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Degradation of trinitrophenol by sequential catalytic wet air oxidation and solar TiO_2 photocatalysis

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ABSTRACT

Catalytic wet air oxidation (CWAO) and solar TiO_2 photocatalysis were investigated as advanced oxidation processes to degrade trinitrophenol (TNP) in model aqueous solutions. An activated carbon (AC) treated with sulphuric acid of different concentrations (5, 10 and 18 M) at two different temperatures (353 and 423 K) was investigated as a metal-free CWAO catalyst, while a commercially available P25 TiO_2 powder was used as a photocatalyst. CWAO experiments were conducted at 448 K, 0.7 MPa oxygen pressure (4.7 MPa of total pressure), 1.3 g L^{-1} AC loading and 270 mg L^{-1} TNP concentration, while photocatalytic experiments were conducted at ambient temperature, 1 g L^{-1} photocatalyst loading, 500–1000 W m^{-2} irradiance provided by a solar simulator and 32–270 mg L^{-1} TNP concentration. Treatment efficiency was assessed by measuring the concentrations of TNP and nitrates, total organic carbon (TOC) and biochemical oxygen demand (BOD_5). Up to 90% TNP degradation was attained during CWAO over 120 min, from an initial concentration of 270 mg L^{-1}. For the same TNP concentration, TiO_2 photocatalysis gives only 13% conversion over the same 120 min. However, for TNP concentrations below 144 mg L^{-1}, photocatalysis can be effectively used: 100 and 80% TNP degradation obtained in 120 min of irradiation for initial TNP concentrations of 64 and 144 mg L^{-1}, respectively. In this respect, CWAO and photocatalysis were employed sequentially to treat TNP; complete TNP conversion being achieved after 120 min of CWAO followed by 60 min of photocatalysis at 1000 W m^{-2} irradiance, and this was accompanied by 82% TOC reduction, as well as an increase of BOD_5/TOC ratio from 0 to 2.28.

1. Introduction

Advanced oxidation processes (AOPs) are remediation solutions based on the generation of non-selective and highly reactive radicals, such as hydroxyl ($HO^\bullet$) and hydroperoxyl ($HOO^\bullet$) radicals, applied to oxidise persistent organic pollutants into carbon dioxide and water, or alternatively into easily biodegradable by-products. Briefly, heterogeneous photocatalysis is based on the irradiation of a semiconductor material with photons of energy equal to or greater than its band-gap energy, to produce reactive electron–hole (e^-/h^+) pairs and, subsequently, highly oxidising species [1,2]. Titanium dioxide (TiO_2) is the most commonly used photocatalyst due to its high efficiency to produce e^-/h^+ pairs and also because it is a chemically stable, non-toxic and low cost material [1,3,4].

Ambient conditions of temperature and pressure are typical in photocatalysis. In contrast, wet air oxidation (WAO) operates at harsh conditions, which can become milder in the presence of active catalysts (400–523 K, 0.5–5.0 MPa) [5–15]. Several heterogeneous catalysts based on supported or unsupported metal oxides (e.g., Cu, Zn, Mn, Fe, Co, and Bi) and noble metals (e.g., Ru, Pt, Pd and Rh) have been tested in the last four decades for catalytic wet air oxidation (CWAO) [5–11,13,14]. However, deactivation phenomena are frequent, such as leaching of active metals to the liquid phase. For this reason, metal-free carbon materials have been tested as catalysts in many CWAO applications, including activated carbons [15–24], carbon xerogels [20,25], multi-walled carbon nanotubes [26–28] and carbon foams and fibres enriched with nitrogen [29]. Carbon materials are very versatile catalysts, since their surface chemistry can be easily

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modified [30] in order to provide adequate active sites for the reaction.

2,4,6-Trinitrophenol (TNP), also known as picric acid, is a by-product of the industrial synthesis of nitrobenzene. The resulting waste is an aqueous stream at the processing temperature (above 348 K) and a solid when left at ambient temperature. The raw effluent resulting from the nitrobenzene synthesis can be treated *in situ* by CWAO, taking advantage of the high temperature at which it is released and allowing for important energy savings. Indeed, recent works show that carbon materials with no added metal phase can be used as highly efficient catalysts for degradation of TNP by CWAO at 473 K [23,25]. In comparison with other AOPs, CWAO is also the most appropriate technology to treat wastewaters with moderate or high organic content (chemical oxygen demand of 10–100 g L^{-1}) [12]. However, since large scale CWAO is capital cost intensive when compared to other AOPs, coupling small cost effective CWAO units with another AOP post-treatment could represent an economically favourable solution for many specific instances.

Amongst AOPs operating at less severe conditions than those used in CWAO, heterogeneous photocatalysis is earning stronger relevance since the degradation process can be driven by solar light. Additionally, it was recently reported that photocatalysis could be beneficial when applied as a secondary treatment to WAO [31].

In the present work, an activated carbon commonly used for wastewater treatment (Norit ROX 0.8), with modified surface chemistry, was studied as a metal-free CWAO catalyst. Then, TiO_2 heterogeneous photocatalysis driven by artificial solar light was investigated as a possible post-treatment to totally degrade TNP.

2. Experimental

2.1. Reagents and materials

2,4,6-Trinitrophenol ($C_6H_3N_3O_7$, 98%), acetic acid (99.8%), sodium dihydrogen phosphate (≥99%) and phosphoric acid (85%) were purchased from Sigma–Aldrich. Acetonitrile (99.8%) and methanol (99.8%) were of HPLC grade (Chromanorm). Ultrapure water was produced in a Direct-Q millipore system.

2.2. CWAO experiments

Different activated carbon samples were tested as CWAO catalysts, namely the as-received original activated carbon Norit ROX 0.8 (AC), and chemically modified carbon materials obtained from the same AC by liquid phase treatments, following the procedure reported elsewhere [32]. Samples were treated with three different sulphuric acid concentrations (5, 10 and 18 M) at two different temperatures (353 and 423 K), and labelled as AC*X*-*Y*, where *X* refers to the sulphuric acid concentration and *Y* to the temperature (e.g., AC5-353 refers to a sample treated with 5 M sulphuric acid at 353 K). In a typical treatment, 10 g of AC were immersed in 200 mL of the sulphuric acid solution for 3 h in a 500 mL round-bottom flask heated by an oil bath at the desired temperature. Then, the recovered samples were thoroughly washed with distilled water until the neutrality of the rinsing waters was reached, and further dried in an oven for 18 h at 383 K. The specific surface area (S_{BET}), the non-microporous surface area determined by the *t*-method (S_{MES}) and the micropore volume (V_{MIC}) were calculated from the N_2 adsorption isotherms that were obtained in a Quantachrome NOVA 4200e analyser. The amounts of surface groups released as SO_2 were determined as described elsewhere [32], by using temperature programmed desorption in a AMI-200 apparatus (Altamira Instruments), equipped with a quadrupole mass spectrometer (Dymaxion, Ametek). Thermogravimetric analysis (TGA) was also performed for selected samples by using a STA 490 PC/4/H Luxx Netzsch thermal analyser and heating the samples at 20 K min^{-1} under nitrogen flow (50 cm^3 min^{-1}) up to 1273 K.

CWAO experiments were performed in a 160 mL 316-stainless steel high pressure batch reactor (Parr Instruments) equipped with a temperature controller (Fig. 1a). The operating conditions were typically as follows: 75 mL of a TNP model solution, 448 K, 500 rpm (confirmed as adequate to ensure the absence of mass transfer limitations), 4.7 MPa of total pressure (0.5 MPa of pure nitrogen, 0.9 MPa of water vapor pressure and 3.3 MPa of air, corresponding to 0.7 MPa of oxygen partial pressure), natural pH and a catalyst loading of 1.33 g L^{-1}. In a typical run, the model solution was placed into the autoclave, flushed with N_2 in order to remove dissolved oxygen, pressurised with 0.5 MPa of nitrogen and pre-heated up to the desired temperature. The introduction of air (3.3 MPa) after this pre-heating period was taken as $t = 0$ min for the reaction. A non-catalytic blank experiment was also performed with air in the absence of catalyst (WAO). Samples were periodically withdrawn and analysed by high performance liquid chromatography (HPLC).

2.3. Solar photocatalytic experiments

A commercial TiO_2 powder (AEROXIDE® TiO_2 P25) supplied by Degussa (now Evonik) was used as catalyst in photocatalytic experiments, referred hereafter as P25 TiO_2. The photocatalytic experiments were performed in a solar simulator (Cofomegra SolarBox 1500e, Fig. 1b). Four different initial TNP concentrations were tested (32, 64, 144 and 270 mg L^{-1}). In a typical run, the TiO_2 catalyst (1 g L^{-1}) was added to 75 mL of the TNP solution. The suspension was first stirred in the dark for 30 min and then irradiated for 120 min. Air was continuously sparged in the suspension under continuous stirring and the temperature maintained at 303 ± 3 K. One trial experiment at 500 W m^{-2} irradiance was performed with 270 mg L^{-1} of TNP and then the power was set at 1000 W m^{-2} for the rest of the experiments at different TNP concentrations. A blank experiment was also performed for 64 mg L^{-1} of TNP in the absence of TiO_2. Samples withdrawn at regular time intervals were centrifuged for 15 min and the supernatant liquid was carefully separated for analysis.

2.4. Analytical techniques

The concentration of TNP and nitrates in liquid samples were monitored by HPLC with a Hitachi Elite LaChrom HPLC system equipped with a diode array detector (L-2450) and a solvent delivery pump (L-2130) at a flow rate of 1 mL min^{-1}. TNP was separated on a Purospher Star RP-18 column (250 mm × 4.6 mm; 5 μm particles) with an isocratic method of an A:B (40:60) mixture of 3% acetic acid and 1% acetonitrile in methanol (A) and 3% acetic acid in water (B). The concentration of nitrates was analysed with another isocratic method (20 mM NaH_2PO_4 acidified with H_3PO_4 at pH 2.8) and using a Hydrosphere C18 column (250 mm × 4.6 mm; 5 μm particles). Quantification was based on the chromatograms by using the EZChrom Elite chromatography data handling software (Version 3.1.7). The concentrations of TNP and nitrates were determined at the maximum absorbance for each species (359 and 201 nm, respectively). Absorbance and concentrations were found to be linear over the whole range of concentrations under consideration (maximum relative standard deviation of 2%).

Total organic carbon (TOC) was determined with a Shimadzu 5000A TOC analyser. This equipment first determines the total carbon (TC) by sample combustion at 973 K over a Pt catalyst bed, and then the total inorganic carbon (TIC) is measured using phosphoric acid. TOC was calculated by subtracting TIC from TC. The uncertainty in this parameter, quoted as the relative deviation of three separate measurements, was never greater than 2%. Low molecular

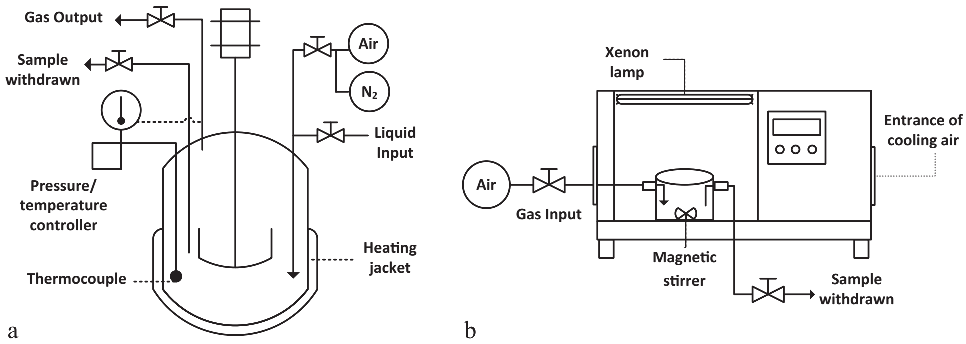

Fig. 1. Experimental set-up for CWAO (a) and photocatalysis (b).

weight carboxylic acids were quantified by ionic chromatography (Dionex DX-600, IonPac AS11-HC column).

The biochemical oxygen demand BOD_5 was determined in a WTW equipment (inoLab BSB/BOD 740 with a StirrOX electrode) by measuring the oxygen consumption of a microorganism culture (obtained from garden soil) after 5 days of incubation, in accordance with standard methods [33].

3. Results and discussion

To test the performance of the CWAO process, several ACs were used to treat the model solution containing TNP. Some textural and chemical properties of these materials are shown in Table 1. The textural properties are very similar for the ACs treated according to different methods: $S_{BET} = 845 \pm 25\,m^2\,g^{-1}$, $S_{MES} = 185 \pm 5\,m^2\,g^{-1}$, and $V_{MIC} = 0.33 \pm 0.01\,cm^3\,g^{-1}$. These textural properties are also similar to those of the original material ($S_{BET} = 850\,m^2\,g^{-1}$, $S_{MES} = 190\,m^2\,g^{-1}$, and $V_{MIC} = 0.33\,cm^3\,g^{-1}$). However, the SO_2 content significantly changes with the conditions applied to prepare each AC (120, 420, 460, 480, 520, 600 and 680 $\mu mol\,g^{-1}$ for AC, AC5-423, AC5-353, AC10-423, AC18-423, AC10-353 and AC18-353, respectively). Therefore, the carbon materials tested as metal-free CWAO catalysts have similar textural properties but different surface chemistry.

Fig. 2 shows the TNP concentration as a function of time in a blank experiment performed in the absence of catalyst (WAO) and in the CWAO experiments performed with the AC and ACX-Y catalysts. It is observed that the removal of TNP is strongly favoured when the carbon materials are used as catalysts. However, the marked decrease in the TNP concentration during the pre-heating period indicates that TNP was removed, to a substantial degree, by pure adsorption during this period (56 ± 7%). The evolution of TNP concentration as a function of time was also determined in experiments performed by introducing 3.3 MPa of nitrogen (instead of air) after the pre-heating period (not shown). For instance, the amount of TNP removed by pure adsorption with the untreated AC was 26% from 0 to 30 min (this experiment yielding no nitrates throughout the course of the experiment) while 44% of TNP was removed in the same period of time in the CWAO experiment (nitrates being detected). Since both processes (adsorption and reaction) occur simultaneously in CWAO, it is quite difficult to discriminate which fraction is removed by pure adsorption or pure reaction when oxygen is injected in the system, but it is evident that TNP is strongly removed by both processes occurring simultaneously.

Also of interest is to note (Fig. 3) the correlation between the amount of sulphur-containing groups in the carbon materials and TNP adsorption at $t = 0$ min. The amount of TNP adsorbed during the pre-heating period increases with the sulphur-containing groups as follows: 9.6, 10.7, 11.1, 11.4, 11.6 and 12.9 mg TNP g^{-1} AC for SO_2 contents in the AC of 420, 460, 480, 520, 600 and 680 $\mu mol\,g^{-1}$, respectively.

Regarding TNP reduction along 30 min of reaction, it is difficult to distinguish differences in the efficiency of the tested materials because the contribution of adsorption is quite significant in all the experiments. Additionally, the final TOC removal was also quite similar for the treated ACs (70–74%) but remarkably different from the TOC removal with the original AC (51%), determined with reference to the initial TNP concentration. Therefore, the effect of the sulphur-containing groups on the catalyst efficiency is not clear, but carbon materials treated with sulphuric acid are in general more efficient than the original AC, not only for TNP removal but also for TOC removal. Although it is quite difficult to distinguish the differences amongst the various ACs treated at 423 K, a decreasing order of efficiency in terms of TNP removal was found for the ACs treated at 353 K; in particular after

Table 1
Textural and chemical characterization of ACs.

	S_{BET} ($m^2\,g^{-1}$)	S_{MES} ($m^2\,g^{-1}$)	V_{MIC} ($cm^3\,g^{-1}$)	SO_2 ($\mu mol\,g^{-1}$)
AC	850	190	0.33	120
AC5-353	820	180	0.32	460
AC10-353	850	180	0.33	600
AC18-353	870	190	0.34	680
AC5-423	840	180	0.33	420
AC10-423	840	180	0.32	480
AC18-423	850	190	0.33	520

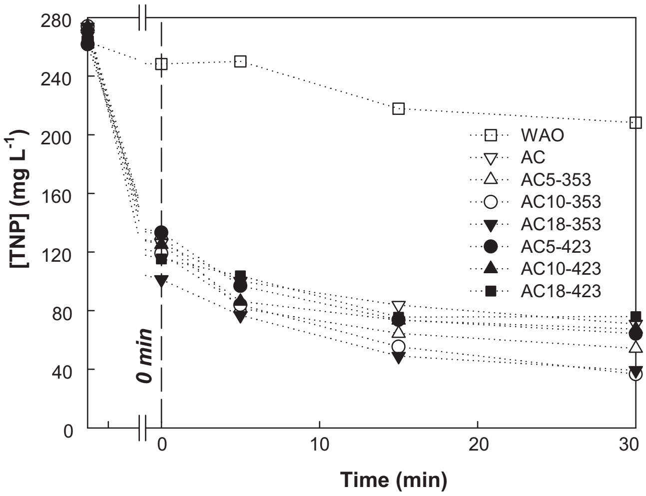

Fig. 2. Evolution of trinitrophenol concentration in non-catalytic and catalytic WAO experiments using the original and treated activated carbons (448 K, 0.7 MPa oxygen pressure, 1.3 g L^{-1} catalyst loading).

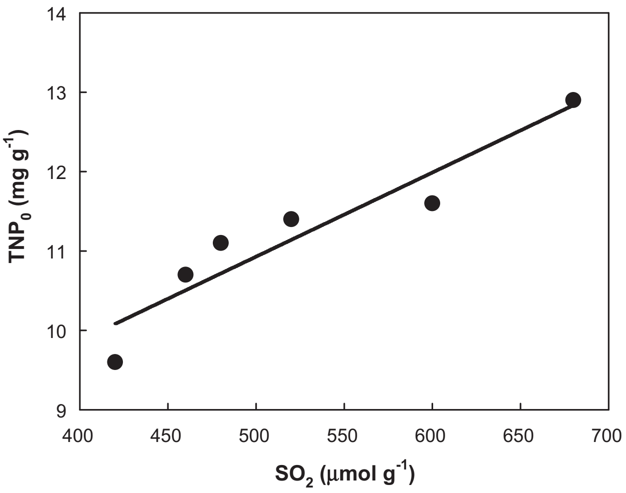

Fig. 3. Amount of TNP adsorbed on different ACs as a function of sulphur concentration in the respective carbon materials.

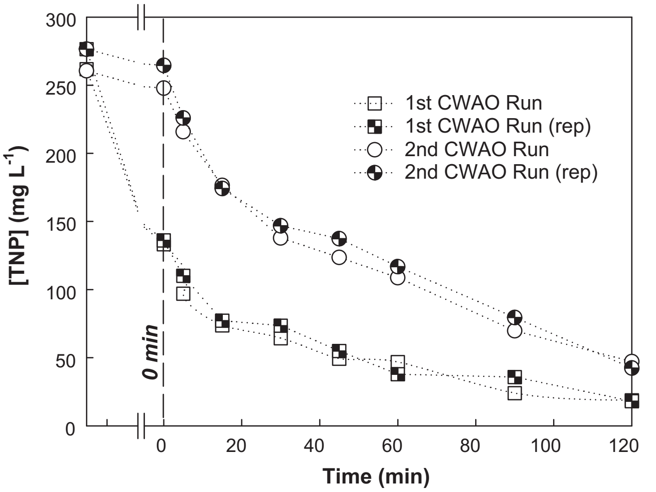

Fig. 4. Evolution of trinitrophenol concentration in CWAO experiments with sample AC5-423 in cyclic (1st and 2nd run) and repeated (rep) runs.

15 min of reaction: AC18-353 > AC10-353 > AC5-353, which seems to be related with the amount of sulphur-containing groups, i.e., 680 µmol g^{-1} > 600 µmol g^{-1} > 460 µmol g^{-1}, respectively.

The amount of nitrates formed during the reaction can give an indication of the extent of oxidation. Once again, the results were quite similar for the materials treated at 423 K but differences could be observed for those treated at 353 K. For this reason, Table 2 shows results for the set of materials treated at 353 K; for comparative purposes, data from the respective CWAO runs with AC5-423 and the original AC material are also given.

The efficiency of the set of materials treated at 353 K decreases in the order: AC5-353 > AC10-353 > AC18-353. This shows that smaller amounts of sulphur-containing groups correspond to larger production of NO_3^-. Since the introduction of sulphur-containing groups increases the acidity of the materials, the previous observation also suggests that the heterogeneous oxidation of TNP occurs to higher extent on carbon materials with lower acidity (the pH at the point of zero charge (pH_{PZC}) is 5.8, 4.1 and 2.4 for AC5-353, AC10-353 and AC18-353, respectively). However, the untreated activated carbon, although it exhibits the lowest acidity (pH_{PZC} = 7.6), yields the smallest amount of nitrates after 30 min of reaction, indicating that there are two opposite effects playing a role in this reaction: the introduction of sulphur-containing groups increases the AC efficiency, but the AC efficiency is also favoured by materials with lower acidity. The better performance of carbon materials with lower acidity was already reported when multi-walled carbon nanotubes were used as catalysts for the degradation of oxalic acid [28].

Two consecutive CWAO runs were performed in order to assess the profile of TNP oxidation with the used carbon material. The second run was performed with fresh TNP solution and with the carbon material recovered after the first run. For this set of experiments, the AC5-423 catalyst was randomly selected amongst all the treated samples, since the observed efficiencies were similar. Between each oxidation run, the recovered catalyst was washed with water and dried in the oven at 383 K for 18 h. These experiments were performed for 120 instead of 30 min. Fig. 4 shows the obtained results, together with the respective duplicates for each experiment (uncertainty of the mean for repeated experiments lower than 5%). For the fresh catalyst, the TNP concentration after the pre-heating period (t = 0 min) was about 135 mg L^{-1}, which is half of the initial concentration (270 mg L^{-1}), while the TNP concentration at t = 0 min for the used catalyst was almost the same as the initial TNP concentration loaded into the reactor. Therefore, TNP removal decreases noticeably from the first (fresh catalyst) to the second run (used catalyst), because after the first run the catalyst is saturated with TNP and/or with its reaction intermediates that remain adsorbed on the carbon material after the first run. In the second run, the TNP concentration after 60, 90 and 120 min of CWAO treatment was about 113, 75 and 45 mg L^{-1}, respectively, while TOC removal after 120 min was nearly 50%. The original untreated TNP solution was aerobically biorecalcitrant with a BOD_5 value equal to zero; nonetheless, CWAO treatment for 120 min increased BOD_5 to 10.2 mg L^{-1}, which corresponds to a BOD_5/TOC ratio of 0.24.

Table 2
Concentration of nitrates in CWAO experiments performed with different ACs (448 K, 0.7 MPa oxygen pressure, 1.3 g L^{-1} catalyst loading).

	$[NO_3^-]_{15\,min}$ (mg L^{-1})	$[NO_3^-]_{30\,min}$ (mg L^{-1})
AC	3.9	6.5
AC5-423	7.3	11.7
AC5-353	8.5	13.2
AC10-353	8.2	12.9
AC18-353	6.6	11.3

In order to study possible changes produced on the carbon material during the CWAO experiments, the treated AC was characterized by N_2 adsorption at 77 K before and after the cyclic CWAO experiments (first and second run). The obtained results are summarized in Fig. 5.

The N_2 adsorption isotherm of the fresh sample is characteristic of microporous materials (as confirmed by the large micropore volume and BET surface area collected in Table 3) with some mesoporosity. Thus, the activated carbon has a porous structure formed by micro- and mesopores. The isotherms obtained for the samples used in CWAO experiments (first and second run) show that there is a clear influence of the CWAO process on the carbon material, namely a marked decrease of S_{BET} (from 840 to 391 m^2 g^{-1}), V_{MIC} (from 0.33 to 0.16 cm^3 g^{-1}) and S_{MES} (from 180 to 88 m^2 g^{-1}) after the first run. A less pronounced decrease of these parameters was observed in the second run (from 391 to 280 m^2 g^{-1} for S_{BET}, from 0.16 to 0.12 cm^3 g^{-1} for V_{MIC} and from 88 to 58 m^3 g^{-1} for S_{MES}). The evolution of the total volume of pores (V_T), determined from the N_2 uptake at P/P_0 = 0.95, as well as the weight loss (WL) obtained by TGA are also presented in Table 3. These results indicate that adsorption of TNP or intermediate compounds occurs, as already reported for CWAO studies for TNP degradation using activated car-

Table 3
Textural characterization and weight loss of the AC5-423 material, before and after cyclic CWAO runs (first and second run).

	S_{BET} (m^2 g^{-1})	V_{MIC} (cm^3 g^{-1})	S_{MES} (m^2 g^{-1})	V_T (cm^3 g^{-1})	WL (%)
AC5-423: fresh	840	0.33	180	0.46	8.3
AC5-423: 1st run	391	0.16	88	0.22	11.1
AC5-423: 2nd run	280	0.12	58	0.16	–

bons produced by chemical activation of olive stones as catalysts [23].

The CWAO mechanism is heterogeneous in nature (as opposed to the homogeneous non-catalytic wet air oxidation), but it can take place in pores of different sizes; thus, the extent of reaction depends on the AC textural properties. The oxidation of TNP takes place into wide micropores (>0.5 nm) when highly microporous ACs are used [23], because all TNP is adsorbed in this type of porosity. The degradation of TNP will also occur on the external surface area (meso- and macropores) when ACs with low microporosity are used, because there is enough TNP available in the liquid phase [23]. Since the ACs tested in the present work have micro- and mesopores, the heterogeneous oxidation mechanism should occur in the wide micropores and larger pores.

In subsequent experiments, the photocatalytic degradation of TNP was investigated. Fig. 6 shows changes in TNP concentration as a function of irradiation time for experiments performed at initial TNP concentrations in the range 32–270 mg L^{-1}. First, it is important to observe that: (i) increased TNP concentrations (270 mg L^{-1}) are very stable regardless of the level of irradiance employed (500 or 1000 W m^{-2}) in photocatalytic experiments, (ii) TNP is not degraded without TiO_2 even when the TNP concentration is low (64 mg L^{-1}) and (iii) light penetration was not reduced at the employed catalyst load of 1 g L^{-1}, the photoactivity at 2 g L^{-1} of TiO_2 being similar to the one obtained at 1 g L^{-1}. In fact, TNP could only be effectively degraded by the photocatalytic treatment at lower concentrations and 1000 W m^{-2} of irradiation. For instance, TNP was reduced by about 78% after 120 min at an initial concentration of 144 mg L^{-1}, while total degradation was achieved in 60 and 45 min when the initial concentration was 64 and 32 mg L^{-1}, respectively. These observations confirm that the photocatalytic process is not appropriate for the degradation of high initial TNP concentrations, but it can effectively be used at lower TNP concentrations; in particular, total degradation was achieved after 60 min for concentrations lower than 64 mg L^{-1}. These results also indicate that photocatalysis can be used as a post-treatment to polish the stream generated from the CWAO of higher TNP concentrations.

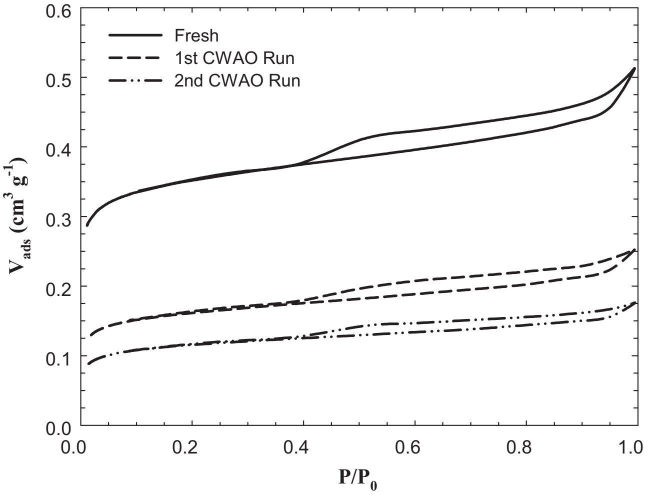

Fig. 5. N_2 adsorption isotherms at 77 K of the AC5-423 material, before and after cyclic CWAO runs (1st and 2nd run). V_{ads} is the amount of N_2 adsorbed expressed as volume of liquid.

To evaluate the eventual process integration, the final effluent from the CWAO treatment with the different modified carbon materials, was treated by photocatalysis. The obtained results are quite similar regardless of the catalyst used, namely complete TNP degradation in 60 min of photocatalytic treatment and final TOC removals of 79–87%. Since TOC removals by single CWAO were 70–74%, it is possible to enhance the TOC removal by about 10–15% with photocatalysis.

It is well known that low molecular weight carboxylic acids are the main by-products of AOPs. For this reason, organic acids were quantified after CWAO experiments performed with the modified carbon materials as well as after the integrated treatment comprising photocatalysis. Maleic acid was always detected after the CWAO experiments in concentrations near 39.7 ± 0.3 mg L^{-1}, decreasing to 33.5 ± 1.7 mg L^{-1} after the photocatalytic treatment. Malonic acid was not detected after CWAO, but seems to be formed by photocatalysis (6.5 ± 0.3 mg L^{-1}) probably due to degradation of maleic acid. Other acids, such as formic and acetic acids are formed by CWAO (12.6 ± 0.8 mg L^{-1} and 7.4 ± 0.4 mg L^{-1}, respectively) but can be effectively degraded by photocatalysis. Only trace amounts of oxalic, citric, pyruvic and valeric acids were detected in some cases (<0.4 mg L^{-1}). The presence of low molecular weight carboxylic acids in the treated solutions can also explain the fact that only a slightly pH increase (from natural solution pH of 3.1 up to a maximum of 3.6) was observed after the CWAO and photocatalytic treatments. It is important to refer that even if low molecular weight carboxylic acids are in general biodegradable compounds, it is known that some other species that were not detected can be harmful to the biological treatment even when their concentrations are lower than 1 mg L^{-1}.

In order to obtain a better picture of the integrated treatment, the results of the photocatalytic treatment of the resulting stream after 120 min of CWAO with the used AC5-423 sample and 270 mg L^{-1} TNP (Fig. 4) are shown in Fig. 6 (pre-treated). As seen, complete degradation of the residual TNP was achieved after 60 min, together with 82% TOC reduction, while the BOD_5 of the final solution increased to 35 mg L^{-1} (this corresponds to a BOD_5/TOC ratio of 2.28). Therefore, since (i) photocatalysis is not effective in treating high TNP concentrations, and (ii) the actual industrial waste would be solid at ambient temperatures but liquid at temperatures typically employed in wet oxidation, CWAO (60–120 min) could be used first followed by photocatalysis (30–120 min) for the complete removal of TNP and effective increase of effluent biodegradability.

4. Conclusions

This work proposes an integrated treatment comprising catalytic wet air oxidation and solar-driven heterogeneous photocatalysis for the efficient removal of trinitrophenol from aqueous streams. Relatively mild operating conditions (e.g., up to 120 min at 448 K and 0.7 MPa oxygen pressure) in the presence of modified

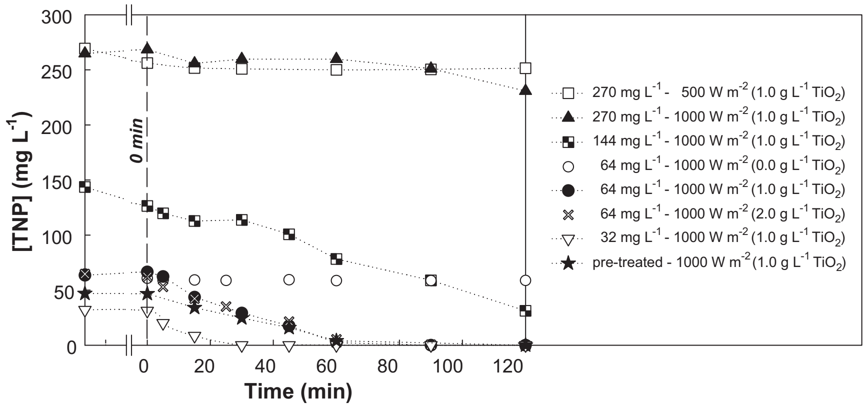

Fig. 6. Evolution of trinitrophenol concentration in photocatalytic experiments with 1 g L^{-1} of TiO$_2$-P25 at various initial concentrations and irradiance values, and blank experiments without catalyst and with 2 g L^{-1} of TiO$_2$-P25 by using 64 mg L^{-1} of trinitrophenol.

metal-free carbon materials lead to the removal of a significant amount of the contaminant by CWAO and partially improve the aerobic biodegradability of the stream. In addition, TiO$_2$ based photocatalysis can polish the resulting waters, thus removing completely the residual contaminant and further improving biodegradability.

Since the development of cost-effective and green processes is critical to achieve sustainable water treatment, coupling CWAO with TiO$_2$ photocatalysis may serve this purpose. The use of (i) materials that can act as low cost and stable CWAO catalysts (activated carbons) and photocatalysts (TiO$_2$), and (ii) renewable energy, as well as selecting the right treatment sequence and conditions, is evidently a step in the right direction.

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