



Post-treatment of real municipal wastewater effluents by means of granular activated carbon (GAC) based catalytic processes: A focus on abatement of pharmaceutically active compounds

Juan José Rueda-Márquez^{a,b,c,d,*}, Javier Moreno-Andrés^d, Ana Rey^e, Carmen Corada-Fernández^f, Anna Mikola^c, Manuel A. Manzano^d, Irina Levchuk^b

^a Department of Separation Science, School of Engineering Science, Lappeenranta-Lahti University of Technology, Sammonkatu 12, 50130 Mikkeli, Finland

^b Fine Particle and Aerosol Technology Laboratory, Department of Environmental and Biological Sciences, University of Eastern Finland, P.O. Box 1627, FI-70211 Kuopio, Finland

^c Water and Wastewater Engineering Research Group, School of Engineering, Aalto University, PO Box 15200, FI-00076 Aalto, Finland

^d Department of Environmental Technologies, Faculty of Marine and Environmental Sciences. INMAR-Marine Research Institute, CEIMAR- International Campus of Excellence of the Sea. University of Cadiz, Spain

^e Departamento de Ingeniería Química y Química Física, Instituto del Agua, Cambio Climático y Sostenibilidad (IACY), Universidad de Extremadura, Av.

Elvas s/n 06006 Badajoz, Spain

^f Instituto Universitario de Investigación Marina (INMAR), Laboratorio de Servicios Periféricos (Cromatografía-Espectrometría de Masas), University of Cadiz, Spain

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ABSTRACT

Pharmaceutically active compounds (PhACs) widely present in urban wastewater effluents pose a threat to ecosystems in the receiving aquatic environment. In this work, efficiency of granular activated carbon (GAC) - based catalytic processes, namely catalytic wet peroxide oxidation (CWPO), peroxydisulfate oxidation (PMS/GAC) and peroxydisulfate oxidation (PDS/GAC) at ambient temperature and pressure were studied for removal of 22 PhACs (ng L⁻¹ level) that were present in secondary effluents of real urban wastewater. Concentrations of PhACs were measured using Ultra Performance Liquid Chromatography – Triple Quadrupole Mass Spectrometry (UPLC-QqQ-MS/MS). Catalytic experiments were conducted in discontinuous mode using up-flow fixed bed reactors with granular activated carbon (GAC) as a catalyst. The catalyst was characterized by means of N₂ adsorption-desorption isotherm, mercury intrusion porosimetry (MIP), elemental analysis, X-ray fluorescence spectroscopy (WDXRF), X-ray diffraction (XRD), thermal gravimetry and differential temperature analyses coupled mass spectrometry (TGA-DTA-MS). Results indicate that the highest efficiency in terms of TOC removal was achieved during CWPO performed at optimal operational conditions (stoichiometric dose of H₂O₂; TOC removal ~ 82%) followed by PMS/GAC (initial PMS concentration 100 mg L⁻¹; TOC removal ~73.7%) and PDS/GAC (initial PDS concentration 100 mg L⁻¹; TOC removal ~ 67.9%) after 5 min of contact time. Full consumption of oxidants was observed in all cases for CWPO and PDS/GAC at contact times of 2.5 min, while for PMS/GAC it was 1.5 min. In general, for 18 out of 22 target PhACs, very high removal efficiencies (> 92%) were achieved in all tested processes (including adsorption) performed at optimal operational conditions during 5 min of contact time. However, moderate (40 – 70%) and poor (< 40%) removal efficiencies were achieved for salicylic acid, ofloxacin, norfloxacin and ciprofloxacin, which can be possibly attributed to insufficient contact time. Despite high efficiency of all studied processes for PhACs elimination from urban wastewater effluent, CWPO seems to be more promising for continuous operation.

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1. Introduction

Presence of pharmaceutically active compounds (PhACs) in urban wastewater effluents is attracting significant attention recently,

* Corresponding author.

E-mail addresses: Juan.Rueda.Marquez@lut.fi (J.J. Rueda-Márquez), irina.levchuk@uef.fi (I. Levchuk).

which can be explained by the ability of these pollutants (even at very low levels) to cause biological effects (Suárez et al., 2008). It can be expected that constant discharge of pharmaceutical compounds to the aquatic environment could pose a threat to the aquatic ecosystems (François et al., 2015; Quinn, Gagné and Blaise, 2009; Quinn et al., 2011). A list of these substances was recently included in the Watch List by EU Water Framework Directive (EU Decision 2018/840).

Municipal wastewater treatment plants (WWTP) are the main barrier preventing the release of pollutants into the receiving water bodies. During the secondary wastewater treatment step (biological) some PhACs can be eliminated. The tertiary treatment step at conventional urban wastewater treatment plants usually aims at elimination of pathogens, turbidity and nutrients. Hence, filtration, chlorination as well as UVC disinfection are often used as a tertiary treatment step. However, commonly applied tertiary treatment processes do not lead to efficient elimination of recalcitrant organic contaminants. As a result, emerging contaminants are often released to the aquatic environment with urban wastewater effluents (Gracia-Lor et al., 2012; Luo et al., 2014). Tertiary treatment of urban wastewater aiming at elimination of contaminants of emerging concern (CECs), pathogens, etc. is of high interest especially in view of recent EU regulation 2020/741 for wastewater reuse.

Advanced Oxidation Processes (AOPs) can be considered as an alternative option for post-treatment of urban wastewater effluents (Rueda-Marquez et al., 2020; Sichel, Garcia and Andre, 2011; Rizzo, Agovino et al., 2019; Huang et al., 2020; Michael-Kordatou, Karaolia and Fatta-Kassinos, 2018; Rizzo et al., 2019). Currently, AOPs are extensively studied by many researchers mainly due to non-selective behaviour and potential for pollutant oxidation as well as lack of solid waste formation during majority of AOPs. Among the different AOPs, catalytic wet peroxide oxidation (CWPO) and persulfate oxidation processes are of significant promise. Main advantages of CWPO include absence of sludge generation and possibility to work in a wide pH range (Wang et al., 2016). Mainly iron-based catalysts are used for CWPO (Munoz et al., 2017), while carbon-based catalysts are not so widely studied. Similarly, carbon-based materials for the activation of different persulfate salts have been mainly addressed using dyes or phenol as model pollutants (Wang and Wang, 2018). Accordingly, the persulfate activation efficiency by carbonaceous-based materials, especially metal-free, is worth further research (Zhao et al., 2017). Thus, the application of activated carbon as a catalyst for CWPO and persulfates at ambient temperature and pressure is emerging as a technique of significant promise. Recent studies have demonstrated formation of hydroxyl radicals during decomposition of H_2O_2 by carbon materials (Santos et al., 2009; Rueda-Márquez et al., 2015a; Rueda-Márquez et al., 2015b).

To the best of our knowledge, there is only one study (Munoz et al., 2017) devoted to post-treatment of real urban wastewater effluents by CWPO (iron-based catalyst) aiming at removal of pharmaceutical compounds at environmentally relevant concentrations. Thus, there is an important knowledge gap in application of carbon-based catalysts for the elimination of emerging pharmaceutical compounds from real urban wastewater effluents by CWPO and persulfate oxidation at ambient temperature and pressure (Rueda-Márquez, Levchuk and Sillanpää, 2018). This study aims at taking a step forward towards existing research gap. In this work we have studied granular activated carbon (GAC) as a catalyst for CWPO and persulfate oxidation performed in up-flow fixed bed reactors for treatment of real urban wastewater effluents. The effect of initial concentration of oxidizing agents (H_2O_2 for CWPO; peroxymonosulfate (PMS) and peroxydisulfate (PDS) for persulfate oxidation) was studied in order to identify optimal reaction conditions leading to highest TOC conversion. When optimal conditions were established, removal of 22 PhACs present in

real urban wastewater effluents (not spiked) by CWPO, PDS/GAC and PMS/GAC was studied. Moreover, catalyst stability was investigated. As far as we are aware, this is the first work focused on treatment of real urban wastewater effluents (decrease of TOC and elimination of 22 PhACs) by CWPO and persulfate oxidation using carbon-based catalyst.

2. Materials and methods

2.1. Chemicals

Sodium Peroxydisulfate (PDS, reagent grade, $\geq 98\%$), monoperoxysulfate compound OXONE® (PMS), sodium bicarbonate (ACS reagent, $\geq 99.7\%$), and potassium iodide (ACS reagent, $\geq 99\%$) were purchased from Sigma-Aldrich. Hydrogen peroxide (30%), methanol (ACS, ISO, Reag. Ph Eur) and titanium (IV) oxysulfate were received from Merck. Analytical standards of monitored PhACs were obtained from suppliers listed elsewhere by Baena-Nogueras et al. (2016). Orange (II) was received from ACROS Organics®. The solid phase extraction cartridges Oasis HLB 200 mg were purchased from Waters Chromatography Europe BV. A granular activated carbon (GAC) from coconut shell (PQ-0602-02) purchased from Hidrowater was used as catalyst.

2.2. Sampling and characterization of municipal wastewater effluent

Municipal wastewater effluent from the largest Wastewater Treatment Plant (WWTP) in Finland, namely, Viikinmäki (Helsinki, Finland) was used for experiments. This WWTP processes industrial (approx. 15%) and domestic (approx. 85%) wastewater of over 800 000 inhabitants from capital area with average flow 280 000 m^3/day . The Viikinmäki WWTP is conducting conventional wastewater treatment based on the activated sludge process. The wastewater is processed in nine activated sludge process lines which also include biological denitrification. Besides mechanical, biological and chemical treatment, a biological filter has been added in order to improve nitrogen removal. The process unit operations include intake, screening, grit and grease removal, preliminary settling and activated sludge treatment with nitrification/denitrification steps. More details regarding wastewater treatment process can be found elsewhere (Helsinki Region Environmental Services Authority HSY, 2018). Prior to experiments, composite 48 h samples (during weekend, winter) of wastewater influent and effluent from WWTPs were collected in order to perform complete analysis of typical PhACs (in total 83 compounds were analyzed; list of analyzed compounds is in Table 1 SM). It should be noticed that during the weekend when composite sample was collected, it was raining heavily. Wastewater samples were collected into specifically cleaned amber glass and bottles and Solid Phase Extraction (SPE) was performed as soon as samples were received. This wastewater effluent was used for optimization of operational conditions of CWPO, PMS/GAC, and PDS/GAC processes. When the optimal conditions were selected, experiments at optimal conditions with CWPO, PMS/GAC, PDS/GAC and GAC (as a reference test) were repeated using wastewater effluent collected in summer, which was used for the experiments in the same day. Concentration of 22 PhACs (Table 2 SM) was measured using Ultra Performance Liquid Chromatography – Triple Quadrupole Mass Spectrometry (UPLC-QqQ-MS/MS) before and after all experiments performed at optimal conditions. Wastewater effluent before and after treatment by CWPO, PMS/GAC, PDS/GAC and GAC was collected inside amber glass bottles, which were specially cleaned. The physicochemical characterization of wastewater effluent was conducted using standard methods (APHA 2008). The Total Organic Carbon (TOC) analysis was conducted using Shimadzu TOC-L analyzer in non-purgeable organic carbon (NPOC) mode.

Table 1
Results of UPLC-QqQ-MS/MS analysis of pharmaceutically active compounds (PhACs) in influent and effluent of studied WWTP.

Compound	Concentration influent, ng L ⁻¹	effluent, ng L ⁻¹	Reduction, %*	LOD**, ng L ⁻¹	LOQ***, ng L ⁻¹
Lincosamides					
Chloramphenicol	20.8 ± 4.0	14.4 ± 0.4	30.9	<0.1	<0.1
Lincomycin	9.8 ± 0.4	0.4 ± 0.3	96.8	<0.1	<0.1
Anti-inflammatory					
Acetaminophen	69072.9 ± 2161	<LOD	100	0.5	1.8
Salicylic Acid	1183.1 ± 191.8	33.7 ± 1.6	97.2	1.3	4.4
Phenylbutazone	131.2 ± 130.5	<LOD	100	0.8	2.8
Fenoprofen	197.1 ± 30.9	98.4 ± 9.7	50.1	0.1	0.5
Ibuprofen	35827.7 ± 754.5	361 ± 8.8	99	1	3.5
Indomethacin	20 ± 1.2	18.7 ± 1.7	6.5	0.6	2.1
Naproxen	3972.5 ± 579.8	764.2 ± 46.5	80.8	0.3	0.9
Mefenamic acid	75 ± 5.2	60.4 ± 5.3	19.4	<0.1	<0.1
Diclofenac	1499.2 ± 13.4	1362.1 ± 31.3	9.1	0.1	0.2
Ketoprofen	117.3 ± 13	93.8 ± 1.5	20	0.1	0.3
Phenazone	1.9 ± 0.3	3.6 ± 0.1	negative	0.1	0.2
Lipid Regulators					
Bezafibrate	93.7 ± 0.9	51.4 ± 1.8	45.1	<0.1	<0.1
Clofibric acid	4.8 ± 4.7	1.3 ± 1.2	74.2	0.1	0.2
Gemfibrozil	58.6 ± 21	92.2 ± 14.7	negative	<0.1	<0.1
Pravastatin	88 ± 4.9	20.3 ± 6.2	100	<0.1	0.1
Diuretics					
Furosemide	2564 ± 58.7	1810.7 ± 23.8	29.4	<0.1	<0.1
Hydrochlorothiazide	625.9 ± 8.3	518.5 ± 18.5	17.2	<0.1	<0.1
Other antibiotics and surfactants					
Triclocarban (TCC)	14.9 ± 1	<LOD	100	<0.1	0.1
Triclosan (TCS)	344.1 ± 12.2	357.9 ± 33.1	negative	<0.1	0.1
Monensin	<LOD	13.3 ± 1	negative	<0.1	<0.1
Macrolides					
Roxithromycin	13.4 ± 0.1	5.2 ± 2.9	61.1	<0.1	<0.1
Azithromycin	1499.1 ± 68.2	946.1 ± 62.9	36.9	<0.1	<0.1
Clarithromycin	238.5 ± 12.8	160.8 ± 9.8	32.6	<0.1	<0.1
Sulfonamides					
Sulfathiazole	0.4 ± 0.04	0.5 ± 0.02	negative	<0.1	<0.1
Sulfadiazine	14.1 ± 0.1	24.9 ± 0.6	negative	<0.1	<0.1
Sulfamethoxazole	49 ± 2.7	69.6 ± 2	negative	<0.1	<0.1
Sulfanilamide	40.8 ± 7.6	122.4 ± 12.3	negative	0.4	1.2
Quinolones					
Flumequine	<LOD	3.2 ± 3	negative	<0.1	<0.1
Ofloxacin	5729.2 ± 446.6	2226.7 ± 67.1	61.1	<0.1	<0.1
Norfloxacin	273.7 ± 98.8	1216.6 ± 1088.9	negative	<0.1	0.1
Danofloxacin	297.8 ± 35.4	1104.9 ± 829	negative	0.1	0.2
Sparfloxacin	8502.4 ± 137.3	241.6 ± 210	97.2	<0.1	<0.1
Nitroimidazols					
Metronidazole	324 ± 22.7	371.9 ± 1.5	negative	<0.1	0.1
Ornidazole	8 ± 7	5.6 ± 5.4	30.1	<0.1	<0.1
Dihydrofolate					
Trimethoprim	60.4 ± 0.4	102.1 ± 7.3	negative	<0.1	<0.1
Beta-blockers					
Propranolol	146.7 ± 3.4	171.1 ± 1.1	negative	<0.1	0.1
Timolol	4.9 ± 0.04	9 ± 0.4	negative	<0.1	<0.1
Atenolol	118.7 ± 3.3	78.9 ± 0.3	33.5	<0.1	<0.1
Metoprolol	320.6 ± 5.5	366.8 ± 20.6	negative	0.1	0.2
Histamine receptor antagonist					
Ranitidine	187.4 ± 10.9	60.7 ± 58.9	67.6	<0.1	0.1
Psychiatric drugs and stimulants					
Amitriptiline	12.2 ± 1.7	7.6 ± 1.8	37.7	<0.1	0.1
Carbamazepine	13.1 ± 0.3	28.6 ± 0.5	negative	<0.1	<0.1
Caffeine	492223.2 ± 143239	0.3 ± 0.2	100	0.1	0.3
Asthma medication					
Albuterol	8.7 ± 1.5	5.3 ± 5	39.8	<0.1	0.1
Tetracyclines					
Tetracycline	4562.1 ± 120	<LOD	100	1	3.5

* It should be noticed that hydraulic retention time was not considered.

** LOD – Limit of Detection.

*** LOQ – Limit of Quantification.

Concentrations of PhACs were determined in duplicate as reported earlier (Baena-Nogueras et al., 2016). Briefly, Solid Phase Extraction (SPE) was used as pre-treatment method (HLB cartridges Oasis, 200 mg). Conditioning of HLB cartridges was performed using 8 mL of methanol and 8 mL of Milli-Q water. Consequently, samples (100 mL) were passed through the cartridges. Finally, car-

tridges were washed with Milli-Q water (10 mL) and dried in air. Elution was performed using 10 mL of methanol. Evaporation of extracts was carried out under a nitrogen stream and a mixture of water and methanol (75:25) was used for reconstruction. Identification and quantification of PhACs were performed by means of Bruker EVOQ Elite (Bruker, Billerica, MA) UPLC-QqQ-MS/MS with

Table 2
Physico-chemical characterization of urban wastewater effluent.

Parameter (unit)	Concentration	Parameter (unit)	Concentration
Chemical Oxygen Demand (mg L ⁻¹)	49	NO ₃ -N (mg L ⁻¹)	1.46
Total Organic Carbon (mg L ⁻¹)	14.4	Alkalinity (mmol L ⁻¹)	2.13
Biochemical oxygen demand 7 (mg L ⁻¹)	9.16	Total iron (mg L ⁻¹)	0.55
Suspended Solids (mg L ⁻¹)	4.8	pH	7.13
Total Phosphorous (mg L ⁻¹)	0.23	Conductivity (mS cm ⁻¹)	0.68
Total Nitrogen (mg L ⁻¹)	4.9	SO ₄ ²⁻ (mg L ⁻¹)	89.83
NH ₄ -N (mg L ⁻¹)	1.38	Cl ⁻ (mg L ⁻¹)	87.12

C-18 column (100 × 2.1 mm; particle size 2 μm) and electrospray interface. The injection volume was 10 μL and the flow rate was 0.4 mL/min in positive and negative ionization modes. The aqueous mobile phases used for measurements conducted in positive ionization mode were a mixture of 10 mmol formic acid and ammonium formate (pH 3.2), while 100% methanol was used as organic mobile phase. Aqueous mobile phases applied for analysis performed in negative ionization mode were 5 mmol ammonium acetate/ammonia (pH 8), while organic mobile phase consisted of 100% methanol. Multiple reaction monitoring (MRM) was used for data acquisition. Obtained data were processed with Bruker MS Workstation 8.1 Software.

2.3. Characterization of granular activated carbon

Different GAC samples were characterized: fresh (GAC), GAC after adsorption runs (GAC-Ads) and after AOPs experiments (GAC-AOPs). Textural properties were determined combining N₂ adsorption-desorption isotherm and mercury intrusion porosimetry (MIP). N₂ isotherms were obtained at -196°C with a Quadrasorb Evo apparatus (Quantachrome). Before measurements, the samples were outgassed at 150°C for 24 h under high vacuum (residual pressure <10⁻⁴ Pa). BET surface area was calculated, and t-plot method was used for micropore analysis. Mercury intrusion porosimetry was used to determine the meso and macropore volumes (Poremaster 60 apparatus from Quantachrome). The mesopore volume in the range not covered by MIP was obtained from the N₂ isotherm. Elemental analyses were performed in a LECO CHNS628 elemental analyser. Complementary chemical analysis was carried out by wavelength dispersive X-ray fluorescence spectroscopy (WDXRF) to check for the presence of different elements with a S8 Tiger apparatus (Bruker). X-ray diffraction (XRD) pattern was performed in a Bruker D8 Advance XRD diffractometer with a Cu Kα radiation (λ=0.1541 nm) in the 2θ range 10–80° at a scan rate of 0.02°/s and 0.5 s per point.

Thermal gravimetry and differential temperature analyses coupled mass spectrometry (TGA-DTA-MS) were performed with a STA 449 F3 Jupiter (Netzsch) coupled to a mass spectrometer (QMS 403D Aëolos III from Netzsch) in order to analyse the evolution of CO₂, CO and H₂O during the temperature programmed treatments. Two different experiments were carried out in inert (temperature programmed desorption (TPD) in Ar) and in oxidizing flows (temperature programmed oxidation (TPO) runs in Ar/O₂, 80/20) with a flow rate of 100 mL/min, using a heating rate of 10°C/min from 40°C to 1100°C. The pH of the GAC suspension slurry (pH_{pZC}) can be equivalent to the point of zero charge under certain conditions (Moreno-Castilla et al., 1995; Menendez et al., 1995). It was determined by mass titration with 5 wt.% GAC loading in ultrapure water as described in the literature (Moreno-Castilla et al., 1995; Menendez et al., 1995) in dark conditions and continuous stirring until the pH of the slurry was stabilized. A calibrated pH-meter (Crison GLP21+) was used for pH measurement.

2.4. Experimental set-up

All CWPO, PMS/GAC, PDS/GAC and GAC experiments for urban wastewater treatment were conducted in discontinuous mode using up-flow fixed bed reactors at ambient pressure and temperature (20 ± 2°C). Methacrylate tubes with diameter of 4.5 cm and length of 13 cm were used as reactors (Fig. 1 SM). Each reactor was charged with 68.825 ± 0.345 g of GAC (catalyst). Real urban wastewater effluent (410 mL) was placed in glass beaker (volume 750 mL) and mechanically stirred, then the appropriate amount of H₂O₂ (for CWPO), PMS (for PMS/GAC) or PDS (for PDS/GAC) was added to the effluent and pumped to the fixed-bed reactor using peristaltic pump (Masterflex®). Adsorption experiments (blank/reference test) were conducted in parallel with catalytic experiments (CWPO, PMS/GAC, PDS/GAC) in order to reach similar saturation of GAC used for catalytic and adsorption tests. The time zero of each experiment was considered when the effluent reached the top of the GAC bed. Experimental set up for CWPO, PMS/GAC and PDS/GAC experiments is shown in Fig. 2 SM. Residual concentration of hydrogen peroxide was measured during all CWPO experiments by means of colorimetric method reported elsewhere (Eisenberg, 1943). Persulfate concentration was monitored using spectrophotometric methods according to the protocols proposed in (Liang et al., 2008; Waclawek, Grübel and Černík, 2015).

Long-term CWPO tests were also performed in order to evaluate the stability of the catalyst using two different experimental set ups. The first long-term test was conducted using the experimental set up described above and shown in Fig. 2 SM. For this test a model solution consisting of tap water and Orange II (initial concentration 500 mg/L) was continuously pumped (flow rate about 20 mL/min) through the fixed-bed reactors during 47 h. Taking into consideration that the theoretical COD of Orange II model solution was estimated to be about 760 mg L⁻¹, the amount of H₂O₂ was chosen based on optimum stoichiometric ratio obtained in previous experiments with wastewater effluent. No hydrogen peroxide was added in adsorption column (CWPO and adsorption tests were performed in parallel). The contact time was decreased as compared to experiments with wastewater in order to ensure presence of residual H₂O₂ in the CWPO effluent. Concentration of Orange II in water was measured by means of UV-Visible spectrophotometer (Jenway 7315) at the wavelength 486 nm. Taking into account the large amount of catalyst used in this experimental set up it was difficult to reach saturation of GAC. Hence, similar tests were performed using smaller amounts of catalyst (experimental set up shown in Fig. 3 SM). Two up-flow fixed bed reactors (polystyrene, 1 cm diameter, 5 cm bed length, 22 cm total length) filled with 2 g of GAC each were used and operated in parallel (one for CWPO and one for adsorption). Model solution (except that pH was adjusted to 3) and concentration of H₂O₂ were similar to these used in the first long-term test. Experiments were performed continuously during 400 min and model solution was pumped through reactors with flow rate of 2 mL min⁻¹.

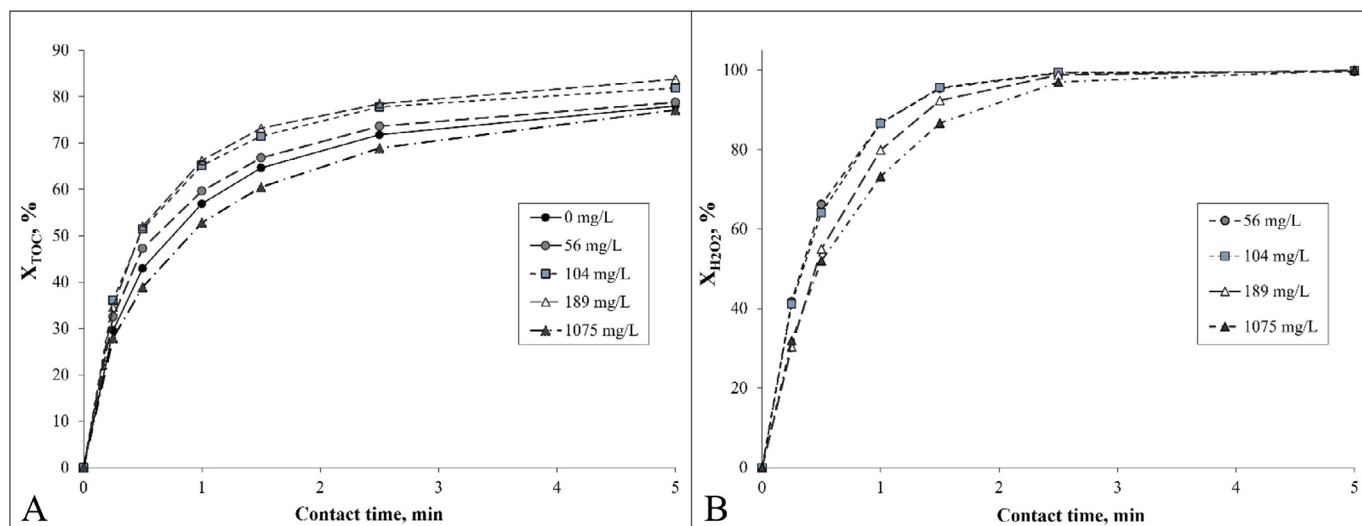


Fig. 1. (A) Effect of hydrogen peroxide concentration on conversion of TOC of urban wastewater effluent (initial TOC = 12.28 ± 0.33 mg L⁻¹; initial pH = 7.6); (B) hydrogen peroxide consumption.

3. Results and discussion

3.1. Optimization of operational conditions of CWPO, PMS/GAC and PDS/GAC

3.1.1. CWPO

The CWPO experiments were conducted at ambient pressure and temperature with various concentrations of hydrogen peroxide in order to choose the optimal concentration of the oxidant to treat the wastewater effluent. Performance of the CWPO process with different initial hydrogen peroxide concentrations was evaluated based on TOC conversion (X_{TOC},%), calculated as shown in Equation (1), while hydrogen peroxide consumption (X_{H₂O₂},%) was estimated using Equation (2).

$$X_{TOC} = \frac{([TOC]_{inlet} - [TOC]_{outlet})}{[TOC]_{inlet}} \cdot 100 \quad (1)$$

$$X_{H_2O_2} = \frac{([H_2O_2]_{inlet} - [H_2O_2]_{outlet})}{[H_2O_2]_{inlet}} \cdot 100 \quad (2)$$

It is well known that concentration of hydrogen peroxide is a critical parameter for CWPO. According to Pliego et al. (2012), the stoichiometric amount of hydrogen peroxide required for the complete mineralization of wastewater is 2.125 g per g of COD. The initial COD and TOC values of wastewater effluent used for CWPO experiments were 49 mg L⁻¹ and 12.3 mg L⁻¹, respectively. Thus, the theoretical stoichiometric concentration of hydrogen peroxide was estimated to be about 104 mg L⁻¹ taking into consideration the COD value (49 mg L⁻¹) of the tested wastewater effluent. Following concentrations of hydrogen peroxide: 104 mg L⁻¹ (H₂O₂:COD 1 stoichiometric), 56 mg L⁻¹ (H₂O₂:COD 0.5 stoichiometric), 189 mg L⁻¹ (H₂O₂:COD 1.8 stoichiometric) and 1075 mg L⁻¹ (H₂O₂:COD 10.3 stoichiometric) were tested. Results (TOC conversion and H₂O₂ consumption profiles) are shown in Fig. 1.

As it can be seen from Fig. 1 (A), with an initial increase of hydrogen peroxide concentration (H₂O₂:COD from 0.5 to 1.8 stoichiometric) the TOC conversion increased, while when the H₂O₂ concentration was too high (H₂O₂:COD 10.3 stoichiometric) the efficiency of CWPO decreased. Similar observations have been reported earlier (Fang et al., 2018) and can be explained by the fact that an excess of hydrogen peroxide acts as scavenger of hydroxyl radicals (reactions 3 and 4 (Chou and Huang, 1999)).



The highest TOC conversion was achieved with initial H₂O₂ concentrations of 104 mg L⁻¹ (H₂O₂:COD 1 stoichiometric) and 189 mg L⁻¹ (H₂O₂:COD 1.8 stoichiometric), leading to approx. 82% and 84% of TOC removal, respectively. Obtained results are in agreement with data reported earlier as in most of recent studies devoted to wastewater treatment by CWPO the H₂O₂:(COD or TOC) ratios were with the range of 0.5 – 2 (Rueda-Márquez, Levchuk and Sillanpää, 2018). It should be mentioned that hydrogen peroxide was fully consumed during all CWPO tests (Fig. 1B), which is highly beneficial as the presence of H₂O₂ in effluents even at low concentrations can be possibly toxic for the receiving environment (Drábková et al., 2007). The pH and conductivity values were measured before and after each CWPO test and similar results were obtained for all tested H₂O₂:COD ratios, namely pH increased from 7.6 ± 0.03 (initial wastewater effluent) to 8.04 ± 0.03, while conductivity raised from 0.9 ± 0.01 mS cm⁻¹ to 1.08 ± 0.04 mS cm⁻¹. The values of pH and conductivity after adsorption test were 8.38 ± 0.01 and 1.13 ± 0.01 mS cm⁻¹, respectively. The H₂O₂:COD ratio 1 stoichiometric was chosen as the optimal among all CWPO tests and used for further experiments, although TOC conversion was slightly higher at ratio 1.8 stoichiometric. However, required amount of H₂O₂ at ratio 1.8 is almost two times higher as compared with ratio 1, while the TOC removal is very similar. Reference (blank) test in absence of catalyst with 1 stoichiometric concentration of hydrogen peroxide was conducted and no changes in TOC were observed. The adsorption capacity of GAC in absence of hydrogen peroxide was relatively high (Fig. 1A) as expected due to high GAC load in the fixed-bed reactor. However, experiments confirming that chemical oxidation and not sorption takes place when H₂O₂ is added to the GAC column have been performed in our previous study (Rueda-Márquez et al., 2015b). Briefly, deionized water spiked with 4-chlorophenol and H₂O₂ was pumped through the GAC column (mass of catalyst 140.10 g) and a stoichiometric amount of chloride ions was detected after treatment, confirming that oxidation occurred. It should be mentioned that the same GAC was used in previous (Rueda-Márquez et al., 2015b) and current study.

In this sense, this GAC will promote H₂O₂ decomposition into reactive oxidizing species (ROS), mainly HO[•] radicals (Oliveira et al., 2004; Santos et al., 2009; Georgi and Kopinke, 2005; Rey et al., 2008). This reaction is favoured by surface defects, unsaturated

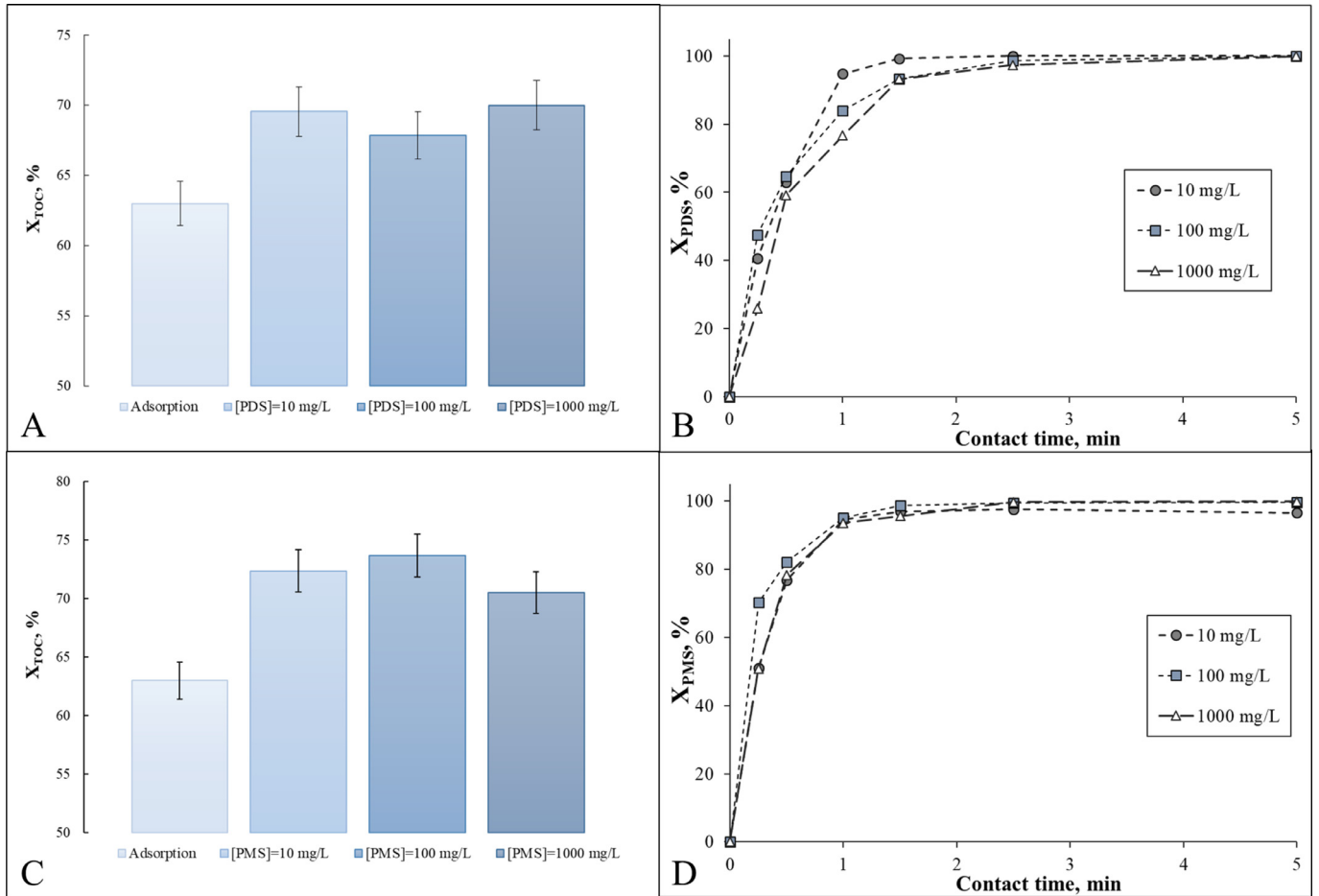


Fig. 2. (A) Effect of PDS concentration on conversion of TOC (after 5 min of contact time) of urban wastewater effluent (initial TOC = 11.59 ± 0.72 mg L⁻¹); (B) PDS consumption; (C) Effect of PMS concentration on conversion of TOC (after 5 min of contact time) of urban wastewater effluent (initial TOC = 11.51 ± 0.82 mg L⁻¹; initial pH = 7.6); (D) PMS consumption.

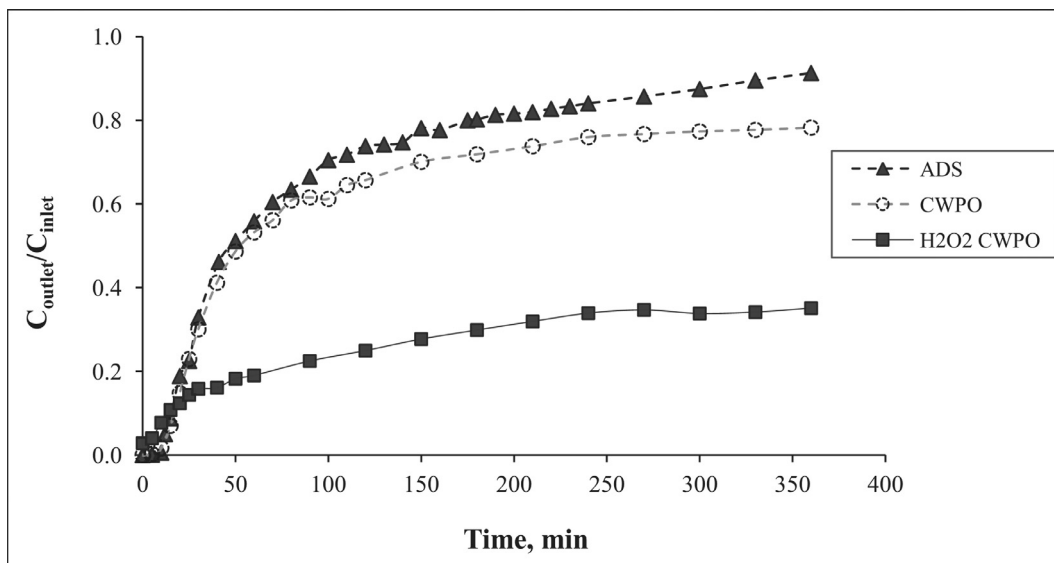


Fig. 3. Results of Orange II conversion during adsorption (ADS) and catalytic wet peroxide oxidation (CWPO), and H₂O₂ conversion during CWPO (H₂O₂ CWPO). Experiments were conducted as during long-term test (2 g GAC experimental set up).

sites and basic surface oxygen groups (SOGs) in activated carbons, but also by the presence of metallic species (mainly Fe) on their surface (Domínguez et al., 2013b; Rey et al., 2011; Santos et al., 2009), this latter being very low in the GAC used in this study. However, the vast number of active sites in activated carbons is a disadvantage for the use of H₂O₂ during CWPO due to the recombination of the ROS generated. Adsorption of organic molecules blocking some of the active sites has demonstrated to favour the overall process making the hydrogen peroxide decomposition more controllable (Domínguez et al., 2013a). More evidence about the mechanism during CWPO is presented in the long-term test results (Section 3.3.2) with the characterization of the used GAC samples.

3.1.2. PDS/GAC and PMS/GAC

The PDS/GAC and PMS/GAC experiments were conducted at ambient pressure and temperature with various concentrations of PDS or PMS in order to choose the optimal concentration of the oxidant to treat the wastewater effluent. Performance of PDS/GAC and PMS/GAC process with different initial PDS or PMS concentrations was evaluated based on TOC conversion ($X_{\text{TOC},\%}$), calculated as shown above in Equation (1), while PDS consumption ($X_{\text{PDS},\%}$) or PMS consumption ($X_{\text{PMS},\%}$) was estimated using Equation (5, 6).

$$X_{\text{PDS}} = \left(\frac{[\text{PDS}]_{\text{inlet}} - [\text{PDS}]_{\text{outlet}}}{[\text{PDS}]_{\text{inlet}}} \right) \cdot 100 \quad (5)$$

$$X_{\text{PMS}} = \left(\frac{[\text{PMS}]_{\text{inlet}} - [\text{PMS}]_{\text{outlet}}}{[\text{PMS}]_{\text{inlet}}} \right) \cdot 100 \quad (6)$$

In order to get comparable results with CWPO (with H₂O₂ as an oxidant), similar concentrations of persulfates (PDS/PMS) have been used, i.e., 10, 100, 1000 mg L⁻¹. Results obtained for each system (PDS/GAC, PMS/GAC) are shown in Fig. 2, where the TOC conversion (Fig. 2 A, B) and the oxidant consumption profiles (Fig. 2 C, D) are reported.

In PDS/GAC system, similar behaviour on TOC conversion was obtained for all the concentrations tested, in which 70% conversion was reached at 5 min of contact time. Regarding PDS consumption (Fig. 2 C), it should be noted that at 2.5 min all PDS has been consumed. In fact, the PDS decomposition decreased as the concentration increased. On the other hand, PMS was practically consumed (independently of initial concentration) at 1.5 minutes of contact time. Accordingly, PMS/GAC system shows better performance than PDS/GAC, as PMS is more efficiently decomposed than PDS, and also shows better TOC conversion rates (about 72% vs. about 69%; Fig. 2). No major changes were detected in pH and conductivity values, being similar to that reported on CWPO experiments, although at 1000 mg PMS·L⁻¹ the pH decreased to 5.80 at initial conditions and raised up to 7.98 at the end of the experiments with a conductivity of 1.3 mS·cm⁻¹. Similar conclusions were obtained in the literature (Saputra et al., 2013), in which authors showed that the ability of activated carbons (ACs) to produce sulfate radicals was much higher in a PMS system compared to PDS (Saputra et al., 2013).

Activated carbon (AC) is an electron transfer mediator in persulfates activation. However, a non-radical activation pathway has also been reported (Yao et al., 2019), which makes difficult to strictly explain activation mechanisms. Nevertheless, the persulfates might be decomposed by the AC surface with the release of organic radicals and sulfate radicals, via radical or non-radical pathway (Zhang et al., 2013; Zhao et al., 2017). Accordingly, it is assumed that as persulfates are decomposed, they produce chemical oxidation in some way, and major TOC mineralization rates can be achieved rather than sorption. Also, taking into account that GAC with very low iron content (0.03 wt.%) was used in this study, catalytic performance in PDS/GAC or PMS/GAC might be lower (Zhao et al., 2017; Xiao et al., 2020).

These systems have been previously studied by means of dyes (Yang et al., 2011; Zhang et al., 2013) and phenol degradation (Saputra et al., 2013) as well as antibiotic metronidazole (Forouzesheh et al., 2019; Forouzesheh, Ebadi and Aghaeinejad-Meybodi, 2019). Generally, the persulfate/GAC system shows promising degradation rates for dyes removal; however when mineralization rates are analysed in form of TOC it reduces its efficacy (Zhang et al., 2013; Yang et al., 2011). The presence of other organic substances could imply the reduction of active surface sites available for the activation of persulfates, and it is of high importance as real effluent was used in the experiments. When more specific pollutants are studied, for instance, antibiotics (Forouzesheh, Ebadi and Aghaeinejad-Meybodi, 2019; Forouzesheh et al., 2019), significantly higher amounts of persulfates (~ 3000 mg L⁻¹) have been used in order to increase the degradation performance by comparison with single adsorption, which can agree with our results.

The persulfates:TOC ratio 8.6 was selected for further PDS/GAC or PMS/GAC experiments due to (i) highest TOC conversion obtained in PMS/GAC (100 mg·L⁻¹ of PMS), (ii) comparative purposes (in terms of initial oxidant concentration, mg L⁻¹) with CWPO, which was the most efficient among studied AOPs.

3.2. Comparison of CWPO, PMS/GAC and PDS/GAC for elimination of PhACs from real urban wastewater effluent

3.2.1. Occurrence of PhACs in urban wastewater influent and effluent

Composite samples (48 h) of urban wastewater influent and effluent were collected for screening and identifying PhACs (83 in total, see Table 1 SM) with higher concentrations to be monitored during further post-treatment experiments (CWPO, PMS/GAC, PDS/GAC at optimal conditions). Moreover, some PhACs, the concentrations of which significantly increased after treatment (negative removal efficiency) were taken into consideration because those would be especially interesting to follow during possible post-treatment (CWPO, PMS/GAC, PDS/GAC). Results are shown in Table 1.

Forty seven out of eighty three analysed PhACs were detected in influent and effluent wastewater. Obtained concentrations of PhACs in wastewater influent and effluent (Table 1) are in agreement with PhACs concentration ranges previously reported for influents and effluents of conventional WWTPs in different countries (Luo et al., 2014), except for concentrations of acetaminophen (in influent), diclofenac (in effluent) and metoprolol (in effluent), which were slightly higher. Interestingly, concentration of caffeine in wastewater influent measured in this study (492.223 ± 143.239 µg L⁻¹) was significantly higher than caffeine concentrations reported in wastewater influents of various countries (0.22 – 209 µg L⁻¹) (Luo et al., 2014). This result can be explained by the fact that coffee consumption in Finland is among the highest in the world (Kempf et al., 2010).

Out of all detected PhACs only acetaminophen, phenylbutazone, pravastatin, triclocarban (TCC), and tetracycline were completely removed (concentration in effluent was < LOD) after conventional wastewater treatment process. High removal efficiency (> 70%) was observed for lincomycin, salicylic acid, ibuprofen, naproxen, clofibrac acid, sparfloxacin and caffeine, which is generally in agreement with the removal efficiency for micropollutants reported by Luo et al. (2014). Moderate removal efficiency (40 – 70%) was achieved for fenpropfen, bezafibrate, roxithromycin, ofloxacin and ranitidine. Chloramphenicol, indomethacin, mefenamic acid, diclofenac, ketoprofen, furosemide, hydrochlorothiazide, azithromycin, clarithromycin, ornidazole, atenolol, amitriptyline and albuterol were poorly removed (< 40%), which is in agreement with removal efficiencies reported earlier for some of these compounds (e.g. di-

clofenac, mefenamic acid) (Luo et al., 2014). Concentrations of some PhACs, such as phenazone, gemfibrozil, triclosan (TCS), monensin, sulfathiazole, sulfadiazine, sulfamethoxazole, sulfanilamide, flumequine, norfloxacin, danofloxacin, metronidazole, trimethoprim, propranolol, timolol, metoprolol, carbamazepine were higher in effluent than in influent wastewater (negative removal efficiency). Consulting the scientific literature, similar results have been reported earlier (Rivera-Jaimes et al., 2018; Luo et al., 2014; Kasprzyk-Hordern, Dinsdale and Guwy, 2009; Sun et al., 2014; Villar-Navarro et al., 2018). Observation of higher concentrations of some PhACs in wastewater effluent in comparison with influent can possibly be ascribed to (i) desorption from activated sludge or suspended particulate matter during wastewater treatment process; (ii) transformation of some PhACs to their original state during wastewater treatment from metabolites present in influent (e.g. carbamazepine, sulfamethoxazole) (Kasprzyk-Hordern, Dinsdale and Guwy, 2009); (iii) seasonal variations, sampling and analytical uncertainties (Sun et al., 2014).

Obtained results suggest that several PhACs were poorly or negatively removed after conventional wastewater treatment. Thus, it is of high importance to monitor such PhACs during tertiary treatment of secondary wastewater effluent in order to ensure complete elimination of these compounds.

3.2.2. Removal of PhACs from wastewater effluent by CWPO, PMS/GAC and PDS/GAC

Efficiency of catalytic processes, namely, CWPO, PMS/GAC and PDS/GAC was compared for removal of selected PhACs (in total 22) from real urban wastewater effluent. Physico-chemical characterization of wastewater effluent used for experiments is shown in Table 2.

Taking into account that the initial TOC of urban wastewater used for PhACs removal was higher than in previous experiments, the optimal ratio of oxidant to organic matter obtained from previous experiments was kept for each process. Samples were collected after 5 min of contact time. Removal percentages of PhACs after CWPO, PMS/GAC and PDS/GAC are shown in Table 3.

Results shown in Table 3 revealed that concentrations of PhACs in urban wastewater effluents may significantly vary in summer (Table 3) compared to winter (Table 1), which is in agreement with previously published works (Luo et al., 2014). For instance, concentrations of ibuprofen and caffeine were significantly higher in effluent collected in summer.

Complete removal of acetaminophen, ketoprofen, sulfadiazine, trimethoprim, propranolol, atenolol and albuterol was achieved after treatment by CWPO, PMS/GAC, PDS/GAC and GAC only (adsorption). Interestingly, sulfamethoxazole was fully eliminated by all applied processes except GAC (adsorption). Complete decomposition of gemfibrozil and clarithromycin (compound included in Watch List by EU Decision 2018/840) was observed after CWPO, while azithromycin (compound included in Watch List by EU Decision 2018/840) was fully eliminated after PMS/GAC. In general, for 18 out of 22 target PhACs very high removal efficiencies (> 92%) were achieved by all tested processes. However, moderate (40 – 70%) and poor (< 40%) removal efficiencies were achieved for salicylic acid, ofloxacin, norfloxacin and ciprofloxacin (the last compound included in Watch List by EU Decision 2018/840). Thus, ofloxacin was poorly removed after GAC (9.5%), PDS/GAC (35.7%) and PMS/GAC (33%), while no removal was reached after CWPO. Observed differences in removal efficiency of ofloxacin by tested processes can be possibly attributed to more selective nature of sulfate radicals (Ye et al., 2017) generated during PDS/GAC and PMS/GAC as compared to only hydroxyl radicals formed during CWPO. Poor removal efficiency of norfloxacin (26%) was achieved after GAC/PDS, while this compound was not eliminated after CWPO, GAC and PMS/GAC. Salicylic acid was poorly removed af-

ter CWPO (1.6%) and PMS/GAC (8.7%) and not eliminated after GAC/ PDS and GAC. Poor elimination of ciprofloxacin was reached after CWPO (11.2%), GAC (30.5%) and PMS/GAC (19%), while it was moderately removed after PDS/GAC (62.8%). Complete elimination of a mixture of six pharmaceuticals (sulfamethoxazole, atenolol, metronidazole, trimethoprim, diltiazem, ranitidine) with initial concentration $10 \mu\text{g L}^{-1}$ each has been reported after application of CWPO (30 min of contact time; 75°C ; $\text{Fe}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3 - 2 \text{ g L}^{-1}$; $\text{H}_2\text{O}_2 - 100 \text{ mg L}^{-1}$; $\text{pH}_0 - 3$) (Munoz et al., 2017). Higher contact time (60 – 90 min) was required for the removal of pharmaceuticals listed in EU Watch List (Decision 2015/495) spiked to urban wastewater effluent ($1000 \mu\text{g L}^{-1}$) by CWPO (25°C ; modified magnetite - 2 g L^{-1} ; $\text{H}_2\text{O}_2 - 35 \text{ mg L}^{-1}$). In another study (Díaz-Garduño et al., 2017), combination of UV/ H_2O_2 and CWPO (ambient temperature; GAC - 144.1 g ; $\text{H}_2\text{O}_2 - 160 \text{ mg L}^{-1}$; contact time - 3.5 min) for the treatment of three different urban wastewater effluents was demonstrated to be extremely efficient and completely remove 53 compounds originally detected in used effluents, except for fenofibrate (W3) and bezafibrate (W1). Considering that in the current study the contact time was only 5 min, it can be expected that with increase of contact time higher/complete removal of salicylic acid and quinolones can be possibly achieved. As far as authors are aware, relatively few studies have been reported focused on elimination of pharmaceutical compounds (mg L^{-1} level) from deionized water using persulfates oxidation activated by carbonaceous-based materials (Chen and Carroll, 2016; Kang et al., 2016), while there are no studies conducted in real wastewater matrices using environmentally representative concentrations ($\text{ng L}^{-1} - \mu\text{g L}^{-1}$) of pharmaceuticals.

The results suggest that adsorption by GAC was also very efficient for the elimination of studied PhACs from wastewater effluent, which can be explained by relatively low concentration of target PhACs and high dose of GAC. Obtained results are in agreement with earlier studies (Luo et al., 2014). However, keeping in mind the different nature of studied catalytic and sorption processes, it can be expected that in a long-term perspective catalytic processes may be more beneficial due to lower saturation of catalyst with organic compounds.

3.3. Long-term CWPO and adsorption test

3.3.1. Performance of long-term tests

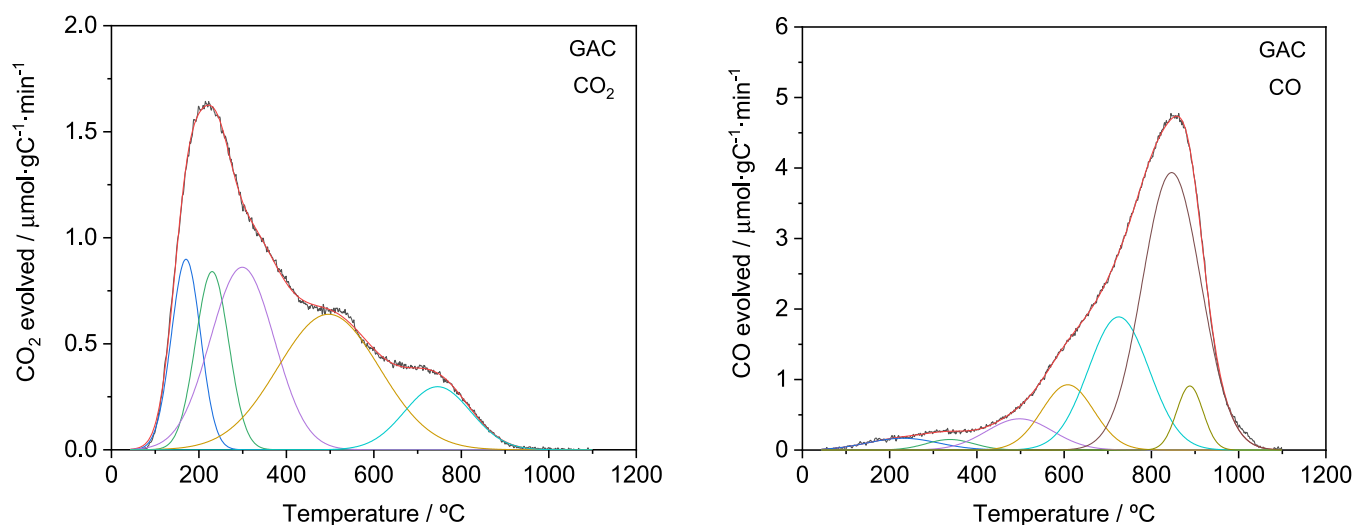
Based on results obtained with real urban wastewater effluents, it can be concluded that among the studied processes under chosen operational conditions (ambient temperature and pressure, carbon-based catalyst) the highest performance was achieved for CWPO using the stoichiometric concentration of H_2O_2 . Hence additional experiments were performed in order to evaluate catalysts stability during long-term continuous operation and get better understanding of studied processes nature. Long-term test was performed using the same fixed-bed reactors, which were used for experiments with urban wastewater. Orange II was used as a model compound. The flow rate was adjusted to 20 mL min^{-1} in order to ensure availability of residual H_2O_2 concentration in the effluent of fixed-bed reactor. Long-term adsorption experiments (GAC-Ads) were conducted in parallel with CWPO (GAC-AOPs) test during 47 h. Judging from obtained results (Fig. 4 SM) 47 h was not sufficient for saturating GAC column (adsorption experiment). Hence, no significant difference was observed in performance of CWPO and adsorption.

In order to get more evidence in the different nature of the studied CWPO and adsorption processes, an additional long-term experiment was conducted using fresh GAC (2 g) and Orange II as a model solution (500 mg L^{-1} , pH 3). The model solution with pH 3 was selected and used at this part of the work only in order to check the differences between adsorption-oxidation perfor-

Table 3

Results of UPLC-QqQ-MS/MS analysis of pharmaceutically active compounds before and after CWPO, PMS/GAC, PDS/GAC and GAC treatment of real urban wastewater effluent.

Compound	effluent, ng L ⁻¹	GAC, ng L ⁻¹	CWPO, ng L ⁻¹	PDS/GAC, ng L ⁻¹	PMS/GAC, ng L ⁻¹
Anti-inflammatories					
Acetaminophen	168.7 ± 5.4	<LOD	<LOD	<LOD	<LOD
Salicylic Acid	24.3 ± 6.1	24.7 ± 6.2	23.9 ± 3.9	27.5 ± 6.9	22.2 ± 5.6
Ibuprofen	20612.4 ± 342.5	29.9 ± 0.5	19 ± 0.9	30.2 ± 0.5	21.7 ± 0.4
Naproxen	3294.9 ± 84	9.2 ± 0.2	3 ± 4	7.3 ± 0.2	7.6 ± 0.2
Diclofenac	1575 ± 154.9	16.5 ± 1.7	8.4 ± 0.5	19.8 ± 2	13.9 ± 1.2
Ketoprofen	261.9 ± 12.6	<LOD	<LOD	<LOD	<LOD
Lipid Regulators					
Gemfibrozil	45.5 ± 2.3	1.4 ± 0.1	<LOD	3.2 ± 0.2	0.6 ± 0.1
Diuretics					
Furosemide	2047.8 ± 31.8	9.8 ± 1.5	6.3 ± 1	10.8 ± 1.7	7.8 ± 1.2
Hydrochlorothiazide	604.2 ± 39.7	1.9 ± 0.2	1.1 ± 0.1	1 ± 0.1	1.3 ± 0.2
Macrolides					
Azithromycin	748.8 ± 24.4	8.1 ± 2	2.7 ± 3	7.3 ± 1.8	<LOD
Clarithromycin	123.3 ± 3	3.6 ± 0.4	<LOD	2.6 ± 0.4	3.6 ± 0.5
Sulfonamides					
Sulfadiazine	30.6 ± 0.1	<LOD	<LOD	<LOD	<LOD
Sulfamethoxazole	80.6 ± 5.1	1.2 ± 0.2	<LOD	<LOD	<LOD
Quinolones					
Ofloxacin	745.4 ± 108.4	674.8 ± 101.2	766.1 ± 41.4	479 ± 81.4	498.5 ± 69.8
Norfloxacin	55.1 ± 17.2	84 ± 14.3	59.5 ± 3	40.7 ± 5.8	67.9 ± 7
Ciprofloxacin	5545.2 ± 1612.7	3852.2 ± 269	4923.1 ± 63.6	2062.9 ± 103	4489.7 ± 168
Dihydrofolate					
Trimethoprim	78 ± 1	<LOD	<LOD	<LOD	<LOD
Beta-blockers					
Propranolol	81.9 ± 1.2	<LOD	<LOD	<LOD	<LOD
Atenolol	76.3 ± 4.3	<LOD	<LOD	<LOD	<LOD
Psychiatric drugs and stimulants					
Carbamazepine	20.6 ± 1	0.3 ± 0.03	0.3 ± 0.02	0.3 ± 0.1	0.3 ± 0.1
Caffeine	349442 ± 7410.7	362.4 ± 86.8	256.5 ± 58.9	221 ± 44	365.7 ± 76.5
Asthma treatment					
Albuterol	10.1 ± 0.2	<LOD	<LOD	<LOD	<LOD

**Fig. 4.** Evolution of H₂O, CO and CO₂ during TGA-DTA in Ar.

mance of GAC when saturation with Orange II is reached at the tested conditions. It was demonstrated in the literature that higher pH at low temperature can induce the inefficient decomposition of H₂O₂ or hydroxyl radical scavenging (Khalil, Girgis and Tawfik, 2001; Buxton et al., 1988; Pignatello, Oliveros and MacKay, 2006; Rivas et al., 1998; Thomsen, 1998), hence, pH near 3 used in many cases (Rey et al., 2008; Domínguez et al., 2013a; Pinho et al., 2015). Experimental set up is shown in Fig. 3 SM. Results are presented in Fig. 3 and GAC characterization after these tests is discussed below.

At these conditions, after 360 min almost all the GAC was saturated with Orange II in the adsorption experiment. During CWPO

(GAC-AOPs*, where * indicates that experimental set up presented in Fig. 3 SM was used), a stationary H₂O₂ conversion of about 65% was reached whereas only 22% of Orange II in the influent was eliminated at 360 min. It should be mentioned that the objective of this long-term test was not to achieve high removal of Orange II, but to observe the differences in GAC saturation during CWPO and adsorption. The difference between Orange II profiles during adsorption (GAC-Ads*, where * indicates that experimental set up presented in Fig. 3 SM was used) and CWPO tests was 13% indicating the oxidation of the dye by radical species produced onto the GAC surface through H₂O₂ decomposition. However, at tested conditions an important part of H₂O₂ on GAC was decom-

Table 4
Textural properties of GAC.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{MICRO} ($\text{m}^2 \text{g}^{-1}$)	S_{EXT} ($\text{m}^2 \text{g}^{-1}$)	V_{MICRO} ($\text{cm}^3 \text{g}^{-1}$)	V_{MESO} ($\text{cm}^3 \text{g}^{-1}$)	V_{MACRO} ($\text{cm}^3 \text{g}^{-1}$)	$V_{\text{TOTAL(N}_2)}$ ($\text{cm}^3 \text{g}^{-1}$)	$V_{\text{TOTAL(N}_2+\text{Hg})}$ ($\text{cm}^3 \text{g}^{-1}$)
GAC	1040	1023	17	0.435	0.031	0.270	0.470	0.736
GAC-Ads	759	744	15	0.318	0.029	0.200	0.348	0.547
GAC-AOPs	758	739	19	0.314	0.030	0.220	0.347	0.564
GAC-Ads*	638	624	14	0.276	0.028	n.m.	0.304	n.m.
GAC-AOPs*	822	810	11	0.336	0.025	n.m.	0.362	n.m.

Table 5
TGA-DTA-MS-Ar results.

Sample	H_2O ($\mu\text{mol g}^{-1}$)	CO ($\mu\text{mol g}^{-1}$)	CO-Oil^* ($\mu\text{mol g}^{-1}$)	CO_2 ($\mu\text{mol g}^{-1}$)	M/M ₀ (%)	$\text{pH}_{\text{slurry}}$
GAC	429	1337	16	558	7.0	9.4
GAC-Ads	960	1481	105	751	9.2	7.2
GAC-AOPs	698	1371	67	699	8.3	7.1
GAC-Ads*	1161	1913	117	983	11.7	n.m.
GAC-AOPs*	835	1307	85	609	7.9	n.m.

posed into oxygen and water, which was supported by our observations and is in agreement with earlier studies (Oliveira et al., 2004; Huang et al., 2003; Rey et al., 2016). Further differences in nature of tested processes are discussed in the Section 3.3.2.2.

3.3.2. Characterization of GAC before and after CWPO and adsorption tests

3.3.2.1. Fresh GAC characterization. According to the supplier, the commercial GAC used had a mesh size of 4–8 mm and average particle density of 0.47 g cm^{-3} . Textural characteristics of the GAC samples calculated from N_2 -isotherm and Hg porosimetry are summarized in Table 4.

The isotherm shape (Fig. 5 SM) of fresh GAC is characteristic of microporous materials (type I) with H4 type hysteresis loop associated to some mesoporosity (Brunauer et al., 1940). Macropore volume was calculated by Hg porosimetry (Figure 6 SM). The GAC presented a high BET surface area, mainly because of its microporous structure but also an important contribution of macroporosity to the total pore volume was observed.

Regarding the composition of the activated carbon (Tables 3 SM and 4 SM), it is essentially constituted by C with H, N and S in small amount. The ashes content calculated from TGA-DTA-MS in oxidizing environment was 5.84 wt%. These ashes are composed mainly of K, Na, Cl, Si and Mg according to WDXRF results. For the relevance in CWPO and other AOPs (Domínguez et al., 2013b), the amount of Fe in the GAC structure was determined as c.a. 0.03 wt%.

By XRD only graphitic carbon was detected (Figure 7 SM), with the main reflection signals at 2θ values of 24.3° , 43.6° and 79.2° corresponding to (002), (100)-(101) and (110) diffraction planes of graphene layers in activated carbon (Nieto-Márquez, Valverde and Keane, 2007; Zhao et al., 2009; Lueking et al., 2007). The wide peaks indicate a poor degree of graphitization in a common turbostratic carbon structure, typical of activated carbons (AC). The values of the interplanar distance between graphene sheets in the activated carbon (d_{002}) and the crystal thickness (L_c) were 0.365 and 2.82 nm, respectively, confirming the amorphous character of the activated carbon used in this study. The structural distortion and defects may play a key role in the AC as catalyst for hydrogen peroxide decomposition (Rey et al., 2011). No diffraction peaks corresponding to any other inorganic structure were observed in agreement with the WDXRF results and the vegetal origin of the GAC.

The role of the surface composition of the activated carbon as catalyst is also well known. The presence and distribution of surface oxygen groups in GAC has been determined by Ar-TPD (Fig. 4).

Table 5 summarizes the amount of CO and CO_2 evolved and also the $\text{pH}_{\text{slurry}}$ of the GAC. The assessment of the different SOGs has been performed according to the literature (Moreno-Castilla, López-Ramón and Carrasco-Mariñ, 2000; Moreno-Castilla et al., 1998; Figueiredo et al., 1999; Szymański et al., 2002). The profile of CO_2 presents a main contribution of carboxylic (100 - 400°C), followed by anhydride (400 - 600°C) and lactone-type (700 - 900°C) SOGs. These structures, mainly carboxylic acids, would confer acidic character to the AC surface to some extent. On the other hand, the CO profile presents a small contribution of the anhydride-type SOGs, followed by phenolic structures (600 - 700°C), with predominance of basic structures like carbonyl (700 - 900°C), ether and chromene ($\sim 800^\circ\text{C}$) and pyrone-like SOG (800 - 1000°C). The highest contribution of the basic SOG compared to the acidic type (evolving mainly as CO_2) is evident from the basic value of the $\text{pH}_{\text{slurry}}$ for this GAC. The importance of the SOGs content and distribution in the processes of adsorption of organic compounds or catalytic decomposition of hydrogen peroxide, PMS and PDS, has been previously reported (Jung et al., 2001; Vidic, Tessmer and Uranowski, 1997; Georgi and Kopinke, 2005; Rey et al., 2008; Rey et al., 2011; Domínguez et al., 2013b).

3.3.2.2. GAC characterization after long-term CWPO and adsorption tests. Textural characterization of fresh and used GAC after adsorption (GAC-Ads) and AOPs (GAC-AOPs) tests (including the long-term tests, experimental set up shown in Fig. 2 SM) is presented in Table 4 and Figure 8 SM. The decrease observed in the BET surface areas (mainly microporous area) and micropore volumes indicates that some organic compounds remain adsorbed onto the GAC surface after both type of treatments (adsorption and oxidation), which is not surprising taking into consideration the relatively high concentration of chosen organic pollutant and short contact time. Macroporosity seems to be slightly affected also by the applied treatments. The reduction of BET surface area of activated carbon or Fe-activated carbon catalysts has been previously reported after CWPO of phenol and Orange II (Zazo et al., 2006; Domínguez et al., 2013a; Duarte, Maldonado-Hódar and Madeira, 2013). Condensation by-products due to oxidative coupling of aromatic structures usually remain adsorbed and cannot be oxidized at the conditions of CWPO (Vidic, Tessmer and Uranowski, 1997; Domínguez et al., 2013a). The presence of organic compounds adsorbed in used GAC was analysed by TGA-DTA-MS in Ar. At this point it is necessary to highlight that the contribution of previous organic compounds from batch experiments can be considered negligible according to the TOC of the water samples compared to Orange II long-term

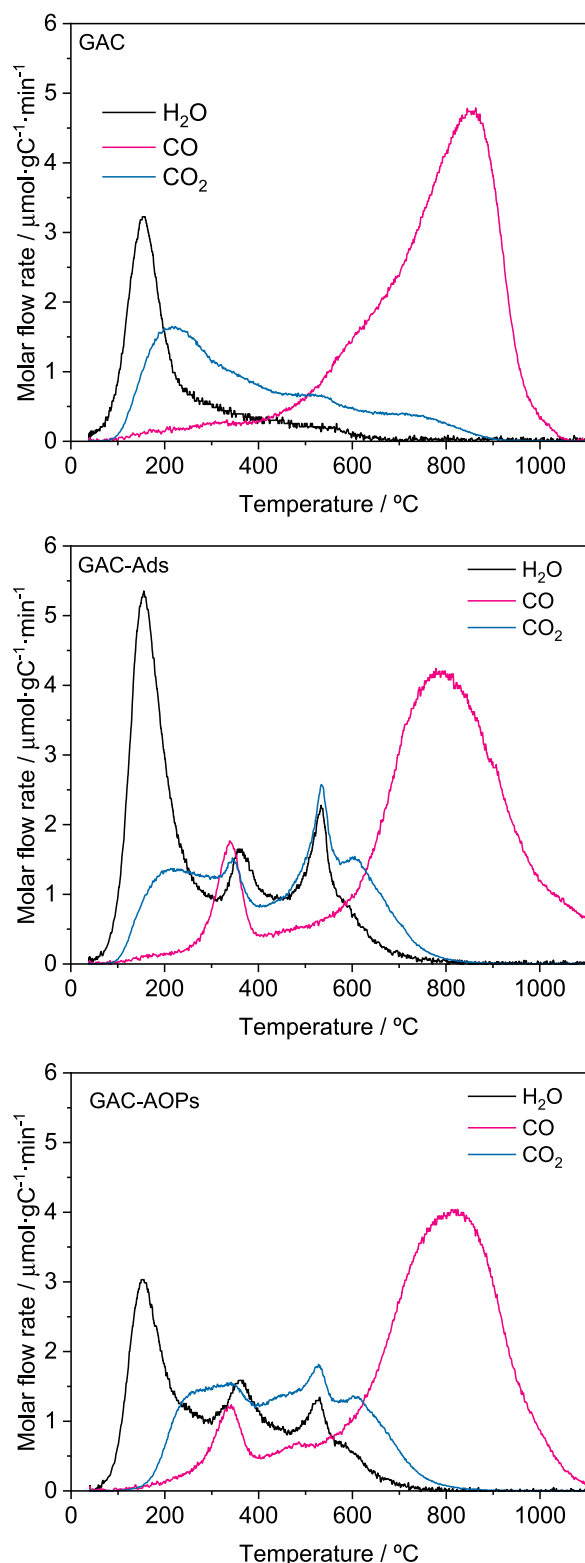


Fig. 5. Evolution of H₂O, CO₂ and CO evolved upon TGA-DTA-MS in Ar in fresh and used GAC samples.

experiments. Figure 9 SM shows the TGA and calculated differential thermogravimetry (DTG) profiles of fresh and used GAC, the final mass loss is presented in Table 5. The highest mass loss was found for GAC-Ads confirming a high loading of organic compounds, mainly Orange II, in its surface. The DTG profiles in Figure 9 SM (down) agree with the results by Duarte, Maldonado-Hódar and Madeira (2013). For GAC, physisorbed water is released

at around 100 - 150°C with a weight loss overlapped with some CO₂ evolution from SOGs. This was confirmed by the coupled MS analysis during TGA (see Fig. 5). The next important mass loss between 600 - 1000°C is attributed to the decomposition of CO-evolving SOGs. On the other hand, DTG of GAC-Ads and GAC-AOPs samples presented two additional contributions at 346°C and 530°C that have been assigned to the thermal decomposition of Orange II (Duarte, Maldonado-Hódar and Madeira, 2013). Besides, the weight loss corresponding to physisorbed water can be affected by some dehydration of Orange II. Regarding to the differences found between both used samples (GAC-Ads and GAC-AOPs), the weight loss assigned to Orange II seems to be lower for oxidation sample. Thus, around 346°C a peak in the profile of H₂O, CO₂ and CO is observed (Fig. 5); and around 530°C clear peaks of H₂O and CO₂ were detected.

The total amounts of H₂O, CO₂ and CO evolved during TGA-DTA-MS/Ar analysis are summarized in Table 5. The highest values of the three compounds were detected for the adsorption sample (GAC-Ads) confirming the presence of the highest amount of adsorbed organic matter. The differences in the profiles of H₂O, CO₂ and CO between both used samples in Fig. 5, in which different height ratio are observed for the same species, can suggest some differences in the nature of adsorbed organic matter in both samples. Thus, mainly Orange II is expected to be adsorbed onto GAC-Ads but some oxidation intermediates can be also present in GAC-AOPs (Duarte, Maldonado-Hódar and Madeira, 2013). Hence, according to the profiles in Fig. 5, the CO peak located at 346°C can be a good indicator of Orange II (or similar structures) adsorbed onto GAC. Thus, the CO profile has been decomposed in individual contributions (see Figure 9 SM) and the value of the 346°C peak (OII-CO) has been included in Table 5. From these results, a higher amount of Orange II remained adsorbed onto GAC after adsorption tests compared to oxidation. Finally, the increase in the percentage of S determined by elemental analysis and WDXRF (Tables 3 SM and 4 SM) can also confirm the presence of Orange II or S-containing by-products in the GAC samples, which was higher for GAC-Ads.

GAC samples (GAC-Ads* and GAC-AOPs*) after the second long-term test (experimental set up is shown in Fig. 3 SM) were characterized by N₂ adsorption-desorption isotherms and TGA-DTA-MS in Ar. According to textural characterization (Fig. 5 SM and Table 4), a higher decrease of the BET surface area and pore volumes was observed after adsorption (GAC-Ads*) as compared to CWPO (GAC-AOPs*). These results reveal a higher load of Orange II, blocking the porous structure, onto GAC used for adsorption test in comparison with GAC used for CWPO. Higher loading of Orange II on the surface of GAC used for adsorption test can be also confirmed by higher mass loss and higher amounts of H₂O, CO₂ and CO evolved during TGA-DTA-MS/Ar analysis observed for GAC-Ads* in comparison with GAC-AOPs* (Table 5). Moreover, differences in profiles of H₂O, CO₂ and CO obtained from TGA-DTA-MS analysis for GAC-Ads* and GAC-AOPs* indicate differences in nature of adsorbed organic compounds (Figure 10 SM), which is similar to results obtained after the first long-term test. Additionally, the peak at 346°C (OII-CO) was higher for GAC-Ads* in comparison with GAC-AOPs* (Figure 11 SM).

Results of GAC characterization confirm the ability of the GAC to promote catalytic decomposition of H₂O₂ and the subsequent organic matter oxidation despite the fact that difference between removal of organic pollutants by adsorption and CWPO was not very significant. Despite the high efficiency of GAC only (adsorption) observed in experiments with wastewater effluent, it should be noticed that oxidation processes are more beneficial for post-treatment of wastewater effluents mainly due to higher long-term performance.

4. Conclusions

Catalytic wet peroxide oxidation (CWPO) and persulfate oxidation (PMS/GAC and PDS/GAC) performed at ambient temperature and pressure using an up-flow fixed bed reactor exhibit high efficiency for the treatment of urban wastewater effluents. Thus, in terms of TOC mineralization difference in performance was observed with trend CWPO > PMS/GAC > PDS/GAC. In terms of PhACs removal from urban wastewater effluent, similar performance was observed for all tested processes. In general, for 18 out of 22 target PhACs very high removal efficiencies (> 92%) were achieved after 5 min of contact time (all tested processes, including adsorption). However, moderate (40 – 70%) and poor (< 40%) removal efficiencies were achieved for salicylic acid, ofloxacin, norfloxacin and ciprofloxacin, which can be attributed to insufficient contact time for elimination of these compounds.

Results of GAC characterization (mainly by TGA-DTA-MS and N₂ adsorption-desorption isotherm) after long-term adsorption and CWPO tests with Orange II indicate that a higher amount of Orange II was loaded on GAC used for adsorption tests. This, in turn, confirms the different nature of processes (CWPO and adsorption), and the catalytic ability of GAC.

Results obtained in this study indicate possible practical application of CWPO and/or persulfate oxidation for post-treatment of urban wastewater effluents aiming at removal of contaminants of emerging concern.

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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Supplementary materials

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