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# Thermal regeneration of activated carbons saturated with *ortho*- and *meta*-chlorophenols

M. Mercedes Maroto-Valer[a,*], Ion Dranca[b,c,1], David Clifford[b],
Tudor Lupascu[c], Raisa Nastas[c], Carlos A. Leon y Leon[d,2]

[a] *School of Chemical, Environmental and Mining Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK*
[b] *The Energy Institute of the Penn State University, University Park, PA 16802, USA*
[c] *Institute of Chemistry of the Academy of Sciences, Chisinau MD 2028, Republic of Moldova*
[d] *Quantachrome Instruments, Boynton Beach, FL 33426, USA*

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## Abstract

Activated carbons (ACs) made from peach and plum stones were oxidized and impregnated with salts of Cu(II), Fe(III), Ni(II) and Cr(III). The chemically modified ACs, along with a commercial AC (S208c), were saturated with *ortho*- (OCP) and *meta*-chlorophenol (MCP) to investigate the potential for thermally regenerating the spent ACs. The thermal regeneration process was monitored by thermal analysis (TGA/DSC), gas chromatography and mass spectrometry (GC/MS). Thermal desorption profiles showed that in most cases weight losses occur in two steps (weak physisorption at ∼220 °C and strong chemisorption at ∼620 °C). Intermediate steps at ∼400 °C appeared in samples whose chemical treatments successfully weakened the interactions between strongly chemisorbed chlorophenol (CP) molecules and AC surfaces. The type and quantity of products of OCP and MCP desorption during the thermal regeneration of a spent AC depend on the chemical modification given to the AC prior to its use as CP adsorbent. Besides the original chlorophenols, thermal regeneration products can include chlorobenzene, dichloro-dibenzofuran, phenol, aliphatic and aromatic hydrocarbons, water, chlorides, carbon oxides, hydrogen, and char deposits. Mechanisms for the formation of these compounds are discussed. The char deposits built during this study did not appear to diminish the surface area or porosity of the chemically modified ACs following their thermal regeneration.

*Keywords:* Activated carbon; Thermal analysis; Adsorption properties; Impregnation; Oxidation

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## 1. Introduction

Activated carbons (ACs) are widely used as adsorbents for water purification [1]. Their principal role in water treatment is to remove pollutants that may otherwise pose health risks or introduce unpleasant odors or taste. Once an AC is spent, the material is currently discarded (e.g., by incineration) and substituted with fresh AC, or it is treated to remove the pollutant(s). Both chemical and thermal treatments are known to be effective [1], but their overall effectiveness depends on the nature of the pollutant and the adsorbent itself [2–5].

Chlorophenols (CPs) pose special challenges as pollutants. Potentially hazardous levels of CPs and their degradation products are often found in natural waters [6]. A wide variety of methods have been applied to remove CPs from water, including adsorption on ACs [7–13], bacterial degradation [14–16], exposure to immobilized enzymes [17], catalytic oxidation with metal salt solutions [18], metal-catalyzed dechlorination [19,20], oxide-catalyzed ozonation [21], ionizing radiation [22], UV photodecomposition [23,24], ultrasonication [25] and electrochemical treatments [26]. Currently, adsorption on ACs offers the most practical route for CP removal from contaminated water. However, CPs adsorb strongly on ACs, especially at low

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[*] Corresponding author. Tel.: +44 115 846 6893; fax: +44 115 951 4115.
*E-mail address:* Mercedes.maroto-valer@nottingham.ac.uk (M.M. Maroto-Valer).

[1] Current address: Department of Chemistry, University of Alabama in Birmingham, Birmingham, AL 35294, USA.

[2] Current address: Hexcel Corporation, Decatur, AL 35609, USA.

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pH values [7,8,13]. This complicates the use of ACs because a portion of the adsorbed CPs can react chemically with AC surfaces before or during the regeneration step [27,28]. Hence the degree of AC regeneration achievable and the nature of the CP degradation products are of concern.

Both thermal and chemical methods have been employed to regenerate ACs saturated with CPs. Chemical methods consist of washing the spent ACs with one or more solvents. Ferro-Garcia et al. [27,29] investigated the removal of *ortho*-chlorophenol (OCP) and *meta*-chlorophenol (MCP) from saturated olive stone-based ACs using different organic solvents. The efficiency of OCP and MCP removal was found to depend on the pore structure of the AC and the type of solvent used. Mesoporosity favored pollutant removal, but none of the organic solvents tested was able to remove more than ∼38% of the preadsorbed OCP or MCP. Moreover, it was found that MCP was more difficult to remove than OCP. This was attributed to stronger adsorbate–surface interactions with MCP than OCP. Subsequent thermal regeneration was needed to remove additional chlorophenols. However, thermal regeneration led to the degradation of the strongly bound CPs, particularly MCP molecules. This degradation has a negative impact on the efficiency and cost of spent AC regeneration. Rivera-Utrilla et al. [30] reduced this impact by using water at high pressure (150 atm) and temperature (350 °C) to remove deposits that appeared to block the porosity following chemical and thermal regeneration steps. San Miguel et al. [31] found that steam gasification at 800 °C to low burn-off levels could also be used to regenerate spent ACs. However, steam gasification also caused the undesirable loss of some of the original AC. The most cost-effective route to reusing spent ACs continues to be the direct thermal regeneration process.

This study was undertaken to assess the thermal regeneration potential of ACs (derived from agricultural by-products) following their saturation with CPs. The ACs were chemically modified by oxidation and impregnation with salts of various metals in an attempt to: (a) increase the efficiency of AC regeneration; (b) decrease the regeneration temperature via a catalytic effect.

## 2. Experimental

### 2.1. Materials

Three types of ACs were selected for this study: (a) peach stone-based AC; (b) plum stone-based AC; (c) coconut shell-based AC. Peach stones and plum stones were obtained as agricultural by-products from Moldova. Each of these materials was cleaned, ground, washed, dried at 105 °C, and sieved to obtain particles of sizes ∼2–3 mm. The grains were then carbonized in $N_2$ at 10 °C/min to 400 °C for 1 h, and subsequently activated in steam at 900 °C in a horizontal tube furnace [32]. The activated samples were ground, washed in deionized water to remove the smallest (colloidal) particles, and dried at 120 °C, to obtain particles of sizes ∼0.63–1.00 mm. In this study, the peach and plum stone-based AC will be termed CA23 and CA36, respectively. The third AC investigated was a commercially available material identified as S208c by its manufacturer (Waterlink Barnebey Suttcliffe). This coconut shell-based commercial AC is widely used in water purification applications worldwide.

Highly pure metal salts and chlorophenols were obtained from Sigma–Aldrich. In this investigation the following metal salts were used: $FeCl_3{\cdot}6H_2O$, $CuCl_2{\cdot}6H_2O$, $NiSO_4{\cdot}7H_2O$, and $Cr(NO_3)_3{\cdot}9H_2O$. Also, *ortho*-CP (2-CP or OCP) and *meta*-CP (3-CP or MCP) were selected to facilitate comparisons with prior literature reports of CP adsorption on chemically unmodified ACs [7,28].

### 2.2. AC oxidation and impregnation with metal salts

Portions of samples CA23 and CA36 were oxidized by contacting them with an excess of boiling nitric acid (50 wt.%) for 8 h. The freshly oxidized samples were neutralized with NaOH, thoroughly washed with water, and dried at 105 °C, to obtain oxidized samples labeled CAO23 and CAO36, respectively.

Selected AC samples were impregnated with various metal salts following an ion exchange method described elsewhere [33]. Briefly, 10 g portions of each AC were added to 250 ml of 1 wt.% aqueous solutions of the salts chosen. The slurries were stirred at room temperature for 72 h to allow adsorption to proceed to equilibrium. Then the samples were filtered, washed with deionized water, and dried in an air convection oven at 120 °C, to obtain the impregnated ACs.

Metal contents in various samples were determined by atomic absorption spectrophotometry (AA-3, Zeiss Jena, Germany). For that purpose, about 2 g of each sample were ashed at 500 °C. The ash was treated with 4 ml of concentrated nitric acid solution (1:1, v/v) and the product was diluted to 25 ml with deionized water. Aliquots of these diluted solutions were exposed to an acetylene–air flame (Fe, Ni, Cr) or a propane–air flame (Cu). The absorption signals were quantified by comparison with standard calibration curves generated for each metal solution.

### 2.3. Sample saturation with CPs

Small dried portions of each sample (100 mg) were soaked in 100 ml aqueous solutions containing 500 mg/l of *ortho*-CP (OCP) or *meta*-CP (MCP). The resulting slurries were thermostated at 25 °C and were mechanically shaken for 1 week to complete the sample saturation step.

### 2.4. Thermal desorption and analysis

Simultaneous thermal analysis by a variety of techniques was employed to simulate the thermal regeneration of CP-saturated (or spent) AC samples. This was accomplished using a TGA2050/SDT2960 thermal analyzer (TA Instruments, USA) capable of simultaneously recording thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) data. In each case, about 30 mg of sample was heated at 10 °C/min up to 1000 °C in ultrapure argon flowing at 130 ml/min.

Thermal desorption products from various samples were also analyzed by subjecting the samples to controlled pyrolysis coupled with in-line gas chromatography and mass spectrometry

Table 1
Metal loadings (wt.%) of selected AC samples

| Sample | Ni(II) | Fe(III) | Cu(II) | Cr(III) |
|---|---|---|---|---|
| CA23Ni | 0.22 | – | – | – |
| CAO23Ni | 0.88 | – | – | – |
| CAO23Fe | – | 1.46 | – | – |
| CAO23Cu | – | – | 1.39 | – |
| CA36Cr | – | – | – | 0.062 |
| CA36Cu | – | – | 0.94 | – |
| CAO36Cu | – | – | 1.50 | – |

(py-GC/MS). Initially the samples were heated at 40 °C for 5 min, followed by ramping at 4 °C/min to 290 °C and holding for 10 min in order to thermally desorb the unbound chlorophenols. Then the samples were heated at 10 °C/min up to 800 °C in ultrapure helium to induce further desorption by bond cleavage reactions. The GC column used was filled with either a 5% diphenyl/95% dimethyl polysiloxane (Restek XTi-5) or a (50%-phenyl)-methylpolysiloxane (Agilent DB-17ht). The range covered during MS analyses was 40–500 amu.

### 2.5. *Surface area and pore structure analysis*

Nitrogen adsorption measurements were carried out at 77 K using an automated volumetric gas sorption analyzer (Autosorb-1, Quantachrome, USA). Each sample was outgassed at 250 °C under vacuum to remove adsorbed impurities prior to its evaluation. Structural information was derived by interpreting the experimental data using standard models [34].

## 3. Results and discussion

### 3.1. *Metal loadings of chemically modified ACs*

Table 1 confirms that moderate amounts of metals were introduced in the ACs by the impregnation procedure adopted. And, as expected, oxidizing ACs led to higher metal loadings. Oxidizing CA23 increased its nickel(II) adsorption capacity by 0.66 wt.%. Similarly, oxidizing CA36 increased its copper(II) adsorption capacity by 0.56 wt.%. Oxidation promotes cation adsorption on ACs in two ways [35]: (a) it introduces new cation exchange sites on AC surfaces; (b) it lowers the point of zero charge of ACs, thereby activating additional or pre-existing sites for cation exchange. The differences in uptakes by the different metal cations can be explained in terms of differences in solution chemistry of the different salts employed [36]. In addition, in the present study the slightly lower initial molar concentration of chromium in solution (∼25 mmol/l versus ∼36–41 mmol/l of the other metals tested) may have contributed to its relatively low uptake.

For the present purposes it suffices to note that ion exchange procedures are expected to result in highly dispersed and relatively homogeneous metal particle distributions on AC surfaces [37]. In fact, a ∼1 wt.% loading of any of the metals used would correspond to up to ∼10 $m^2/g$ of surface coverage by the metal. This value is much lower than the total surface area available for CP adsorption (Section 3.2). However, it is comparable to the ∼10 $m^2/g$ monolayer coverage by OCP or MCP if one assumes a saturation uptake of ∼300 mg/g for these ACs [7]. Therefore, the metals loaded can interact to a significant extent with adsorbed CP molecules.

### 3.2. *Surface properties of chemically modified ACs*

The extent to which loaded metals or other surface sites interact with adsorbed CP molecules depends on their accessibility. In highly porous samples, either oxidation or impregnation treatments can decrease the accessibility of pollutant molecules to pores by: (a) physically blocking pore entrances, or (b) electrostatically repelling incoming adsorptives [35,36]. To examine these possibilities, the textural characteristics of selected samples were evaluated. The results are listed in Table 2. The effects of each preparation step on the textural properties of the ACs prepared for this study will be discussed in turn below.

#### 3.2.1. *Effect of fruit-stone activation treatment*

Table 2 shows that the activation of peach-based CA23 and plum-based CA36 led to the generation of high surface area,

Table 2
Textural characteristics[a] of selected AC samples

| Sample | $S_{BET}$ ($m^2/g$) | $S_{meso}$ ($m^2/g$) | $S_{micro}$ ($m^2/g$) | $S_{meso}$ (%) | $V_{total}$ (ml/g) | $V_{micro}$ (ml/g) | $V_{micro}$ (%) | Average pore diameter (Å) |
|---|---|---|---|---|---|---|---|---|
| CA23 | 957 | 110 | 846 | 11.5 | 0.57 | 0.42 | 73.7 | 24 |
| CA23Ni | 926 | 113 | 814 | 12.2 | 0.54 | 0.38 | 70.4 | 23 |
| CA23Cu | 905 | 95 | 810 | 10.5 | 0.52 | 0.39 | 75.0 | 23 |
| CAO23 | 869 | 130 | 739 | 15.0 | 0.52 | 0.35 | 67.3 | 24 |
| CAO23Cu | 839 | 120 | 719 | 14.3 | 0.50 | 0.34 | 68.0 | 24 |
| CAO23Fe | 811 | 110 | 700 | 13.6 | 0.48 | 0.37 | 77.1 | 24 |
| CA36 | 1199 | 128 | 1071 | 10.7 | 0.68 | 0.51 | 75.0 | 23 |
| CA36Cr | 1024 | 76 | 948 | 7.4 | 0.60 | 0.49 | 81.7 | 23 |
| CAO36Cu | 1028 | 91 | 937 | 8.9 | 0.59 | 0.48 | 81.4 | 23 |
| S208c | 926 | 62 | 865 | 6.7 | 0.51 | 0.44 | 83.6 | 22 |
| CAO23Cu[b] | 805 | 115 | 690 | 14.2 | 0.49 | 0.33 | 67.3 | 24 |
| CAO23Fe[b] | 875 | 110 | 745 | 12.9 | 0.51 | 0.34 | 66.7 | 23 |

[a] $S_{BET}$, $S_{meso}$ and $S_{micro}$: BET, mesopore and micropore surface areas; $V_{total}$ and $V_{micro}$: total pore volume and micropore volume. $V_{micro}$ and $S_{meso}$ were determined by de Boer's *t*-method [34].

[b] Structural parameters measured after one thermal regeneration cycle.

predominantly microporous, ACs. Sample CA36 has a ∼25% higher surface area and a ∼20% higher pore volume than CA23. However, both CA23 and CA36 have essentially the same % microporosity (∼75%) and average pore diameter (∼23 Å). The textural characteristics of both CA23 and CA36 are in fact comparable to those of the commercial coconut-based S208c. Hence, their performance for pollutant removal should not depend on relatively minor differences in their structure.

### *3.2.2. Effect of oxidation treatment*

Treatments with nitric acid have been reported to enhance or degrade the textural features of ACs, depending on the starting material and the treatment severity [35]. Table 2 shows that sample CA23 lost ∼9% of its surface area and total pore volume following its oxidation step. These losses translated to lower micropore volume and area, but did not prevent the mesopore area from increasing by ∼18%. Larger mesoporosity should facilitate the access of pollutant molecules to internal AC surfaces. However, the average pore diameter remained unchanged at ∼24 Å. These results imply that the physical changes induced by AC oxidation should not be detrimental to CP adsorption.

### *3.2.3. Effect of metal impregnation on untreated ACs*

Table 2 shows that loading untreated CA23 with Cu or Ni led to small losses in surface area (∼4%) and total pore volume (∼7%). The fact that $\%S_{\text{meso}}$, $\%V_{\text{micro}}$ and the average pore diameter remained essentially unchanged suggests that Cu and Ni are well dispersed on CA23. On the other hand, adding Cr to CA36 lowered its BET surface area by ∼15%, with the major loss occurring in the proportion of accessible mesopore area (∼41%). It is possible that the accumulation or deposition of Cr species at mesopore entrances (during adsorption or drying) may account in part for the relatively low amount of Cr detected on sample CA36 (see Table 1).

### *3.2.4. Effect of metal impregnation on oxidized ACs*

Loading oxidized sample CAO23 with Cu or Fe led to minor decreases in BET surface area (∼5%) and total pore volume (∼6%). No changes were evident in other textural parameters. The combined effect of oxidation and metal impregnation on CAO23 was a ∼14% loss in BET surface area and total pore volume. This is comparable to the total losses of ∼14% experienced by sample CA36 following oxidation and Cu impregnation. In all cases, the changes in the relative concentrations of mesopores and micropores were small. Average pore diameters remained constant at ∼24 Å regardless of the chemical modification treatments employed. These observations suggest that structural differences among these ACs are not likely to play a major role in altering CP adsorption or thermal regeneration trends of spent ACs.

### *3.3. Thermal analysis of spent ACs*

The thermogravimetric profile under flowing argon of the activated carbon CAO23Cu (oxidized with nitric acid and treated with copper salts but not exposed to CPs) and that of the same sample after saturation with OCP are presented in Figs. 1 and 2, respectively. The desorption profiles before and after OCP saturation are very different. The mass loss in the temperature range up to 140 °C observed for CAO23Cu is probably caused by the thermodesorption of physically adsorbed materials, such as water vapor, hydrocarbons, and residual oxidizing agent (Fig. 1). At higher temperatures, the oxidized and impregnated samples present a gradual and pronounced weight loss up to 1000 °C. This weight loss has been reported to be associated in part with the evolution of $CO_2$ and CO from surface oxygen groups, which were formed during oxidation [33]. Similar behavior was observed for the other samples prior to CPs saturation, where there is an early weight loss below ∼140 °C followed by a gradual weight loss up to 1000 °C. In contrast, after saturation with OCP (Fig. 2), the desorption starts at 120 °C and presents peaks at ∼220, 330, 450 and 630 °C.

All spent ACs tested in this study yielded thermal desorption profiles that fell in one of two broad categories: (a) those exhibiting weight loss in two steps, with differential thermogravimetric (DTG) curves peaking at ∼220 and ∼620 °C; (b) those exhibiting weight loss in three steps, with DTG curves peaking at ∼220, ∼400 and ∼620 °C. Representative examples of these two broad categories are shown in Figs. 3 and 4, respectively. Initial weight

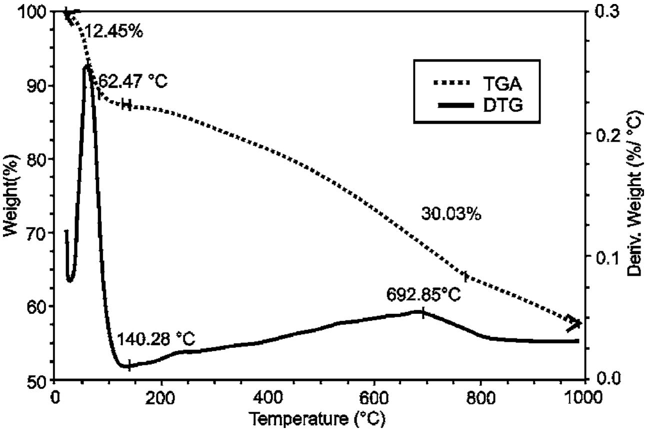

Fig. 1. TGA and DTG curves for the CAO23Cu sample prior to OCP saturation.

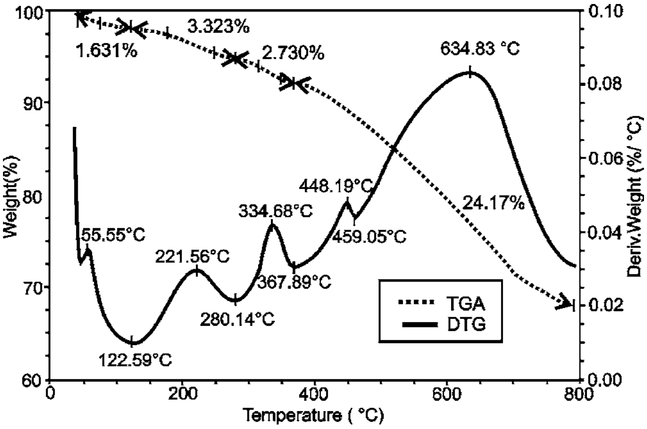

Fig. 2. TGA and DTG curves for CAO23Cu sample saturated with OCP.

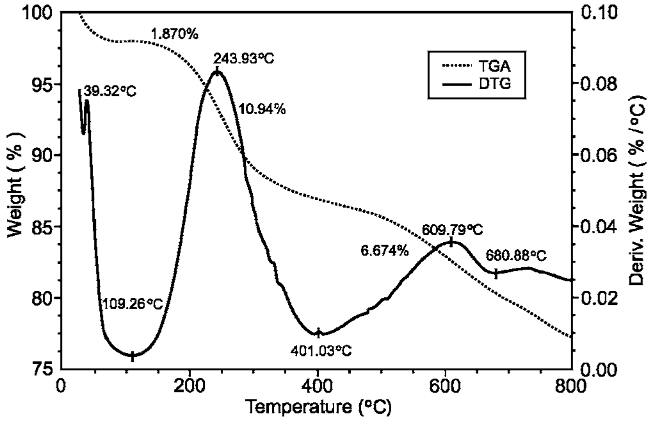

Fig. 3. Cumulative (TGA) and differential (DTG) weight loss of sample S208c saturated with MCP.

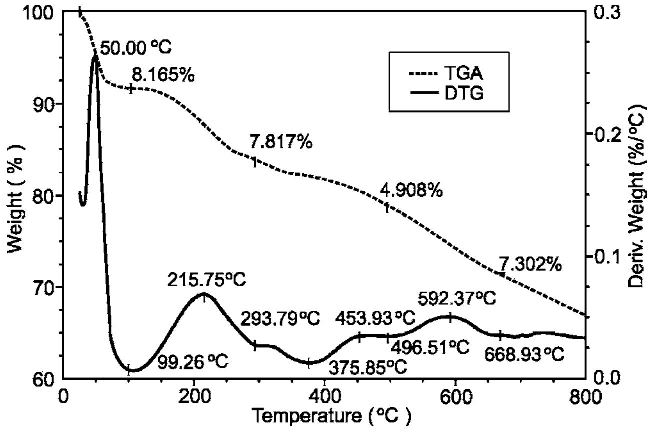

Fig. 4. Cumulative (TGA) and differential (DTG) weight loss of sample CA36Cu saturated with OCP.

losses at <120 °C were due to the evaporation of excess CPs from these ACs. These initial losses could not be quantified reliably, but appeared to amount to up to ∼20–25 wt.%, in agreement with results for oxidized but non-impregnated olive stone-based ACs reported by Ferro-Garcia et al. [27]. At temperatures between ∼120 and 800 °C, the TGA curves reported by Ferro-Garcia et al. [27] exhibited only two weight loss steps (as in Fig. 3). Those two steps were interpreted as arising from the sequential loss of physisorbed and chemisorbed CP molecules.

In this study, the appearance of one or more DTG peaks at intermediate temperatures indicates that some oxidation/impregnation treatments were effective in altering the strength of the CP–AC surface interactions. Table 3 summarizes the results of thermal analyses of selected samples. To facilitate their comparison, the following DGT peak assignments were made: (a) peak 1, at $T_{m1}$ ∼220 ± 20 °C, corresponding to physically adsorbed CPs; (b) peak 2, at $T_{m2}$ ∼400 ± 50 °C, corresponding to weakly bound chemisorbed CPs; (c) peak 3, at $T_{m3}$ ∼620 ± 60 °C, corresponding to strongly bound chemisorbed CPs. Since the samples prior to CP saturation did not present desorption peaks in the regions above, as observed after CP saturation (Figs. 1 and 2), the maximum DTG peak temperature and TGA weight losses reported in Table 3 are those directly measured from the thermogravimetric profiles.

Four samples showed distinct peaks in the intermediate $T_{m2}$ region. When OCP was the adsorbate, only sample CA36Cu showed peaks at $T_{m2}$. When MCP was the adsorbate, samples CAO23, CAO23Cu and CAO23Fe showed peaks at $T_{m2}$. Also listed in Table 3 are selected results from non-impregnated olive stone-based ACs as reported in Ref. [27]. In all cases, the wt.% values are reported directly from TGA curves, i.e., they are uncorrected for the contributions by evaporation losses, AC support pyrolysis, and metal salt decomposition. This allows a more

Table 3
Maximum DTG peak temperatures and TGA weight losses during thermal desorption analysis of spent ACs

| Sample | Chloro-phenol | Desorption peak 1 | | Desorption peak 2 | | Desorption peak 3 | | Total desorbed (wt.%) |
|---|---|---|---|---|---|---|---|---|
| | | $T_{m1}$ (°C) | wt.% | $T_{m2}$ (°C) | wt.% | $T_{m3}$ (°C) | wt.% | |
| CA23Ni | OCP | 226 | 9.3 | – | – | 650 | 22.6 | 31.9 |
| CAO23 | OCP | 225 | 11.6 | – | – | 656 | 18.4 | 30.0 |
| CAO23Ni | OCP | 205 | 10.1 | – | – | 644 | 23.4 | 33.5 |
| CAO23Cu | OCP | 223 | 7.0 | – | – | 585 | 20.8 | 27.8 |
| CAO23Fe | OCP | 205 | 5.0 | – | – | 640 | 15.1 | 20.1 |
| CA23 | MCP | 228 | 11.9 | – | – | 691 | 15.7 | 27.6 |
| CAO23 | MCP | 236 | 5.7 | 442 | 9.4 | 606 | 22.0 | 37.1 |
| CAO23Cu | MCP | 222 | 3.3 | 335[a] | 2.7 | 635 | 24.2 | 30.2 |
| CAO23Fe | MCP | 255 | 6.4 | 350 | 1.7 | 670 | 15.0 | 23.1 |
| CA36Cr | OCP | 216 | 12.4 | – | – | 600 | 14.2 | 26.6 |
| CA36Cu | OCP | 216 | 7.8 | 453 | 4.9 | 592 | 7.3 | 20.0 |
| CAO36Cu | OCP | 235 | 7.0 | – | – | 555 | 23.3 | 30.3 |
| S208c | MCP | 244 | 10.9 | – | – | 610 | 6.7 | 17.6 |
| H13[b] | OCP | 320 | n.r.[c] | – | – | 587 | n.r.[c] | 19.0 |
| H30[b] | OCP | 252 | 11.0 | – | – | 589 | 9.0 | 20.0 |
| H13 | MCP | 395 | n.r.[c] | – | – | 700 | n.r.[c] | 17.0 |
| H30 | MCP | 374 | 8.0 | – | – | 680 | 8.0 | 16.0 |

[a] Shoulder at 448 °C.

[b] Selected results for olive stone-based ACs, taken from Ref. [27].

[c] Not reported.

Table 4
Heat exchanged upon thermal desorption of chlorophenols from selected AC samples

| Sample | BET surface area ($m^2/g$) | Total pore volume (ml/g) | Chloro-phenol | Low temperature peak (kJ/g) | High temperature peak (kJ/g) |
|---|---|---|---|---|---|
| CA23Ni | 926 | 0.54 | OCP | 0.46 | 3.21 |
| CA36Cr | 1024 | 0.60 | OCP | 0.43 | 4.20 |
| H30[a] | 727 | 0.49 | OCP | 0.25 | n.r.[b] |
| H30 | 1030 | 0.68 | MCP | 0.47 | n.r.[b] |

[a] Olive stone-based AC; taken from Ref. [27].

[b] Not reported.

direct comparison of the true impact of thermal regeneration on the regeneration potential of each sample. Although the corrections cannot be accurately made in this study, it is estimated that the chemically modified samples may desorb ~50–70 wt.% of their saturating CP upon thermal treatment at 800 °C. This compares reasonably well with the ~56 and ~51 wt.% removal of OCP and MCP from olive stone-based ACs [27]. The remaining chlorophenols appear to be trapped or degraded on the thermally regenerated AC surfaces. Surprisingly, this high weight retention did not appear to have a negative effect on the surface area and porosity of the regenerated ACs. Table 2 shows that the changes in the structural parameters of representative samples were marginal. These results are consistent with those reported by San Miguel et al. [31], and suggest that the residues may be present in a highly dense and/or dispersed state on AC surfaces.

In principle, two factors can give rise to the intermediate $T_{m2}$ peaks observed in this study: (a) a portion of the physisorbed CP molecules are adsorbed more strongly following specific chemical treatments of ACs and/or (b) a portion of the strongly chemisorbed CP molecules are more weakly adsorbed following specific chemical treatments. DSC and DTA results indicate that the endothermic heat released by the lower temperature peak (attributed to physisorption) is essentially independent of the chemical treatment employed. This finding agrees with the results of Ferro-Garcia et al. [27], as shown in Table 4. However, Ferro-Garcia et al. reported that the heat released by OCP was lower than that released by MCP on two different ACs (labeled H13 and H30). This observation, and the slightly higher $T_{m1}$ values obtained by them for MCP-loaded ACs, led Ferro Garcia et al. to conclude that MCP is physisorbed more strongly to AC surfaces. In this study, MCP yielded $T_{m2}$ peaks more frequently than OCP. This also suggests that MCP molecules are more strongly bound to AC surfaces than OCP molecules. However, the measured heats of physisorption for OCP were as high as those reported in Ref. [27] for MCP (Table 4). The slightly high $T_{m1}$ values reported for MCP in Ref. [27] (see Table 3) suggest that a slight overlap may have occurred between $T_{m1}$ and $T_{m2}$ ranges (perhaps owing to inorganic impurities) in that study. It should also be noted that the heating rate employed for thermal desorption by Ferro-Garcia et al. [27] was twice as high as that used for this study. The effect of heating rate on the results for raw or chemically modified ACs has not been explored systematically to date. Nevertheless, Table 4 indicates that the most significant changes in heat evolution profiles occurred by far on the high temperature (or strong chemisorption) peaks measured during this study. This leads us to conclude that certain oxidation/impregnation treatments were successful in weakening the interaction between strongly chemisorbed CPs and chemically modified AC surfaces.

### 3.4. Desorption products from spent ACs

Pyrolysis experiments coupled with GC/MS analysis of the desorption products (py-GC/MS) enables us to analyze the desorption products released during thermal regeneration of spent ACs. Fig. 5 shows the gas chromatogram of thermal desorption products from MCP-saturated S208c. In all cases, the major product detected was the starting chlorophenol. The release of physically bound CPs at 200 °C (i.e., at temperatures slightly above their boiling point) was followed by a ramped pyrolysis step that led to significant degradation and bond rupture processes. At these higher temperatures, pristine CPs were still detected in significant amounts in all AC–CP combinations tested, with the exception of CAO23Fe, which yields chlorobenzene as its major product. Samples CA23, S208c and CAO23Cu released significant amounts of phenol, chlorobenzene, and dichloro-dibenzofuran. Sample CAO23 also released significant amounts of aliphatic and aromatic compounds in addition to chlorophenols.

Both the product selectivity and the temperatures at which desorption products are evolved are influenced by the specific AC surface modifications and the CP isomer considered. In general, the most effective treatments to lower the desorption temperatures appear to be those involving copper(II) or iron(III) chloride loading on pre-oxidized AC surfaces. This observation

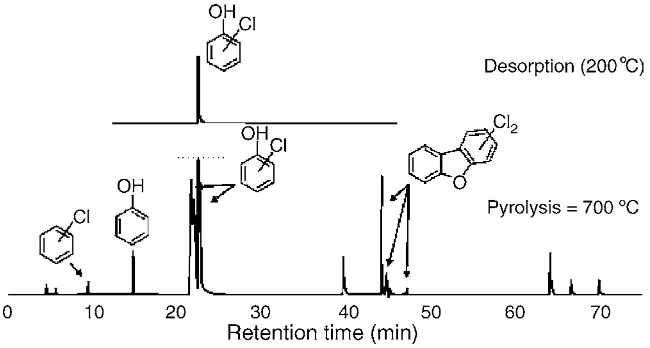

Fig. 5. Gas chromatogram of thermal desorption products from MCP-saturated S208c.

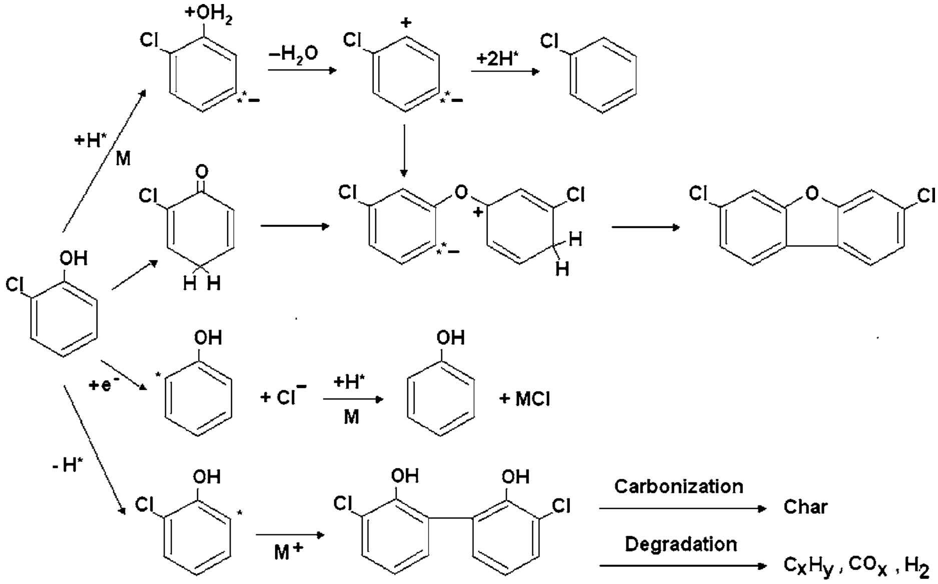

Fig. 6. Generation of thermal desorption products from chlorophenol-saturated ACs.

can also be gathered from Table 3. Note that the most effective treatment for MCP removal from spent ACs was achieved on sample CAO23 (37.1%), followed closely by CAO23Cu (30.2%). Even sample CAO23Fe presented a higher MCP% removal efficiency than the commercial sample S208c (17.6%) or the olive stone-based ACs prepared by Ferro-Garcia et al. (16–20%).

### *3.5. Mechanism of thermal regeneration of spent ACs*

Fig. 6 depicts proposed schemes for the generation of the thermal desorption products from spent ACs as detected in this study. A chlorophenol (shown as *ortho*-CP for illustration) can be physically desorbed from micropores or high sorption energy sites on ACs at a temperature slightly above its boiling point (~200 °C). At higher temperatures ($T_{m2}$), weakly chemisorbed CPs continue to desorb. However, a portion of these CP molecules are converted to other products prior to desorbing. By analogy with alcohol dehydration reactions, phenol groups can become protonated (shown in Fig. 6 as an intramolecular process mediated by a metal catalyst or an AC surface site M, such as a basic oxygen functional group [9]) and subsequently release water molecules and radical-cations. The latter can acquire hydrogen radicals ($H^*$) by abstraction to become chlorobenzene. Alternatively, these radical-cations can participate in oxidative coupling reactions with electronically rearranged (tautomerized) pyrone molecules to ultimately yield dichloro-dibenzofuran. In addition, CPs can lose chlorine by reductive dechlorination [20,38,39], and the products can form phenol molecules (by $H^*$ abstraction) or chlorides (by reaction with metal salts). In this regard, the results of this study agree with Ref. [27] in that the chlorine atoms not released with desorbed CPs during thermal regeneration were not desorbed as HCl, $Cl_2$ or low molecular weight halides [27], even though there are indications that HCl could be directly eliminated from CP molecules by a so-called “ring-walk” mechanism [40]. Finally, CPs may undergo $H^*$ abstraction themselves, and the radicals generated by this route may condense to form a carbonized char, and/or be degraded to release aliphatic or aromatic molecules, carbon oxides, and hydrogen during thermal desorption from spent ACs. In the absence of ACs, pyrolysis of OCP and MCP was reported to yield ~50–70% char, plus naphthalene and other degradation products, at 800 °C [41].

Chemical modifications of ACs alter the activity and the selectivity of the above reactions to different extents. Nearly twice the % CP removal efficiency than that reported previously [22] could be attained through a judicious choice of chemical modification (oxidation and metal impregnation) treatments. The superior % CP removal performance of oxidized and Cu(II)- and Fe(III)-loaded samples is consistent with the fact that Cu(II)

Table 5
Surface and the structural parameters of activated carbons obtained from peach stone shell and saturated with *ortho*-chlorophenol, following their thermal regeneration

| Activated carbon samples | $S_{BET}$ ($m^2/g$), virgin/regenerated | $S_{meso}$ ($m^2/g$), virgin/regenerated | $S_{micro}$ ($m^2/g$) (DR), virgin/regenerated | $V_{total}$ ($cm^3/g$), virgin/regenerated | *t*-Method $V_{micro}$ ($cm^3/g$), virgin/regenerated | Average pore diameter (Å), virgin/regenerated |
|---|---|---|---|---|---|---|
| CAO23Fe | 811/875 | 130/110 | 700/745 | 0.48/0.51 | 0.37/0.34 | 23/24 |
| CAO23Cu | 839/805 | 120/115 | 719/690 | 0.50/0.49 | 0.34/0.33 | 24/23 |

and Fe(III) chlorides are known to be good redox [42] and oxidative coupling [43] agents.

### 3.6. *Effect of thermal regeneration treatments on AC features*

The effect of thermal regeneration (at a final pyrolysis temperature of 800 °C) can be seen from Table 5. In some cases one can observe an enhancement in certain structural parameters (e.g., an increase in BET surface area, increase in mesopore volume) for CAO23Fe. For CAO23Cu, these parameters display a slight decrease. Moreover, Table 5 confirms that the char deposits built during this study did not appear to diminish the surface area or porosity of the chemically modified ACs following their thermal regeneration. Our data are in agreement with the latest work of San Miguel et al. [31] which show that thermal regeneration treatments at 800 °C led to the recovery of the original AC structural features, which in turn restored their sorption capacities. Consequently, the data in Table 5 suggests that the CP sorption capacities of regenerated ACs should not be adversely affected by the regeneration treatments. Therefore, the regenerated ACs should be recyclable without impacting the environment.

## 4. Summary and conclusions

Activated carbons (ACs) were made from agricultural sources (peach and plum stones) from Moldavia. Portions of these ACs were oxidized and impregnated with salts of Cu(II), Fe(III), Ni(II) and Cr(III) in order to modify their surface chemical properties. The chemically modified ACs, along with a commercial AC used for water purification (S208c), were separately saturated with *ortho*- (OCP) and *meta*-chlorophenol (MCP) in order to investigate the potential for thermally regenerating the spent ACs. The thermal regeneration process was monitored by thermal analysis (TGA/DSC), gas chromatography and mass spectrometry (GC/MS). Thermal desorption profiles fell into two distinct categories: (a) profiles showing weight loss in two steps, attributed to physisorption and strong chemisorption; (b) profiles showing weight losses in three (or more) steps, with the new steps appearing at intermediate desorption temperatures. Heat evolution profiles support the notion that the intermediate peaks appear in samples whose chemical treatments were successful in weakening the interactions between strongly chemisorbed CP molecules and AC surfaces. Oxidation of peach stone-based AC followed by impregnation of Cu(II) or Fe(III) proved particularly effective in promoting the removal of preadsorbed CPs during thermal regeneration. In general, the type and quantity of products of OCP and MCP desorption during the thermal regeneration of a spent AC depend on the chemical modification given to the AC prior to its use as CP adsorbent. Besides the original chlorophenols, thermal regeneration products can include chlorobenzene, dichloro-dibenzofuran, phenol, aliphatic and aromatic hydrocarbons, water, chlorides, carbon oxides, hydrogen, and char deposits. The char deposits built during this study did not appear to diminish the surface area or porosity of the chemically modified ACs following their thermal regeneration.

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