1   **LOW TEMPERATURE REGENERATION OF ACTIVATED CARBONS USING**

2   **MICROWAVES: REVISING CONVENTIONAL WISDOM**

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10   **Abstract**

11   The purpose of this work was to explore the application of microwaves for the low

12   temperature regeneration of activated carbons saturated with a pharmaceutical compound

13   (promethazine). Contrary to expectations, microwave-assisted regeneration did not lead to

14   better results than those obtained under conventional electric heating. At low temperatures

15   the regeneration was incomplete either under microwave and conventional heating, being

16   this attributed to the insufficient input energy. At mild temperatures, a fall in the adsorption

17   capacity upon cycling was obtained in both devices, although this was much more

18   pronounced for the microwave. These results contrast with previous studies on the benefits

19   of microwaves for the regeneration of carbon materials. The fall in the adsorption capacity

20   after regeneration was due to the thermal cracking of the adsorbed molecules inside the

21   carbon porous network, although this effect applies to both devices. When microwaves are

22   used, along with the thermal heating of the carbon bed, a fraction of the microwave energy

23   seemed to be directly used in the decomposition of promethazine through the excitation of

24   the molecular bonds by microwaves (microwave-lysis). These results point out the nature

25   of the adsorbate and its ability to interact with microwave are key factors that control the

26   application of microwaves for regeneration of exhausted activated carbons.

27   Keywords: microwave; regeneration; pharmaceuticals; activated carbon; microwave-lysis

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1   **1. INTRODUCTION**

2   Industrial applications of microwave technology were initiated after the commercialization

3   of domestic ovens, and since then it has been used in many fields (food processing, drying

4   processes, polymerization of resins and polymers), most of them based on the ability of

5   microwaves to heat substances (Jones *et al.*, 2002; Meredith, 1998). From a technological

6   point of view, microwaves offer a number of advantages over conventional electric heating

7   such as rapid and selective material heating, quick start-up and stopping, and high level of

8   safety and automatization. Additionally, the microwave heating of a dielectric material is a

9   volumetric heating that occurs from the interior of the material.

10 Microwave heating occurs through the interaction of the electric field component of the

11 microwaves with a) the dipoles (permanent or induced) or b) the charged particles present

12 in some materials. In this regard, carbon materials are good microwave absorbers as a

13 consequence of the interactions of the delocalized π-electrons with the microwaves, thus

14 converting microwave energy into heat. For this reason, the combination of carbon

15 materials and microwave heating has been widely explored in many fields covering soil

16 remediation processes, pyrolysis of biomass and organic wastes, and regeneration of

17 exhausted carbon beds (Menéndez *et al.*, 2010).

18 A number of studies in the literature including our own previous work have reported the

19 use of microwaves for the thermal regeneration of activated carbons (AC) saturated with

20 different pollutants (Ania *et al.*, 2004, 2005, 2007; Bo *et al.*, 2008; Cha *et al.*, 2004; Chang

21 *et al.*, 2010; Emamipur *et al.*, 2007; Fang and Lai, 1996; Hashisho et al., 2005; Kim and

22 Ahn, 2008; Kuo, 2008; Liu *et al.*, 2007; Price and Schmidt, 1997; Robers *et al.*, 2005; Tai

23 and Lee, 2007; Wang *et al.*, 2010; Yuen and Hameed, 2009; Robinson et al., 2008; Jou,

24 2006;). All of them report the supremacy of microwave-assisted regeneration of AC at

25 high temperatures over conventional heating for a number of reasons: fast heating,

26 economic savings due to shorter exposure times, and a superior regeneration efficiency

27 over a larger number of cycles. Furthermore, microwave technology allowed the activated

28 carbons to be recycled and reused several times. And it was shown that the use of this

29 technique causes no damage to the carbon, preserving the porous structure of the

1 regenerated carbons; rather, an increased in the surface area can be achieved during the first

2 regeneration cycles (Ania *et al.*, 2005, 2007).

3 On the other hand, although low temperature regeneration under conventional heating has

4 been investigated by some authors (Cabal *et al.*, 2009; Zhu, 2009), it is still not clear

5 whether this method offers clear advantages over conventional ones (beyond a reduction in

6 the energy penalty). Therefore the main objective of this study was to explore the

7 application of microwave-assisted treatment to the regeneration of AC saturated with a

8 pharmaceutical compound (i.e., promethazine). The efficiency of the low temperature

9 regeneration process and its impact on the characteristics of the adsorbent as well as on its

10 adsorptive performance along subsequent cycles was carefully investigated. The results

11 were compared with those of thermal reactivation conducted under conventional electric

12 heating in similar operating conditions. Our results show that microwave assisted

13 regeneration of exhausted carbon beds may present outstanding disadvantages over

14 conventional heating. The anomalous underperformance of microwave regeneration is

15 herein reported for the first time, and discussed in terms of the nature of the target pollutant.

16

17 **2. MATERIALS AND METHODS**

18 **2.1. Materials**

19 Powdered activated carbon (carbon A) supplied by Norit was chosen for this study. The

20 chemical composition of the carbon is shown in Table S1. Promethazine hydrochloride

21 (PMET) of 98% purity was supplied by Sigma-Aldrich (Spain). All the promethazine

22 solutions were prepared in distilled water without pH adjustment. For the purpose of

23 clarity, the structural formula of PMET is shown in the Supplementary File (Figure S1).

24 **2.2 Regeneration of the saturated activated carbon**

25 Prior to the regeneration studies, the AC was saturated with the pharmaceutical compound

26 in batch experiments using an excess of PMET solution (i.e., 10 g L^{-1}) and kept under

27 stirring for 48 h. The saturated sample (AX) was filtered and dried at 100 ºC for 2 h before

28 regeneration. The procedure and the characteristics of the microwave and electric furnaces

1   used have been described elsewhere (Ania *et al.*, 2005; Fidalgo *et al.*, 2008). For each

2   regeneration, about 10 g of the dried saturated carbon were placed in a quartz reactor and

3   purged with N_2 (60 ml min^{-1}). The inert atmosphere was maintained during the heating-up

4   and cooling-down intervals. Regeneration was carried out at different temperatures between

5   300-500 ºC varying the exposure times (5, 15, 30, 60 min). For regeneration in the

6   microwave device (MW), the time needed to reach the selected temperature was very fast

7   (ca. 5-7 min). This was not the case in the conventional electric furnace (EF). Therefore, in

8   order to minimize the differences between the operating conditions of both systems, the

9   electric device was preheated at 100 ºC and the heating rate was adjusted to the maximum

10 output value, which enabled the target temperature to be reached in 11 min. The samples

11 after regeneration will be denoted as AX (saturated carbon) followed by a reference to the

12 furnace (W and E for microwave and electric furnace, respectively), temperature and time

13 (e.g., AXW300-20 for the sample regenerated in the microwave furnace at 300 ºC for 20

14 minutes). Any likely modifications of the physicochemical features of the AC as a

15 consequence of the thermal treatment itself were evaluated by performing blank

16 experiments, which will be denoted as A followed by the reference to the device,

17 temperature and time (e.g., AW300-15).

18 **2.3 Textural and chemical characterization**

19 Textural characterization was carried out by measuring the N_2 adsorption isotherms at

20 -196 ºC in an automatic apparatus (Tristar 3000, Micromeritics). Before the experiments,

21 the samples were outgassed under vacuum at 120 °C overnight. The isotherms were used to

22 calculate the specific surface area S_{BET}, total pore volume V_T, and pore size distribution

23 using the density functional theory method (Rouquerol *et al.*, 1999).The as-received,

24 saturated and reactivated samples were further characterized by the point of zero charge

25 (Noh and Schwarz, 1989) and thermal analysis. The thermal analyzer (Labsys, Setaram)

26 was set to operate at a heating rate 15 ºC min^{-1} under a nitrogen flow rate of 100 ml min^{-1}.

27 For each measurement about 25 mg of carbon sample was used.

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1 **3. RESULTS AND DISCUSSION**

2 **3.1 Promethazine adsorption on the activated carbon**

3 The saturated carbon (AX) was initially characterized in a thermobalance (Figure 1 A), to

4 investigate the adsorbate-adsorbent interactions and their dependence on temperature. The

5 profiles revealed three desorption peaks centered at around 100, 250 and 500 ºC.
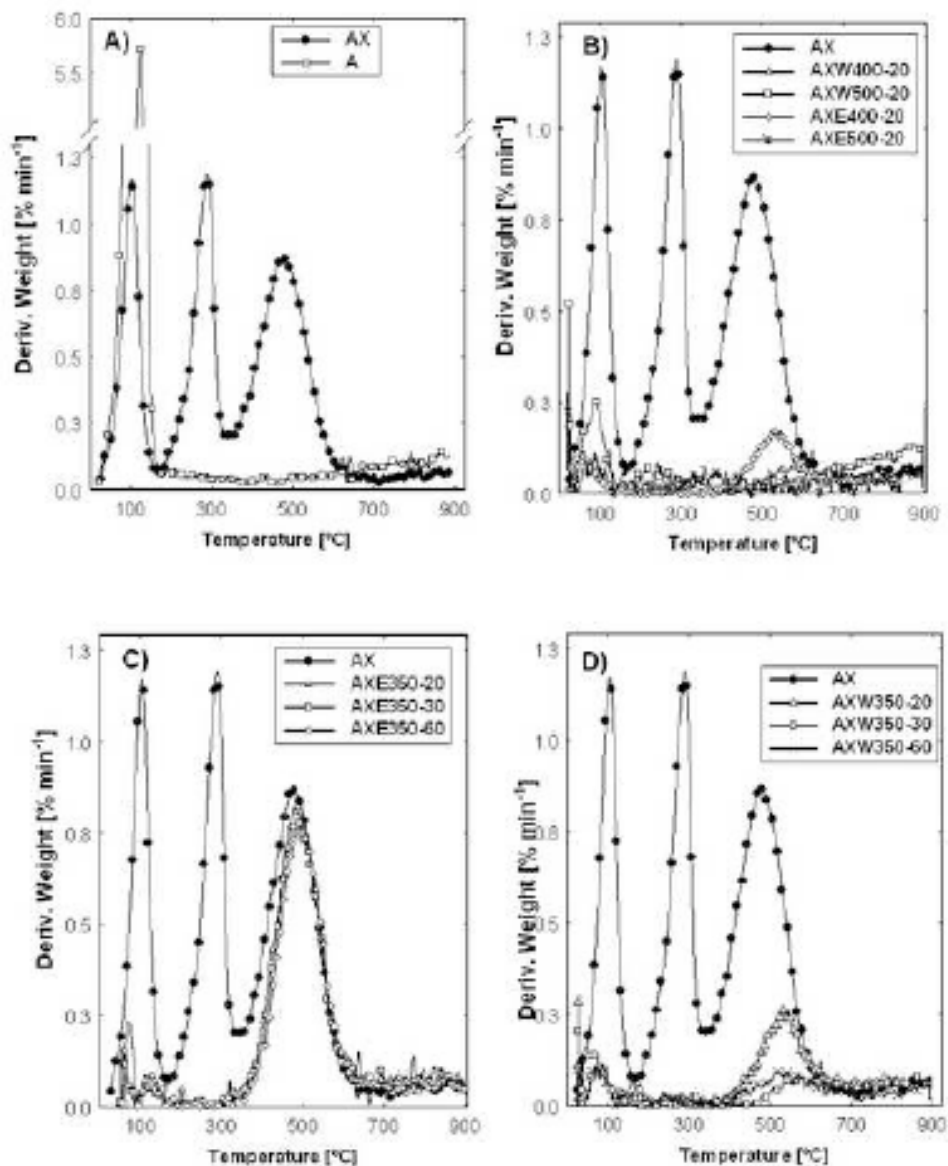
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7 **Figure 1.** Desorption profiles of the initial and saturated activated carbon (A) subjected to

8 regeneration under various conditions: B) 400 and 500 ºC in EF and MW; C) 350 ºC in EF;

9 D) 350 ºC in MW.

1   The first peak was assigned to the moisture present in the AC. Subsequent peaks were only

2   observed for the saturated carbon, and they were attributed to interactions between the

3   pharmaceutical compound and the carbon surface in different sites of adsorption. The peak

4   centered at about 270 ºC was assigned to the desorption of PMET retained in the low

5   energy adsorption sites in the AC (physisorption), whereas the second peak at higher

6   temperature was attributed to the evolution of the chemisorbed compound. Indeed,

7   calculation of the activation energies of the two peaks from the profiles at different heating

8   rates rendered 48 and 155 kJ mol^{-1}, respectively. Analogous desorption profiles showing

9   several peaks have been reported for other aromatic compounds on AC (Cabal *et al.*, 2009).

10   On the basis of the thermogravimetric profiles of the saturated carbon, it seems reasonable

11   to assume that the regeneration temperature has to be a priori high enough to promote the

12   evolution of both the physisorbed and the chemisorbed fractions (between 250 and 650 ºC).

13   Indeed preliminary studies indicated that temperatures below 300 ºC were too low (data

14   non shown), with a small desorption of the physisorbed fraction of PMET even after

15   prolonged regeneration times. Since our objective was to explore the low temperature

16   regeneration process, temperatures between 300 and 500 ºC were chosen for both the

17   microwave and the electric furnaces.

18   **3.2 Low temperature regeneration of the saturated carbon**

19   Blank experiments were conducted at temperatures between 300-500 ºC to evaluate the

20   effect of the thermal treatment itself on the adsorbent. Tables 1 and S1 show that other than

21   a slight fall in the oxygen content, the textural and the chemical properties of the AC

22   remained unchanged due to the thermal treatment. Indeed, because of the hydrophobic

23   character of the carbon and the low temperatures applied, no structural annealing was

24   expected (Rao *et al.*, 1996).

25   During the regeneration, desorption of PMET or its decomposition intermediates occurred

26   between 200-500 ºC (change in the colour of the evolved gases). Simultaneously a whitish

27   precipitate, identified as PMET by infrared analysis, was observed to condense in the cold

28   parts of the reactor. This also occurred in subsequent regeneration cycles. The extent of

29   PMET desorption was evaluated by means of thermal analysis of the regenerated samples.

1   **Table 1.** Nanotextural characterization of the exhausted activated carbon (AX) after

2   thermal regeneration at various temperatures in the electric (E) and microwave

3   (W) furnace.

	S_{BET} [$m^2\ g^{-1}$]	$V_{TOTAL}{}^a$ [$cm^3\ g^{-1}$]	$V_{MICROPORES}{}^b$ [$cm^3\ g^{-1}$]	$V_{MESOPORES}{}^b$ [$cm^3\ g^{-1}$]
A	1062	0.536	0.329	0.107
AX	250	0.162	0.046	0.051
AW350-60	1060	0.536	0.330	0.106
AW500-60	1065	0.536	0.331	0.106
AE350-60	1070	0.540	0.333	0.105
AE500-60	1095	0.550	0.340	0.107
AXW350-20	823	0.457	0.232	0.119
AXW350-30	709	0.390	0.194	0.111
AXW350-60	661	0.360	0.187	0.096
AXE350-20	534	0.307	0.094	0.085
AXE350-30	661	0.362	0.121	0.103
AXE350-60	665	0.360	0.119	0.107
AXW500-C1	578	0.325	0.163	0.101
AXW500-C3	610	0.335	0.104	0.087
AXW500-C5	591	0.338	0.104	0.040
AXE500-C1	717	0.384	0.203	0.111
AXE500-C3	757	0.395	0.217	0.105
AXE500-C5	860	0.480	0.242	0.130

[a] evaluated at relative pressure 0.99

[b] evaluated by DFT method applied to nitrogen adsorption data

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5

6   Figure 1 (plots B,C,D) shows the differential thermogravimetric profiles (DTG) of the

7   saturated carbon subjected to regeneration at different temperatures in both devices. The

8   peak assigned to chemisorbed PMET (i.e., centered at 500 ºC) was still detected in the DTG

9   profiles after regeneration at 350 ºC in both devices, indicating that desorption was

10 incomplete under these conditions. However, at 350 ºC the amount desorbed was much

11 larger when the carbon was heated in the MW. Whereas regeneration in the EF at 350 ºC

12 only provoked the desorption of the physisorbed PMET (as expected bearing in mind the

13 regeneration temperature), microwave heating induced the removal of the physi- and

1   chemisorbed PMET fraction. In other words, microwave heating seemed to be more

2   powerful than heating in a conventional furnace. PMET was almost totally desorbed by

3   heating at 350 ºC in the microwave (ca. mass loss below 1 wt.%), even though the applied

4   temperature was lower than that corresponding to the chemisorbed fraction (Figure 1 A).

5   When the treatment was carried out in the electric furnace at 350 ºC, the DTG profiles

6   show that the amount of PMET that remained inside the AC was very large (even for

7   prolonged times). Therefore, the experiments were conducted at higher temperatures. It

8   appeared that the temperature needed to be raised to 500 ºC to achieve the complete

9   desorption of PMET under conventional heating. The DTG profiles in the MW and the EF

10   at 500 ºC were rather close (Figure 1B), evidencing that the differences between both

11   devices become smaller at high temperatures. The results shown that better desorption

12   yields are obtained for microwave-assisted heating when low temperatures are used.

13   The influence of thermal regeneration on the subsequent adsorption capacity of PMET was

14   investigated at various temperatures and after successive regeneration cycles (Figures 2 and

15   S2). For the sake of comparison, the adsorption capacities of the AC exposed to thermal

16   heating (blanks) have also been included. It can be seen that the adsorption capacity of the

17   raw carbon did not change much when it was exposed to moderate temperatures in the MW

18   and EF (series AW and AE). This was somehow expected since the thermal treatment itself

19   did not substantially modify its porous structure or composition (Tables 1 and S1).
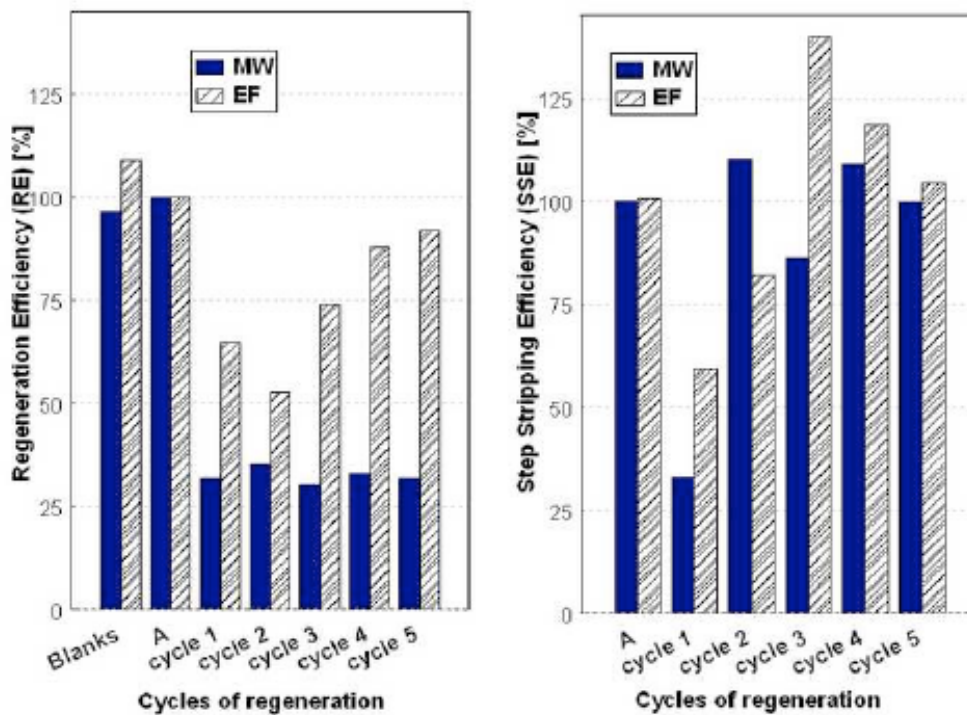
Figure 2. Regeneration Efficiency (RE) and Step Stripping Efficiency (SSE) upon regeneration at 500 ºC in the electric furnace (EF) and the microwave (MW).

Upon regeneration at 350 ºC the PMET adsorption capacity of the carbon decreased drastically for both series treated in the MW and the EF (Figure S2). The DTG profiles (Figure 1C) indicate that this behavior could be due to an incomplete desorption of PMET molecules, assuming that 350 ºC would be too low to promote the desorption of the physi- and chemisorbed fractions of PMET. This hypothesis may be valid for regeneration in the EF (as confirmed by Figure 1C), but not for the MW. A sharp decrease in PMET adsorption capacity was also observed after microwave-assisted regeneration at 350 ºC, which contrasts with the low mass loss of the DTG profiles of the corresponding samples (Figure 1D) that had suggested that PMET is completely desorbed under these conditions. Moreover, when the temperature is raised to 400 and 500 ºC, the fall in the adsorption capacity is still remarkable, but it becomes more pronounced for the sample regenerated in the MW. Indeed, it seems that the better performance of the AC (in terms of PMET retention) after regeneration in the MW compared to EF is only valid for low temperatures, whereas the opposite trend applies from 400 ºC.

1   Our results contrast with previous studies reporting a more efficient regeneration of
2   saturated AC when MW heating is applied (Ania *et al.*, 2004, 2005, 2007; Chang *et al.*,
3   2010; Hashisho *et al.*, 2005; Kuo, 2008; Liu *et al.*, 2007; Price and Schmidt, 1997; Tai *et*
4   *al.*, 2007; Wang *et al.*, 2010; Yuen and Hameed, 2009). In fact, a literature survey of the
5   studies available in the bibliography on the use of microwaves for the regeneration of
6   carbon materials saturated with organic pollutants shows that all of them reported the
7   benefits of MW-assisted heating, particularly when compared to conventional heating. A
8   summary of available data found in the literature (including our previous works) is
9   compiled in Table 2. Consequently, conventional wisdom on this topic supports the
10   supremacy of microwave over conventional electric heating as a general rule.

11   To further comprehend the herein tendency obtained for low and mild temperature
12   regeneration, we have analyzed the process considering different viewpoints that
13   encompass not only the heating mechanism (MW vs EF) but also the characteristics of the
14   system (adsorbent –adsorbate).

15   On the basis of the thermogravimetric analysis (Figure 1), it seems reasonable to assume
16   that the deterioration of the adsorption capacity of the regenerated samples could be linked
17   to the thermal cracking of the adsorbed PMET molecules inside the carbon material during
18   the regeneration step. The decomposition products would cause a pore plugging effect on
19   the adsorbent, preventing the carbon porosity from being reused in subsequent adsorption
20   cycles. This hypothesis is widely found in the literature to explain the decrease (whether
21   low or high) in the adsorption capacity of regenerated carbons, regardless of the heating
22   mechanism (Ania *et al.*, 2004, 2005, 2007; Cabal *et al.*, 2009; Chang *et al.*, 2010; Hashisho
23   *et al.*, 2005; Kuo, 2008; Liu *et al.*, 2007; Price and Schmidt, 1997; Wang *et al.*, 2010; Yuen
24   and Hameed, 2009). However the thermal decomposition of PMET would be expected to
25   occur in both the EF and the MW, and our results suggest that the thermal cracking of this
26   compound is accelerated under microwave irradiation, underlying the importance of the
27   nature of the adsorbate.

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1   **Table 2.** Summary of previous studies on the regeneration of carbonaceous materials using

2   microwave technology. Data of available publications according to ISI Web of

3   Knowledge, 20/12/2010. Search terms: (a) ''microwave AND regeneration AND

4   carbon'', (b) ''carbon AND regeneration AND microwave*''.

Compound	Reference	Remarks
Ethanol, acetone	Fang, 1996	Low carbon losses upon MW irradiation of the saturated carbon; adsorption capacity is maintained upon 3 cycles.
5-chlorophenol	Price, 1997	High level of adsorption capacity after several cycles
Phenol	Ania, 2004	MW outperforms conventional regeneration
Phenol	Ania, 2005	MW outperforms conventional regeneration
Salicylic acid	Ania, 2007	MW outperforms conventional regeneration
Toluene, ethyl acetate, methylene chloride	Cha, 2004	MW restored the original adsorption capacity
Methy-ethyl-ketone	Emamipour, 2007	Dynamic desorption tests; good performance of a microwave swing adsorption system
PAH, VOCs,	Hashisho, 2005	Rapid regeneration; adsorption capacity is maintained after 3 cycles
Acid Orange	Bo, 2008	Initial adsorption capacity was maintained after 2 cycles
Benzene	Kim, 2008	Initial adsorption capacity maintained after 5 cycles
Reactive Red	Kuo, 2008	MW regeneration outperformed NaOH extraction
Reactive Black 5	Chang, 2010	Adsorption capacity is maintained over 7 cycles
2,4,5-trichlorobiphenyl	Liu, 2007	Adsorption capacity maintained high level after five adsorption/regeneration cycles.
Methy-ethyl-ketone	Tai, 2007	MW-induced regeneration restored initial capacity
Dye Reactive Red 3BS	Wang, 2010	High regeneration efficiencies achieved after several cycles; fall in adsorption capacity due to thermal cracking under MW
Acid Orange 7	Yuen, 2009	Initial adsorption capacity and rate maintained at high a level over several cycles. The damage to carbon upon MW irradiation was lower than for conventional regeneration methods.
Triethylamine, acetic acid	Robers, 2005	Best results obtained with MW and ultrasonic–water regeneration
n-alkanes (C_{12}–C_{20})	Robinson, 2008	Technological and energetic advantages of MW-assisted over conventional gas stripping operations are reported in the removal of oils from contaminated drill cuttings.
Pb (II)	Jou, 2006	MW allows the immobilization of heavy metal ions in contaminated soil wastes.

5

6   Promethazine is a polar compound that would so be expected to easily absorb microwaves.

7   Thus, it might occur that along with the heating of the AC (which is a good microwave

1   absorber), a fraction of the microwave energy supplied is being absorbed by the PMET

2   molecules retained in the carbon. The heating mechanism using microwave irradiation is

3   based on a quick molecular level heating. Therefore, the interactions between microwaves

4   and the chemical bonds of the PMET molecules may eventually facilitate the quick thermal

5   cracking of the compound (microwave-lysis), and consequently favor the formation of coke

6   deposits that would block the microporosity of the regenerated adsorbent. The ability of

7   microwaves to break down a given compound would depend on its chemical nature and

8   could be governed by its polarity, polarizability, stability, aromaticity, and so forth.

9   For instance, previous works on the regeneration of AC saturated with two aromatic

10   compounds (phenol and salicylic acid) revealed different behaviors in each case. Salicylic

11   acid is strongly resistant to thermal cracking (both in MW and EF) due to its ability to

12   sublimate at 300 ºC. In contrast, phenol easily undergoes thermal breakdown when it is

13   heated at high temperatures, although no enhancement is observed when microwaves are

14   used maybe due to its high aromatic character (Ania *et al.*, 2004, 2005).

15

16   **3.3 Regeneration efficiency over subsequent cycles**

17   Successive adsorption-regeneration cycles were performed at 500 ºC and the overall

18   efficiency of the regeneration process was evaluated by means of the regeneration

19   efficiency (RE) and the single Step Stripping Efficiency (SSE) parameters (Figure 2)

20   calculated as:

21   $RE = Q_i/Q_o * 100$ (1)

22   $SSE = Q_i/Q_{i-1} * 100$, Q_{i-1} (2)

23   where Q_i is the adsorptive capacity of the regenerated carbon in a given cycle i, and Q_o the

24   adsorptive capacity of the fresh carbon.

25   The RE gradually decreased after several cycles, this effect being more pronounced after

26   the first cycle and when regeneration was carried out using microwave heating (i.e., values

27   below 40% after the first cycle). Comparatively, better results were obtained with

28   conventional heating. After falling during the first cycle, the RE recovered slightly when

1   the regeneration was conducted in the EF, reaching values above 80% after 4 cycles. In

2   contrast, the regeneration efficiency of the samples heated in the MW was very poor and

3   the life span of the AC was dramatically reduced with the number of cycles.

4   The stripping efficiency -SSE- is defined as the ratio between the adsorption capacity of a

5   given cycle and that of the previous one, and allows the desorption yield in the different

6   cycles to be evaluated. Unlike RE, the SSE values did not decrease with the number of

7   cycles with exception of the first one. The gradual increase observed after the second

8   regeneration cycle, particularly for the samples heated in the conventional furnace, suggests

9   that the desorption of fresh PMET molecules from the regenerated carbon becomes easier

10   with the number of cycles. SSE was lower in the MW series, confirming that regeneration

11   for every cycle is more efficient when conventional heating is used.

12   As previously mentioned, the regeneration time (30 min) was chosen on the basis of

13   negligible mass loss of the regenerated samples by thermal analysis. However, to determine

14   whether 30 min was long enough for complete desorption of the retained pollutant, the

15   saturated carbon was also subjected to a thermal treatment at 500 ºC for 60 and 90 min. The

16   RE values were found to be similar to those after heating for 30 min (i.e., 80, 78 and 77%

17   for 30, 60 and 90 min, respectively), demonstrating that longer periods of time would only

18   increase the energy consumption of the process. Similarly, regeneration at 800 ºC -the usual

19   temperature applied in industrial processes- followed the same trend in RE (below 80% in

20   the first cycle).

21   **3.4 Effect of MW regeneration on the textural properties of the activated carbon**

22   Detailed characteristics of the pore structure of the series of as-received, saturated and

23   regenerated carbons are presented in Table 1). As mentioned above, thermal treatment by

24   itself (either in MW or EF) did not modify the textural properties and composition of the

25   carbon. As a general rule, the values of specific surface area and micropore volume of the

26   raw AC were not restored after regeneration, although the shape of the gas adsorption

27   isotherms was not changed (data not shown).

28   For the series of carbons treated in the MW at 350 ºC, a gradual fall in the porosity of the

29   regenerated samples was observed with regeneration time. This finding confirms the pore

1   plugging effect mentioned above. Thus, along with the partial desorption of PMET upon

2   microwave irradiation, the adsorbed molecules could also be irreversibly bound or

3   degraded inside the AC due to their interaction with the microwaves (microwave-lysis).

4   Comparatively, the blockage of the porosity was greater in the case of the carbon

5   regenerated at 350 ºC in the EF than under microwave heating. This seems reasonable

6   considering that at this temperature a large fraction of PMET still remained inside the

7   carbon skeleton (Figure 1C). However, as the regeneration temperature was raised, the

8   collapse of the porous features become more important for the samples treated in the

9   microwave.

10   The most pronounced deterioration of the porous features after successive regeneration

11   cycles corresponded to the regeneration carried out at 500 ºC in the microwave, which is in

12   good agreement with the fall observed in adsorption capacity (Figure S2). The damage to

13   porosity indicates that the thermal cracking of PMET (and thus pore blockage in the

14   regenerated samples) became more evident with the rise in temperature. In contrast, when

15   regeneration was carried out in the EF the porous features of the initial carbon were

16   somehow recovered with the number of cycles. This would explain the increase in the RE

17   and SSE parameters after the second and subsequent cycles, pointing to a gradual recovery

18   of the adsorption capacity of the samples regenerated in the conventional furnace

19   (Figure S2).

20   In sum, improvement of regeneration efficiency would be expected if the regeneration were

21   carried out under oxidizing atmosphere (steam, CO_2, air), which could promote the

22   activation of the coke deposits formed due to thermal cracking of the adsorbate, thereby

23   counteracting the pore plugging effect.

24

25   **4. CONCLUSIONS**

26   As a general rule, microwave heating has long been considered a powerful technology for

27   the regeneration of loaded activated carbons (based on previous works with different

28   pollutants) due to its superior performance vs conventional heating in terms of regeneration

1 efficiency upon several cycles, adsorption capacities of regenerated samples and economic
2 savings due to the fast microwave response. The results of this study show that if the nature
3 of the pollutant is regarded, the use of microwave heating in the regeneration of exhausted
4 carbons does not guarantee a good performance of the regenerated samples upon cycling.
5 This has been herein illustrated with the low temperature regeneration of an activated
6 carbon loaded with a pharmaceutical (promethazine), where microwave-induced
7 modifications of the pollutant have shown to be determinant in the cycle-ability and
8 adsorption performance of the regenerated carbon.

9 Incomplete desorption occurred in both devices (EF and MW) when the applied
10 temperature was too low to promote desorption of the physi- and chemisorbed fractions of
11 the adsorbed compound (even after long regeneration times). Increasing the regeneration
12 temperature favored the desorption of the retained compound, although still low
13 regeneration yields were obtained due to thermal cracking of the adsorbate inside the
14 porosity of the AC. Contrary to expectations based on previous works carried out on a
15 variety of pollutants, this effect was more pronounced in the samples regenerated by
16 microwave irradiation. For this particular compound (promethazine), it seems that
17 microwave heating leads to a decrease in the efficiency of the regeneration process, due to
18 an enhanced cracking of the pollutant caused by direct interaction between the adsorbate
19 and the microwaves (microwave-lysis).

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1   **REFERENCES**

2   Ania, C.O., Menendez, J.A., Parra, J.B., Pis, J.J., 2004. Microwave-induced regeneration of

3   activated carbons polluted with phenol. A comparison with conventional thermal

4   regeneration. Carbon 42, 1377–1381.

5   Ania, C.O., Menendez, J.A., Parra, J.B., Pis, J.J., 2005. Effect of microwave and

6   conventional regeneration on the microporous and mesoporous network and on the

7   adsorptive capacity of activated carbons. Microporous Mesoporous Mater. 85, 7-15.

8   Ania, C.O., Menendez, J.A., Parra, J.B., Pis, J.J., 2007. Microwave-assisted regeneration of

9   activated carbons loaded with pharmaceuticals. Water Res. 41, 3299-3306.

10   Bo, L.L., Wang, X.C., Lu, L., 2008. Study on the purification and regeneration of activated

11   carbon by microwave and its adsorption capacity for Acid Orange. J. Xian Univ. Archit.

12   Technol. 40, 413-417.

13   Cabal, B., Tsyntsarski, B., Budinova, T., Petrov, N., Parra, J.B., Ania, C.O., 2009.

14   Improved phenol adsorption on carbons after mild temperature steam regeneration. J.

15   Hazard. Mater. 166, 1289-1295.

16   Cha, C.Y., Wallace, S., George, A.H., Rogers, S., 2004. Microwave Technology for

17   Treatment of Fume Hood Exhaust. J. Environ. Eng. 130, 338-348.

18   Chang, S.H., Wang, K.S., Liang, H.H., Chen, H.Y., Li, H.C., Peng, T.H., Su, Y.C., Chang,

19   C.Y., 2010. Treatment of Reactive Black 5 by combined electrocoagulation–granular

20   activated carbon adsorption–microwave regeneration process. J. Hazard. Mater. 175, 850–

21   857

22   Emamipour, H., Hashisho, Z., Cevallos, D., Rood, M.J., Thurston, D.L., Hay, K.J., Kim,

23   B.J., Sullivan, P.D., 2007. Steady-State and Dynamic Desorption of Organic Vapor from

24   Activated Carbon with Electrothermal Swing Adsorption. Environ. Sci. Technol. 41, 5063-

25   5069.

26   Fang, C.S., Lai, P.M.C., 1996. Microwave regeneration of spent powder activated carbon,

27   Chem. Eng. Commun. 147, 17-27.

28   Fidalgo, B., Dominguez, A., Pis, J.J., Menendez, J.A., 2008. Microwave-assisted dry

29   reforming of methane. Int. J. Hydrogen Energy 33, 4337-4344.

Hashisho, Z., Rood, M., Botich, L., 2005. Microwave-Swing Adsorption To Capture and Recover Vapors from Air Streams with Activated Carbon Fiber Cloth. J. Environ. Sci. Technol. 39, 6851-6859.

Jones, D.A., Lelyveld, T.P., Mavrofidis, S.D., Kingman, S.W., Miles, N.J., 2002. Microwave heating applications in environmental engineering — a review, Resour. Conserv. Recycl. 34, 75–90.

Jou, C.-J.G. 2006. An efficient technology to treat heavy metal-lead-contaminated soil by microwave radiation, Journal of Environmental Management, 78, 1-4.

Kim, K.J., Ahn, H.G., 2008. A study on adsorption characteristics of benzene over activated carbons coated with insulating materials and desorption by microwave irradiation. J. Korean Ind. Eng. Chem. 19, 445-451.

Kuo, C.Y., 2008. Desorption and re-adsorption of carbon nanotubes: Comparison of sodium hydroxide and microwave irradiation processes. J. Hazard. Mater. 152, 949–954.

Liu, X., Gang, L., Han, W., 2007. Granular activated carbon adsorption and microwave regeneration for the treatment of 2,4,5-trichlorobiphenyl in simulated soil-washing solution, J. Hazard. Mater. 147, 746–751.

Menéndez J.A., A. Arenillas, B. Fidalgo, Y. Fernández, L. Zubizarreta, E.G. Calvo, J.M. Bermúdez, 2010. Microwave heating processes involving carbon materials, Fuel Processing Technology 91, 1–8

Meredith, R., 1998. Engineers' Handbook of Industrial Microwave Heating. The Institution of Electrical Engineers, London, UK.

Noh, J.S., Schwarz, J.A., 1989. Estimation of the point of zero charge of simple oxides by mass titration. J. Colloid Interf. Sci. 130, 157-164.

Price, D.W., Schmidt, P.S., 1997. Microwave regeneration of adsorbents at low pressure: Experimental kinetics studies, J. Microwave Power EE. 32, 145-154.

Rao, A.M., Fung, A.W.P., Dresselhaus, M.S., Endo, M., 1996. Structural characterization of heat-treated activated carbon fibers. J. Mater. Res. 7, 1788-1794.

Robers, A., Figura, M., Thisen, P.H., 2005. Desorption of odor-active compounds by microwaves, ultrasound, and water. AICHe J. 51, 502-510.

1   Robinson, J.P., Kingman, S.W., Onobrakpeya, O. 2008. Microwave-assisted stripping of oil

2   contaminated drill cuttings, Journal of Environmental Management, 88, 211-218.

3   Rouquerol, F., Rouquerol, J., Sing, K., 1999. Adsorption by Powders & Porous Solids,

4   Academic Press, London.

5   Tai, H.S., Lee, C.H., 2007. Desorption of methy-ethyl-ketone from granular activated

6   carbon with microwave radiation, Environ. Prog. 26, 299-303.

7   Wang, J., Peng, X., Luan, Z., Zhao, C., 2010. Regeneration of carbon nanotubes exhausted

8   with dye Reactive Red 3BS using microwave irradiation. J. Hazard. Mater. 178, 1125–

9   1127.

10   Yuen, F.K., Hameed, B.H., 2009. Recent developments in the preparation and regeneration

11   of activated carbons by microwaves, Adv. Colloid Interf. Sci. 149, 19–27

12   Zhu, R., Zhu, J., Ge, F., Yuan, P. 2009. Regeneration of spent organoclays after the

13   sorption of organic pollutants: A review, Journal of Environmental Management, 90, 3212-

14   3216