter degradation and lower ozone consumption. This work verified the positive effects of the ozone dose and the GAC amount on the COD and TOC degradation levels while pH and the initial concentration of polyphenols in the food-processing effluent did not exert noticeable influences.

From a kinetic point of view the process was mass-transfer controlled as the GAC particle size and liquid flow rate had negative and positive effects, respectively, on the degradation level. COD degradation followed apparent first-order kinetics with two stages: the first stage of rapid COD removal mainly due to direct ozonation and adsorption of organic compounds onto the GAC and a second stage, somewhat slower, where COD removal was due to a free-radical mechanism triggered by the decomposition of ozone over the GAC. Through a series of repetitive experiments, no apparent deactivation of a neutral GAC ($\text{PZC} = 6.7$) but a basic GAC ($\text{PZC} = 9.1$). The stability of the neutral GAC was also observed in continuous experiments.

The results of this research call attention to the O_3/GAC treatment as a feasible technology to be considered for full-scale operations, taking into consideration the following aspects: (1) the continual raising of quality standards for treated wastewater, which will make necessary the adoption of advanced treatment in a near future; (2) the ease of implementation of the O_3/GAC technology because of the more widespread use of ozone and GAC in water and wastewater treatment; (3) the lower ozone dosage required to achieve the treatment objective would make the process economically advantageous over ozonation and other AOPs; and (4) the low GAC deactivation and its in situ regeneration through ozone oxidative treatment would extend its lifetime compared with conventional GAC filters.

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