Comparison among Chemical, Thermal, and Electrochemical Regeneration of Phenol-Saturated Activated Carbon[†]

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The regeneration of phenol-saturated activated carbon (AC) by chemical, thermal, and electrochemical techniques has been studied and compared in this work. The influence of the solute (NaOH) concentration and the temperature on the conventional chemical and thermal regenerations, respectively, has been analyzed and compared to the optimal results achieved for the electrochemical method. Comparisons are based on the analysis of the remaining products after regeneration, the regeneration efficiency (RE), and the recovery of the textural properties of a commercial phenol-saturated granular AC. Results show that very low-porosity recoveries are achieved by chemical regeneration, independent of the NaOH concentration, and the optimal REs are 20% lower than those obtained by the thermal and electrochemical ones. REs obtained by thermal treatment in an inert atmosphere increase with the temperature up to 750 °C, reaching the highest REs (80−86%) and porosity recoveries at $T > 600$ °C. The cathodic regeneration in the NaOH medium in an undivided cell, where phenolate desorption is favored and surface blockage is minimized, yields similar RE values (80−85%) and slightly higher porosity than those obtained by thermal treatment. Temperature-programmed desorption (TPD) experiments show that, whereas phenol is almost completely removed electrochemically after 3 h, a temperature of at least 450−600 °C is required to achieve similar results by thermal regeneration.

1. Introduction

Adsorption on activated carbons (ACs) is a technology that has found widespread application to the treatment of industrial water effluents to meet environmental legislations. Specifically, this is the most frequently used method for the removal of highly toxic, refractory, and non-biodegradable phenolic compounds from aqueous solutions.[1]

During the use of the AC, its porosity becomes progressively saturated. Once it is exhausted, AC can be disposed off by incineration or deposited in a landfill, which means a high economical and environmental cost. Alternatively, AC can be reused after an appropriate regeneration step. In view of the high production cost and consumption of AC,[2] the economics and feasibility of the adsorption technology on an industrial scale greatly depends upon the reactivation and reuse of the spent AC.[3] Therefore, more efficient regeneration methods need to be developed and established on an industrial scale.

The ideal AC regeneration process involves the desorption of the pollutants concentrated in the AC without any modification of the initial textural properties of the carbonaceous material. The importance of the regeneration process has stimulated intense research, and hence, a variety of regeneration techniques for exhausted ACs have been proposed.[4−35] However, methods in current use are either not efficient enough or too expensive.

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Because of its simplicity and high efficiency, thermal regeneration in an inert[9−23] or oxidizing atmosphere[18,21−23] is the most widely used regeneration method. However, it has some important problems: (i) it needs *ex situ* operation; that is, exhausted AC has to be transported to a reactivation center, regenerated in a furnace at high temperature, and transported back to the in-process plant; (ii) it may introduce changes in the AC properties, which can modify the adsorption properties; (iii) high energy costs are required to keep the regeneration temperature at about 800−850 °C; and (iv) the loss of AC by attrition, burnoff, and wash-out in the regeneration is considerable (10−20% by weight).[8,20,23] These problems become more serious when the number of regeneration cycles increases.[13,18]

Chemical regeneration is another widely studied regeneration method.[24−30] The method consists of the desorption of adsorbed species, by means of a solvent[10,11,24,25] or a solution containing any other species that modifies the adsorption equilibrium (e.g., NaOH).[24,26−30] In both cases, desorption or extraction of adsorbates is a simple and inexpensive method; however, the regeneration efficiency (RE) is usually below 70%,[11,24] and about 10−15% of the pores of the AC become blocked by the solvent.[11,22,24] Moreover, pollutants are not destroyed, and solvent reuse requires a more expensive purification step, so that it is only recommended when the adsorbate is a high-value product. Another important family of chemical regeneration methods are based on an induced decomposition of the adsorbate by an oxidizing agent.[8,24] In this approach, different oxidizing agents have been studied,[8,24] resulting in a broad variety of REs. In all cases, the main benefit comes from the destruction of the adsorbed pollutant. However, the use of oxidizing conditions not only affects the pollutants but also modifies and/or destroys the original texture and surface chemistry properties of the AC.[8]

Although comparatively less studied,[31−35] electrochemical regeneration appears as a very promising alternative, which presents some advantages compared to the conventional methods. Essentially, it can be conveniently operated *in situ*, with lower energy consumption and short time requirements. The electron is the only reagent, and it requires simple handling and equipment. Moreover, the proper setting of the applied current (or electrode potential) and other operational variables (such as electrolysis time, electrode composition, etc.) can allow for the recovery, modification of organic pollutants into less hazardous compounds, or even complete mineralization.[36,37] In our particular case, it is well-documented that phenol and phenol derivatives can be electro-oxidized both anodically, via direct electron transfer or indirect oxygen transfer from hydroxyl radicals coming from water electrolysis,[38−43] and cathodically, through indirect oxidation by electrogenerated peroxide species.[44−46] In both anodic and cathodic treatments, phenol transformation proceeds through a rather complex mechanism, yielding hydroquinone and benzoquinone as main reaction intermediates. Provided that sufficient electrolysis time is left, these intermediates are further oxidized to a number of less toxic and much more biodegradable organic acids (e.g., maleic, fumaric and oxalic acids) and eventually to CO_2.

We have recently studied the electrochemical regeneration of a commercial granular AC saturated with phenol.[35] The influence of different experimental parameters on the RE and the textural properties of a commercial phenol-saturated granular AC were analyzed, and a general electrochemical regeneration mechanism was proposed. The best results were obtained for the cathodic regeneration in NaOH, in an undivided cell, at moderate current and regeneration times.

However, the efficiency and performance of the different regeneration methods cannot be directly compared to each other if the regenerated carbon materials, the adsorbate, and/ or uptake are different. It is well-known that both the adsorption and regeneration capacities of ACs strongly depend upon their unique physicochemical properties, mainly determined by the carbon precursor nature and the activation procedure. Therefore, a comparison among different regeneration methods has to be performed for the same saturated AC.

In the literature on AC regeneration, only a few contributions[8,10,11] focus on the comparison of different regeneration methods for the same carbon material but, to the best of our knowledge, no comparison including the electrochemical regeneration technique has been reported to date. This work is intended to fill this gap and make a comparative study between electrochemical methods applied under their optimal experimental conditions and the more conventional NaOH chemical and thermal regenerations of the same AC material saturated with phenol. Sodium hydroxide has been chosen in this study because it is used as an electrolyte and blank experiment in the electrochemical regeneration and because it has been found to be one of the most efficient treatments for dissolving and removing weak organic acids from AC.[26,27] The influence of the NaOH concentration and the temperature

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Table 1. Textural Characterization of the Original (W), Saturated (Wsat), and Chemically Regenerated AC Samples with Different NaOH Solution Concentrations

sample	S_{BET} (m²/g)	$V_{DR}(N_2)$ (cm³/g)	$V_{DR}(CO_2)$ (cm³/g)
W	875	0.37	0.29
Wsat	145	0.05	0.09
W0.0OH⁻	170	0.06	0.08
W0.1OH⁻	280	0.10	0.11
W0.5OH⁻	310	0.12	0.13
W1.0OH⁻	350	0.14	0.15

on the chemical and thermal regenerations, respectively, is analyzed.

The comparison is based on the analysis of the remaining products after regeneration, the determination of REs, and the recovery of the textural properties of the original carbon material. This latter issue is seldom considered in the studies on AC regeneration, despite being essential to understand the regeneration process. The resulting data show that the electrochemical method exhibits the best overall performance, although additional specific engineering aspects should be considered to determine the suitability of a given AC regeneration method.

2. Experimental Section

2.1. Materials. The commercial granular AC selected for this work was provided by Waterlink Suctliffe Carbons (207A, pH_{PZC} = 9, mesh = 12 × 20) and is referred to as W. The textural properties of this AC are listed in Table 1. The similarity between micropore volumes measured with N_2 and CO_2 indicates that the employed AC presents a relatively narrow microporous structure, commonly used for the removal of phenol and other aromatic organics in wastewaters.

Before saturation, the AC samples were washed several times with distilled water and dried in an oven at 80 °C overnight. Phenol solutions were prepared using a Merck p.a. chemical, and for the preparation of the NaOH solutions, sodium hydroxide pellets p.a. (Merck) were used, employing in both cases distilled water.

2.2. Phenol Saturation of the AC. Adsorption experiments for the saturation of the ACs were obtained from closed-batch experiments. Phenol solutions (100 mL) with an initial concentration of 20 000 mg/L were added to 100 mL glass flasks with 5 g of AC. The flasks were covered to avoid evaporation and placed on a shaker at a constant shaking speed with a thermostatically controlled bath at 30 °C. These experimental conditions were maintained for 7 days to attain equilibrium. The equilibrium time had been determined previously from preliminary kinetic studies. After the equilibrium period, the ACs were filtered and the phenol concentration in the residual solution was measured by UV−vis absorption spectroscopy (Jasco V-670 UV−vis−NIR spectrometer), at the wavelength of 270 nm. Before electrochemical regeneration experiments, the saturated AC samples were dried in an oven using very mild conditions (40 °C) until a constant mass was achieved.

2.3. Regeneration Methods. *2.3.1. Chemical Regeneration of AC.* Chemical regeneration experiments were carried out by treating 2.5 g of the phenol-exhausted AC with 50 mL of NaOH solution for 3 h at 30 °C. Preliminary kinetic studies have shown that this is the optimal time to desorb most of the adsorbed phenol. Different concentrations were studied to analyze the effect of the NaOH concentration (0.0, 0.1, 0.5, and 1.0 M). The chemically regenerated AC samples will be denoted in the text with the letter W, followed by a number indicating the NaOH concentration, and followed by OH⁻ to indicate the NaOH solution.

2.3.2. Thermal Regeneration of AC. Thermal regeneration experiments were conducted at different temperatures (300, 450,

600, 750, and 900 °C) in a horizontal tube furnace, using a nitrogen flow rate of 100 mL/min and a heating rate of 10 °C/min. The selected temperature for the thermal treatment was maintained for 2 h. The thermally regenerated AC samples will be named with the letter W, followed by the letter t referring to thermal regeneration, and a number indicating the temperature.

2.3.3. Electrochemical Regeneration of AC. The electrochemical regeneration of AC has been carried out in a filter-press electrochemical cell.[35,47] Among the possible electrolytes and configurations, only those results obtained for the most efficient undivided cell configuration and NaOH electrolyte (0.5 M) are discussed in this work.[35]

The detailed experimental conditions have been previously described.[35] Essentially, 2 g of the phenol-saturated original AC (W) was placed in the cell, similar to a granular AC fluidized bed,[35,47] just in contact with the cathode or anode for the performance of the cathodic or anodic regeneration experiments, respectively. Stainless-steel and $SnO_2−Sb−Pt$ electrodes were used as cathode and anode electrodes, respectively, and the area of both electrodes was 20 cm². The electrolyte volume was 200 cm³, and the temperature was controlled at 25 °C during the entire regeneration process. Electrochemical regeneration was carried out at constant current conditions. For the study of the effect of the regeneration time, the duration of experiments was varied in the range of 0−7 h.

During regeneration experiments, the pH and phenol concentration/conversion were monitored with the increasing regeneration time. The amount of phenol was measured by UV−vis absorption spectroscopy (Jasco model V-670).

The electrochemically regenerated AC samples will be designated with the letter W, followed by the letters c or a referring to the electrode polarity in the cathodic or anodic regeneration, respectively, and followed by a number indicating the applied constant current (0.2 or 1.0 A), and finally, the abbreviation of OH⁻ is included to indicate that the NaOH electrolyte solution was used.

2.4. Analysis of the Regenerated AC. After regeneration and prior to their characterization, the regenerated AC samples were dried in an oven (40 °C) and subjected to different tests.

2.4.1. Evaluation of RE. The regenerated AC samples were used for the re-adsorption of phenol, under the same previous conditions (see section 2.2), to determine the percentage of RE, which is defined as the ratio of regenerated to fresh adsorption capacities, according to eq 1.

$$RE = \frac{\text{adsorption capacity of regenerated AC}}{\text{adsorption capacity of fresh AC}} \times 100 \quad (1)$$

Because of the lower amount of regenerated AC, the batch adsorption experiments in this case were performed using 0.5 g of regenerated AC and 10 mL of phenol-concentrated solution (20 000 mg/L), keeping the mass/volume ratio (1:20) constant.

2.4.2. Porous Texture Characterization. The porous texture of all samples was determined by physical adsorption of gases (N_2 at −196 °C and CO_2 at 0 °C) using an automatic adsorption system (Autosorb-6, Quantrachrome Corporation) after sample outgassing at 110 °C under vacuum for 4 h. Nitrogen adsorption at −196 °C has been used to determine the total volume of micropores [$V_{DR}(N_2)$] (pore size smaller than 2 nm) from the Dubinin−Radushkevich (DR) equation (the range of relative pressures used for the DR analysis was $0.005 < P/P_0 < 0.17$) and the apparent specific surface area by the BET equation (S_{BET}), whereas the adsorption of CO_2 at 0 °C has been used to quantify the narrowest micropores [$V_{DR}(CO_2)$] (pore size smaller than around 0.7 nm), also by application of the DR equation for relative pressures below 0.025.[48−50]

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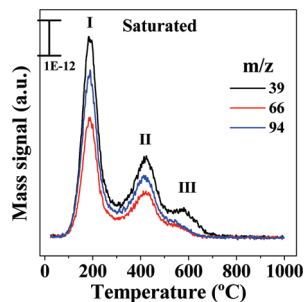(48) Rodríguez-Reinoso, F.; Linares-Solano, A. *Chem. Phys. Carbon* **1988**, *21*, 2–146.

Figure 1. TPD of phenol from the phenol-saturated AC sample.

Figure 2. Effect of the NaOH solution concentration on (a) the REs and (b) the N_2 isotherms (porosity recovery) for chemically regenerated phenol-saturated AC.

257 *2.4.3. Thermal Desorption Studies of the Remaining Products.*
258 The thermal desorption of remaining species was followed by
259 temperature-programmed desorption (TPD) experiments. In
260 these experiments, about 10 mg of the sample were heated to
261 950 °C (heating rate of 20 °C/min) under a helium flow rate of
262 100 mL/min. The analyses were performed in differential scan-
263 ning calorimetry−thermogravimetric analysis (DSC−TGA)
264 equipment (TA Instruments, SDT 2960 Simultaneous) coupled
265 to a mass spectrometer (Thermostar, Balzers, GSD 300 T3).
266 Phenol thermal desorption was monitored by following m/z
267 signals at 94, 66, and 39, which correspond to the main phenol
268 fragments, according to the Wiley Mass Spectra Library 275 L
269 of the electronic database installed in the equipment. The TPD
270 profiles for CO, CO_2, and H_2O are included in the Supporting
271 Information.

3. Results and Discussion

273 **3.1. TPD of the Phenol-Saturated AC.** A representative
274 TPD thermogram of the phenol-saturated AC sample is
275 shown in Figure 1, where only the main m/z signals for
276 phenol have been included. Desorption of phenol can be
277 followed by their corresponding molecular ions with m/z 94,
278 66, and 39 that correspond to $C_6H_6O^+$, $C_5H_6^+$, and $C_3H_3^+$,
279 respectively. The relative intensities of phenol moieties for
280 the mass spectrometer (MS) used in this work were 84, 61 and
281 100, respectively. Above 100 °C, three different peaks can
282 be distinguished, which are related to three different types
283 of interaction. Considering the boiling point of phenol
284 (182 °C)[9] and according to other authors,[12−17] the first peak
285 (peak I) located at about 200 °C is attributed to the desorp-
286 tion of physically adsorbed phenol. On the other hand, the
287 peaks above 300 °C are assigned to chemically adsorbed
288 species. Peak II appearing at about 410 °C corresponds to
289 chemisorbed phenol, and peak III, between 500 and 650 °C,
290 has been attributed to more stable phenol-derivative com-
291 pounds. Interestingly, peak III relative intensities of the three
292 monitored m/z signals do not correspond to those expected
293 for phenol, indicating that, apart from phenol, additional
294 phenol-derivative compounds have been formed.

295 The nature of the compounds desorbed under peak III has
296 been previously under discussion and controversy in differ-
297 ent works. On one hand, these compounds could correspond
298 to thermally transformed products coming from adsorbed
299 phenol, such as benzyl, furans, fragments, and dimers.[17,51,52]
300 On the other hand, they could correspond to irreversibly
301 adsorbed phenol and/or oxidative coupling products, such as
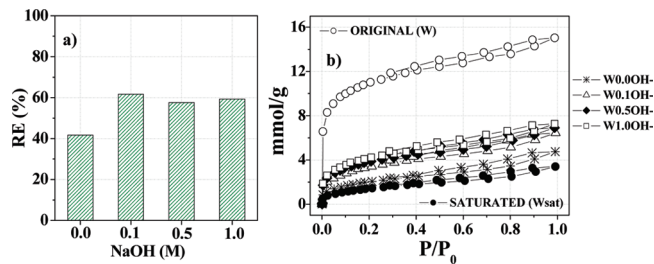
302 dimers (dihydroxybiphenyls or phenoxyphenols) and other
303 phenolic oligomers and polymers catalytically produced by
304 the AC during or after the adsorption process.[7,25,53]

305 Concerning the peak intensities, Figure 1 also shows the
306 following intensity sequence: I > II > III, indicating that
307 phenol is mainly physisorbed. The deconvolution of the
308 phenol desorption peaks using Lorenzt multi-peaks provides
309 a semi-quantitative ratio corresponding to 53% of physisorp-
310 tion (peak I), 37% of phenol chemisorbed (peak II), and 10%
311 of transformed phenol (peak III). These results are in close
312 agreement with those obtained by Castillejos-López et al. for
313 another AC material.[16]

314 TPD results obtained in this section clearly confirm the
315 most accepted adsorption mechanism of phenolic com-
316 pounds on AC proposed in the literature, in which one
317 fraction of the phenolic compounds is physisorbed on the
318 carbon surface by dispersion forces between π electrons of
319 the phenol aromatic ring and π electrons of the graphene
320 layers and the other fraction corresponds to specific surface
321 compounds, chemisorbed phenol, with the formation of
322 electron-transfer bonds between the edges of the graphene
323 layers and the aromatic molecules and ether and ester bonds
324 between phenol hydroxyl groups and surface oxygen
325 groups.[54]

326 **3.2. Chemical Regeneration.** Figure 2 shows the RE values
327 and the N_2 isotherms at 77 K for chemically regenerated AC
328 samples with NaOH solutions of different concentrations.
329 According to the RE results (Figure 2a), the presence of
330 NaOH in the water solution yields a 20% increase in the RE
331 with respect to distilled water. The maximum RE achieved
332 with the NaOH chemical regeneration was about 60% and
333 was found to be independent of the NaOH solution concen-
334 tration, at least in the concentration range studied. These
335 results are in agreement with data reported by others for the
336 chemical regeneration of phenol-saturated AC using NaOH
337 as the regenerating agent.[26−28]

338 The better regeneration performance of the NaOH solu-
339 tion compared to the neutral distilled water can be explained
340 by three mechanisms acting together: (i) in alkaline condi-
341 tions, phenol (pK_a = 9.89) should be in the form of pheno-
342 late ion, and its solubility in water is higher than that of
343 neutral phenol molecules; (ii) in NaOH solutions, both the
344 surface oxygen groups of the AC (pH_{pzc} 9) and the adsorbed
345 phenol are deprotonated and, because of electrostatic repul-
346 sions between phenolate and AC oxygen groups and also
347 between phenolate molecules, phenol is favorably desorbed

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as phenolate species; and (iii) considering the chemical adsorption mechanism of phenol postulated by some authors,[54] NaOH solution can hydrolyze some chemical bonds between phenol hydroxyl groups and the surface oxygen groups of the AC.

The N_2 adsorption isotherms for the original, saturated, and chemically regenerated AC samples (Figure 2b) reveal that, after the marked porosity reduction caused by phenol saturation, the chemical regeneration with NaOH solutions brings about a small recovery of the porosity (Table 1). Moreover, a higher blockage of the micropores of about 0.7 nm may account for the similarity between $V_{DR}(CO_2)$ and $V_{DR}(N_2)$ in the regenerated samples. Similar results were found after regeneration in dynamic regime performed in the electrochemical cell but without application of current.[35] The observed low-porosity recoveries do not seem to match with 60% RE values; i.e., although the surface is considerably blocked, the blocking species may participate on the re-adsorption of phenol after regeneration. Earlier authors[25,53] suggested that dimeric or oligomeric phenol compounds, formed during NaOH regeneration by coupling reactions favored at high pH and oxic conditions, are the blocking species involved in phenol re-adsorption.

Figure 3 shows the TPD thermogram and AC sample chemically regenerated in 0.5 M NaOH showing the main m/z signals for phenol. In comparison to Figure 1, it can be observed that the NaOH treatment removes the physisorbed phenol almost completely (peak I) but chemisorbed phenol (peak II) and phenol-derivative compounds (peak III) still remain in the AC. After the removal of the physisorbed phenol, an additional peak or shoulder at about 310 °C can be distinguished. This finding suggests that the desorption signal of chemisorbed phenol is indeed composed of two contributions: the first on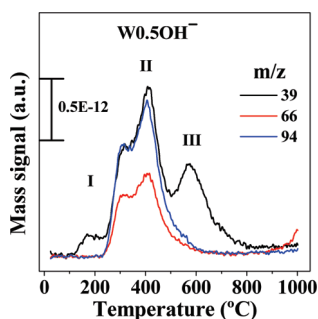e desorbing at lower temperatures (310 °C) is considered to be the weakly chemisorbed phenol, and the other centered at temperatures about 410 °C is considered to be the most stable or strongly chemisorbed phenol. The signal corresponding to weakly chemisorbed phenol is probably obscured by strong overlapping between physisorbed and strongly chemisorbed phenol peaks in Figure 1.

3.3. Thermal Regeneration. The results of thermal regeneration of phenol-saturated AC are shown in Figure 4, where the RE percentage is represented as a function of the temperature. From the obtained results, it can be observed that the RE increases with the temperature up to a maximum value of 86% at 750 °C. Higher regeneration percentages are difficult to achieve by pyrolysis treatment because phenol decomposition products are known to be retained on the carbon surface.[9,13,15,17,18]

The influence of the temperature on the textural properties of the thermally treated ACs was also analyzed. Figure 4b and Table 2 contains the porosity characterization of the thermally treated carbon materials. The results show that the porosity recovery increases with the temperature and that thermal regeneration produces a high recovery of the porosity at temperatures above 600 °C. These results can be easily explained considering that the higher the temperature, the higher the phenol removal. However, further improvements in the AC porosity may be difficult because of the remaining cracking products.

TPD spectra of the regenerated AC samples at different temperatures are shown in Figure 5. As observed (Figure 5a), physisorbed phenol is completely removed at 300 °C and only chemically adsorbed species (peaks II and III) remain on the AC. Nevertheless and in comparison to the phenol-saturated AC sample (Figure 1) and the sample regenerated by NaOH (Figure 3), a significant shift of the two peaks toward higher temperatures is observed. Thus, peaks II and III appear at 495 and 615 °C, respectively. Furthermore, there is an important change in the relative intensities of

Figure 3. TPD of phenol from a chemically regenerated AC sample (0.5 M NaOH).

Table 2. Textural Characterization of the Original (W), Saturated (Wsat), and Thermally Regenerated AC Samples at Different Temperatures

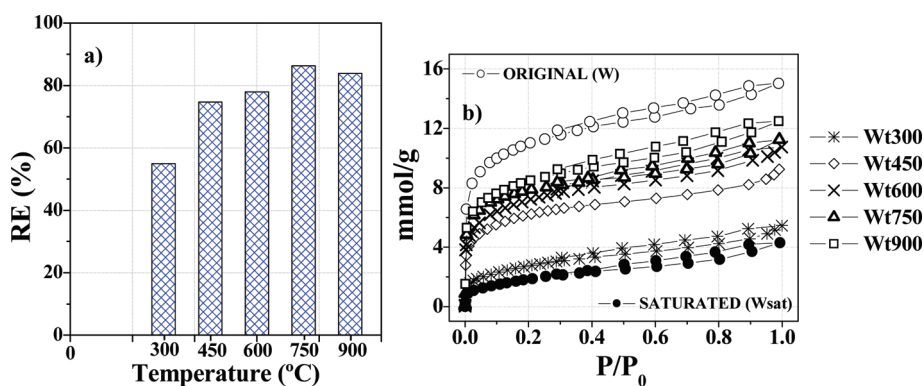| sample	S_{BET} (m²/g)	$V_{DR}(N_2)$ (cm³/g)	$V_{DR}(CO_2)$ (cm³/g)
W	875	0.37	0.29
Wsat	145	0.05	0.09
Wt300	225	0.08	0.10
Wt450	477	0.20	0.19
Wt600	560	0.23	0.17
Wt750	635	0.27	0.20
Wt900	675	0.28	0.21

Figure 4. Effect of the temperature on (a) the REs and (b) the N_2 isotherms (porosity recovery) for thermally regenerated phenol-saturated AC.
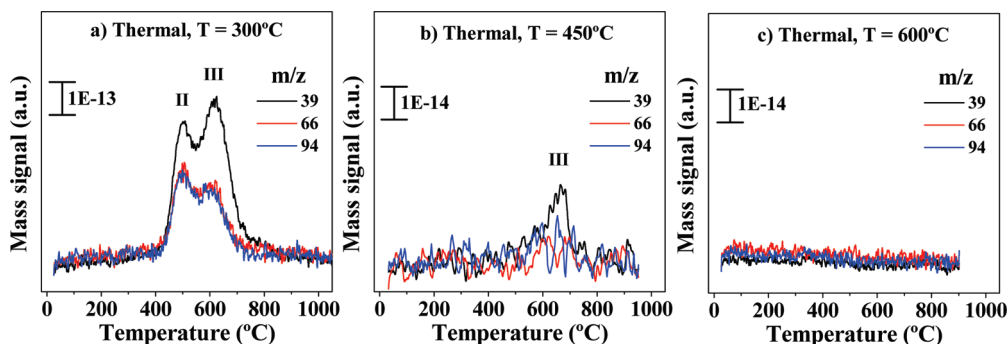
Figure 5. TPD of phenol from thermally regenerated AC samples at different temperatures.
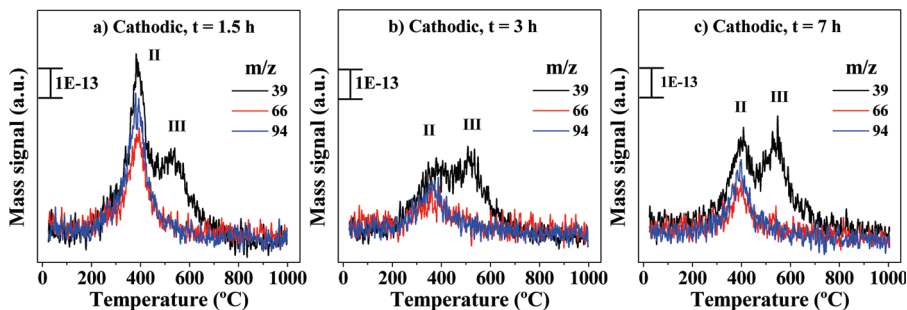

Figure 6. TPD of phenol from cathodically regenerated AC samples for different times, at 0.2 A in 0.5 M NaOH solution.

peak II *m/z* signals compared to peak II for the phenol-saturated AC (Figure 1), suggesting that phenol decomposition compounds have been formed and that they have higher stability than those resulting from NaOH regeneration.

When the regeneration temperature is increased up to 450 °C (Figure 5b), chemisorbed phenol is completely removed and only a low-intensity peak III, corresponding to reaction products, is detected. After thermal regeneration at 600 °C, phenol characteristic *m/z* signals are not detected (Figure 5c). These results clearly agree with the increase of RE values and porosity recoveries with increasing temperature. However, textural characterization (Table 2) indicates that the porosities of AC samples regenerated at 450 and 600 °C are not completely recovered, and on the other hand, both REs and porosity recoveries reach a maximum value with the temperature, so that some carbonization products keep blocking the surface of the regenerated AC samples.

3.4. Electrochemical Regeneration of Granular AC and Comparison to the Conventional Methods. As previously mentioned in the Introduction, we have recently studied the electrochemical regeneration of phenol-saturated AC, analyzing the influence of different parameters, such as the electrode polarity, the compartment separation, the applied current, and the regeneration time, on both the RE and porosity recovery.[35]

The blank experiment for the electrochemical regeneration in a filter-press cell, in which a 0.5 M NaOH flow is recirculated and no current is applied, was used to analyze the influence of dynamic desorption conditions (as commented in section 3.2). In this case, similar REs (60−65%) to chemically regenerated AC were obtained (Figure 2a).

In this paper,[35] we found that the electro-oxidation of desorbed phenol during the electrochemical regeneration of AC favors phenol desorption but can also hinder the regeneration process because of the blockage of porosity of the AC by the electro-oxidation products (quinones, polymers, etc.), which increase with the current and the regeneration time.

Then, the best results, in terms of both RE and porosity recovery, were obtained for the cathodic regeneration in 0.5 M NaOH in an undivided configuration cell for an electrolysis time of 3 h under a wide range of applied currents (RE ~ 80%). These results were attributed to a combination of factors, namely, maximum enhancement of phenol desorption, phenol electro-oxidation occurring on both the cathode and the counterelectrode, and consequently, a lower concentration of electro-oxidation products that may adsorb on the AC. At longer electrolysis times, RE remains constant, which was explained as a result of the combination of the sluggish phenolate diffusion through the narrowest micropores and the increasing amount of blocking oxidation products, whose adsorption on the granular AC may also increase with the regeneration time.

To further deepen the mechanism and optimization of this regeneration method, the adsorbed species remaining on electrochemically regenerated AC were analyzed by TPD. The analysis was restricted to AC treated by cathodic regeneration in an undivided cell, which was proven to yield the best results as stated above. Figure 6 presents the TPD experiments for the cathodically regenerated AC samples at 0.2 A, in 0.5 M NaOH, for different electrolysis times. As follows from the figure, unlike physisorbed phenol, the chemically adsorbed phenol is not completely removed and only some desorption at high temperatures appears. The amount of chemisorbed phenol and phenol decomposition products (peaks II and III) decreases with increasing the time of treatment within the first 3 h of electrolysis, and then they seem to reach a constant value in the investigated time interval, thus accounting for the evolution of RE with the electrolysis time.[35]

The similarity between TPD spectra of samples regenerated for 3 and 7 h (Figure 6) suggests that that the amount of remaining species on the AC sample regenerated after 7 h may be of similar nature to those for the sample regenerated after 3 h. However, the much higher porosity recovery
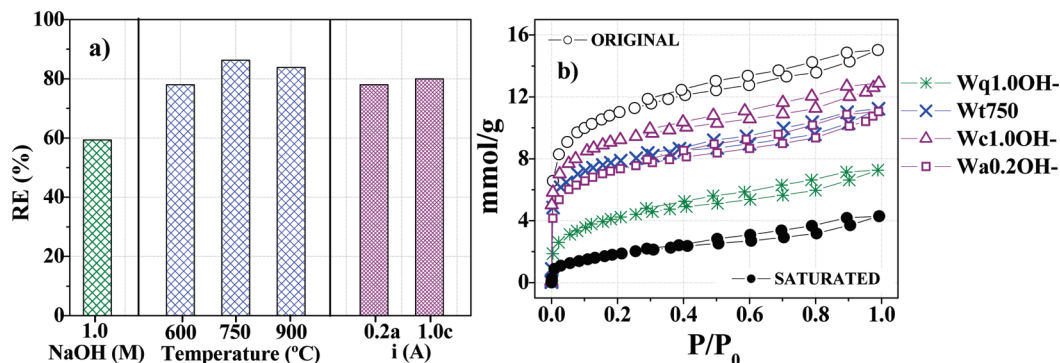
Figure 7. Comparison of (a) the REs and (b) the N_2 isotherms (porosity recovery) for the regeneration of phenol-saturated AC at the experimental conditions, yielding the best results for each regeneration method.

Table 3. Textural Characterization of the Original (W), Saturated (Wsat), and Regenerated AC Samples at the Experimental Conditions of the Best Results for Each Regeneration Method

sample	S_{BET} (m^2/g)	$V_{DR}(N_2)$ (cm^3/g)	$V_{DR}(CO_2)$ (cm^3/g)
W	875	0.37	0.29
Wsat	145	0.05	0.09
W1.0OH$^-$	350	0.14	0.15
Wt600	560	0.23	0.17
Wt750	635	0.27	0.20
Wt900	675	0.28	0.21
Wa0.2OH$^-$	585	0.26	0.12
Wc1.0OH$^-$	735	0.32	0.19

achieved after 3 h (579 m^2/g compared to 233 m^2/g for the 7 h treatment)[35] points to a much higher amount or volume of remaining species after a 7 h regeneration process than after the 3 h experiment. These results could be explained considering that the products formed by electro-oxidation of phenol after 7 h are adsorbed on the AC.

Figure 7 compares the REs and the N_2 adsorption isotherms at −196 °C for the regenerated AC samples at the optimal experimental conditions for each regeneration method studied in this work. Table 3 includes the textural characterization of these samples. The chemical regeneration of the studied AC produces RE values by 20% lower than those obtained by the thermal and electrochemical ones. Interestingly, similar REs of about 80% are achieved by electrochemical and thermal regenerations (provided that temperatures above 600 °C are applied in this latter case).

Textural characterization (Figure 7b and Table 3) shows that the porosity recoveries achieved by chemical regeneration are rather low and that the cathodic regeneration is the most effective treatment for the porosity recovery of the AC, even more effective than the thermal treatments at the highest temperature. The RE and porosity recovery achieved by anodic treatment at low currents are slightly lower than those obtained by cathodic treatment at 1.0 A but high enough to also be considered as a promising regeneration treatment.

As a final remark, it appears clear from data reported in this work that, even under the optimal experimental conditions, the electrochemical and thermal regeneration methods are not capable of yielding REs higher than 80−85% and the initial textural properties of the original AC cannot be completely recovered. These limitations in the regeneration performance could be conditioned by the nature of the studied AC and, more specifically, by its characteristic surface chemistry and microporous structure. With regard to this latter factor, we believe that the narrow microporosity that favors phenol uptake may also hinder subsequent phenol desorption and, consequently, the RE and porosity recovery achieved by a given regeneration method. In this sense, further research on the influence of the pore size distribution on the performance of AC regeneration should be carried out.

4. Conclusions

The presence of NaOH increases the efficiency of phenol desorption with respect to distilled water. However, it is difficult to achieve regeneration efficiencies above 60% by chemical regeneration with NaOH, and low-porosity recovery occurs.

TPD experiments show that, whereas phenol is almost completely removed electrochemically after 3 h, at least 450−600 °C is required to achieve similar results by thermal regeneration.

The analysis of REs and porosity recoveries after regeneration by the different methods shows that the electrochemical regeneration run under the optimal conditions can produce similar RE values (about 80%) and higher porosity recovery than those obtained by thermal treatment. Through electrochemical regeneration, the AC can recover about 84% of the surface area compared to the pristine AC, whereas 77% of surface recovery is attained by thermal treatment at 900 °C. Thus, it can be concluded that, in terms of both RE and porosity recovery, electrochemical regeneration is more efficient than thermal regeneration.

However, all of the regeneration treatments explored in this work leads to a degradation of adsorbed phenol and generation of strongly bound compounds. These degradation compounds probably have a detrimental effect on the efficiency, and therefore, further research must be carried out toward avoiding or removing these strongly adsorbed compounds.

Results presented in this work provide contrasted information on the feasibility of the electrochemical regeneration method of AC, which appears as a real alternative to replace the conventional less efficient chemical treatment and the much more expensive thermal one. However, for practical applications, specific engineering considerations may play a key role and may also determine the choice of the suitable AC regeneration method.

Supporting Information Available: TPD profiles of CO, CO_2, and H_2O from the pristine AC, phenol-saturated AC, and regenerated AC samples. This material is available free of charge via the Internet at http://pubs.acs.org.