

Electrochemical regeneration and porosity recovery of phenol-saturated granular activated carbon in alkaline medium

R. Berenguer^a, J.P. Marco-Lozar^b, C. Quijada^c, D. Cazorla-Amorós^b and E. Morallón^{a,*}

^aDpto. Química Física e Instituto Universitario de Materiales. Univ. Alicante. Apartado 99. E-03080 Alicante. Spain

^bDpto. Química Inorgánica. Universidad de Alicante. Apartado 99. E-03080 Alicante. Spain

^cDpto. Ingeniería Textil y Papelera, Universidad Politécnica de Valencia, Pza. Ferrandiz y Carbonell, s/n, E-03801 Alcoy (Alicante). Spain

* Corresponding author. Fax: +34 965903537. E-mail address: morallon@ua.es (E. Morallón)

Abstract

The electrochemical regeneration of phenol-saturated activated carbon has been carried out in a filter-press electrochemical cell. The feasibility of the electrochemical regeneration has been assessed by monitoring the regeneration efficiency and the textural properties of a phenol-saturated granular activated carbon (GAC) electrolysed in alkaline medium. The influence of parameters including i) the electrolysis treatment (either anodic or cathodic) ; ii) the separation of compartments; iii) applied current and iv) electrolysis time has been studied. Based on the obtained results, an overall phenomenological mechanism for the electrochemical regeneration has been proposed. The general worse performance of anodic regenerations can be attributed to a surface blockage of the GAC by reaction products such as quinones, phenolic oligomers and polymers coming from phenol electrooxidation. The cathodic regeneration in NaOH medium, where phenolate desorption is favoured, and in an undivided configuration, where surface blockage is minimized, produces a significant recovery of the porosity of the original GAC, in agreement with the highest RE values (close to 80%).

1. Introduction

Activated carbons (AC) present several important applications in liquid and gas phases and for energy storage [1,2], owing to their unique properties, such as high surface area, wide variety of porosity, rich surface chemistry and high adsorption capacity. Among these applications, activated carbons are currently being widely used for the treatment of industrial water effluents to meet environmental legislations [3,4]. In this particular case, the unique properties of activated carbons make the adsorption technology the most frequently used method for the removal of aqueous pollutants from waste waters [4].

During the use of the activated carbon, the porosity becomes progressively saturated and inactive. Once it is exhausted, AC can be disposed off by incineration or deposited in a landfill, what means a high cost and an environmental problem. On the contrary, the AC could be reused after an appropriate regeneration step. In the view of the high production cost and consumption of AC [5], the economics and feasibility of the adsorption technology on an industrial scale greatly depends on the reactivation and reuse of the spent activated carbon [6].

The ideal AC regeneration process involves desorption of the pollutants concentrated in the activated carbon without any modification in the initial properties of the carbonaceous material. A variety of regeneration techniques for exhausted activated carbons have been proposed [7-22]. However, the methods that are applied today are either not efficient enough or too expensive. The most widely used regeneration methods are the thermal regeneration and solvent regeneration. Thermal regeneration shows a high efficiency, but it presents some disadvantages such as: i) the need of ex-

situ operation, that is, exhausted AC has to be transported to a reactivation center, where it is regenerated in a furnace at high temperature, and then it has to be transported back to the wastewater purification unit; ii) the possible changes in the AC properties, which can modify the adsorption properties; iii) the requirement of high energy costs to keep the regeneration temperature around 800–850°C and iv) the considerable loss (~10-15% by weight) of AC during the process [8,13]. In addition, these problems become more serious when the number of regeneration cycles increase [14,15]. Regarding the solvent extraction, about 10–15% of the pores of the activated carbon remains blocked after the treatment [12,16,17] and the efficiency is usually below 70% [12,17].

An alternative route which has been less studied is the electrochemical regeneration [18-22]. This technique presents some advantages compared with the conventional methods. Essentially, it can be conveniently operated in-situ at ambient temperature and pressure, with low energy consumption and with short time requirements. Moreover, the electrode potential allows recovery, destruction or transformation of the pollutants into less hazardous compounds, exploiting either oxidative or reductive chemistries, and using electrons as the only reagent. Thus, with this method, the adsorbed pollutants can be treated without additional oxidants.

Because of their extreme toxicity, and their inhibitory, refractory and non-biodegradable character, the phenolic compounds constitute one of the most important groups of pollutants in industrial wastewaters [4, 23] and their presence, even at low concentrations, can be an obstacle to the use or the reuse of water. For this reason, this work is aimed at the investigation of the electrochemical regeneration of a commercial granular activated carbon (GAC) saturated with phenol.

To the best of our knowledge, most of the studies on the electrochemical regeneration of AC have focused primarily on regeneration efficiencies. However, fundamental information on the regeneration mechanism and the influence of the treatments on the adsorption properties of the original adsorbent is lacking. Therefore, it is worth investigating the influence of the electrochemical parameters on both the electrochemical regeneration efficiencies (REs) and the AC properties. Thus, the influence of type of treatment (anodic or cathodic), the separation of compartments, applied current and electrolysis time on the regeneration efficiency and on the textural properties of the phenol-saturated GAC has been studied in this work. The electrochemical regeneration process of an adsorbent like GAC can be envisaged as a very complex process, in which the adsorbate (phenol) may be involved in many coupled and/or competing steps. Data reported in this study will be helpful to identify such steps and to eventually propose an overall phenomenological mechanism for the electrochemical regeneration of exhausted GAC.

2. Experimental

2.1. Materials

The commercial granular activated carbon selected for this work was provided by Waterlink Suctcliffe Carbons (207A, $\text{pH}_{\text{PZC}} = 9$, Mesh: 12×20) and it is referred to as W. Before saturation, the GAC samples were washed several times with distilled water and dried in an oven at 80 °C overnight. Phenol, NaOH, H₂SO₄ and NaCl solutions were made up by dissolving analytical grade reagents (Merck) in deionised water.

2.2. Phenol saturation of the activated carbon

Adsorption experiments for the saturation of the activated carbons were obtained from closed batch experiments. Phenol solutions (100 ml) with an initial concentration of 20000 mg/l were added to 100 ml glass flasks with 5 g of GAC. The flasks were sealed to avoid evaporation and placed on a shaker at constant shaking speed with a thermostatically controlled bath at 30 °C. These experimental conditions were maintained for 7 days in order to attain equilibrium. The equilibrium time was determined previously from preliminary kinetic studies. After the equilibrium period, the carbons were filtered and the phenol concentration in the residual solution was measured by UV-Vis absorption, at the wavelength of 270 nm. Before electrochemical regeneration experiments, the saturated GAC samples were dried in an oven using very mild conditions (40 °C) until constant mass was achieved.

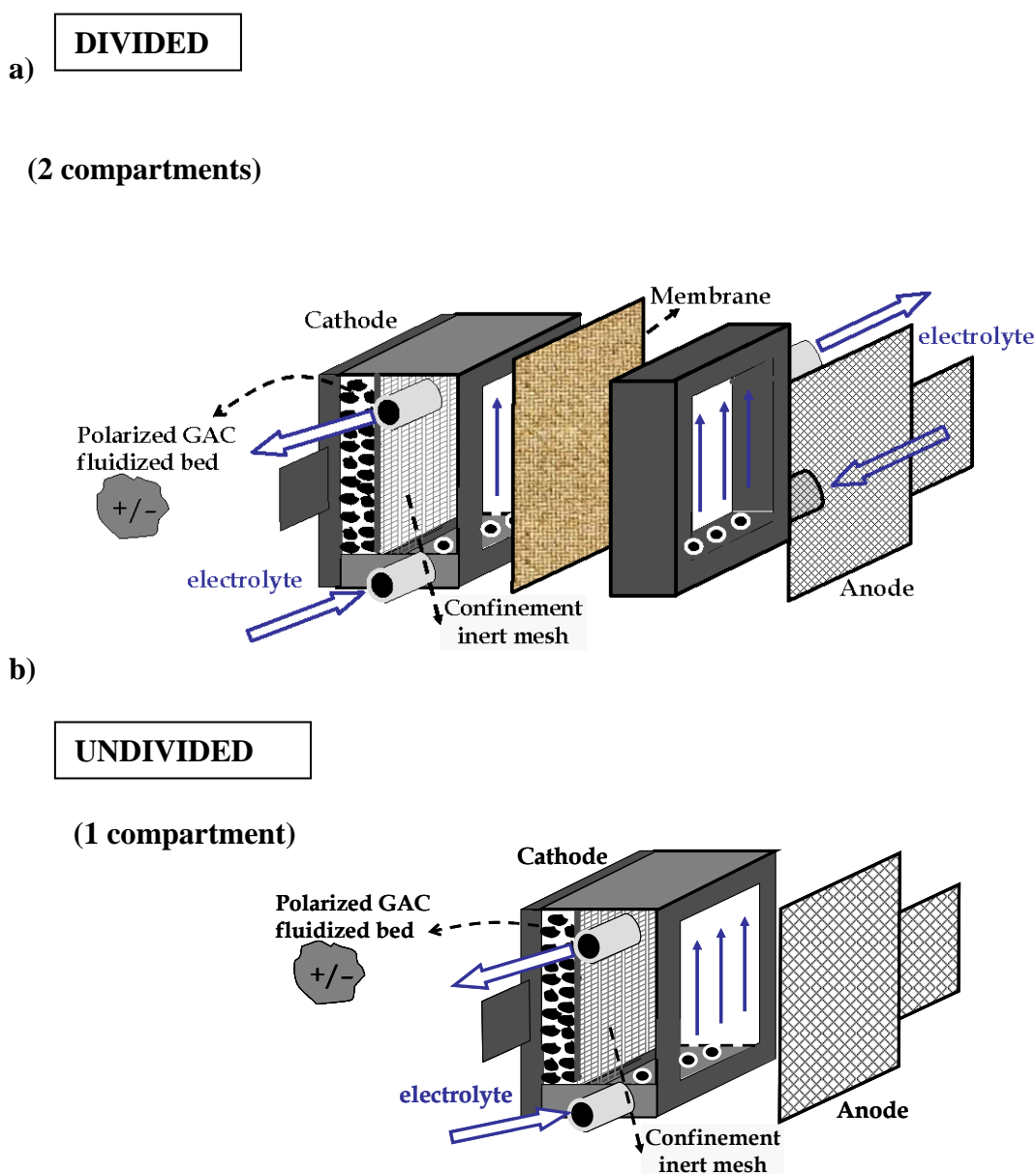
2.3. Electrochemical regeneration of activated carbon

In this work, the electrochemical regeneration of activated carbon was carried out in a filter-press electrochemical cell, which has been described elsewhere [24]. The filter-press cell is provided with electrodes of a geometric area of 20 cm². The cell is sketched in Figure 1, in both divided and undivided assemblies. In the first configuration, the cell is composed of two compartments separated by an appropriate ionic exchange membrane. Each compartment is defined by an electrode, a flow distributor and the ionic membrane (Fig. 1(a)). This assembly allows the GAC to be electrochemically regenerated at the desired electrode. The membrane hampers the transport of desorbed phenol or phenol ionic species to the counterelectrode, making it negligible within the electrolysis timescale. In other words, the electrochemical regeneration is effectively decoupled from electrochemical reactions occurring at the counterelectrode side. In the undivided configuration, the ionic membrane is removed

and there is only one compartment with a common flow distributor between the two electrodes (Fig. 1(b)). Thus, in this case the influence on the regeneration process of electrochemical reactions at the counterelectrode (i.e. solvent decomposition, electrolyte reaction or desorbed phenol degradation) should be considered.

The experimental conditions for a typical electrochemical regeneration process have been reported elsewhere [24]. Typically, 2 g of the phenol-saturated original GAC were placed in the cell, and kept in close contact with either the anode (anodic regeneration experiments) or the cathode (cathodic regeneration experiments) by means of a polypropylene confinement mesh (Fig 1a-b), thus behaving like a GAC fluidized bed. The electrolytic solution (200 ml) was continuously stirred and recirculated through the compartments by means of centrifugal pumps. The temperature was controlled at 25°C during all the regeneration process. Electrochemical regeneration was carried out under constant current conditions (galvanostatic regeneration) at 0.2, 0.5, 1.0, 1.5 and 2.0 A for 3 h in alkaline medium. The electrode potentials were measured against a Ag/AgCl/Cl⁻ (3 M) reference electrode. For the study of the effect of the regeneration time, it was varied in the range of 0-7 h.

Figure 1. Diagram of the electrochemical filter-press cell: (a) Divided configuration; (b) Undivided configuration.



A stainless steel plate electrode was used as the cathode in all experiments. A platinized titanium (Pt/Ti) electrode was employed as the anode in cathodic regeneration experiments performed in divided cells, whereas an antimony- and platinum-doped tin dioxide (SnO₂-Sb-Pt) DSA-like electrode was used in anodic regeneration experiments. The performance and electrocatalytic activity of these anodes towards phenol oxidation

have been previously reported [25]. These latter electrode materials were also utilized as anodes in non-divided assemblies, regardless of whether the GAC is anodically or cathodically regenerated. The geometric projected area of all electrodes was 20 cm². The cell compartment separation for the regeneration experiments was by an anionic membrane.

The electrolyte for the electrolysis of saturated GAC was 0.5 M NaOH. Non electrochemical phenol desorption experiments were also attempted in 0.5 M NaOH, 0.5 M H₂SO₄ and 2wt% NaCl (0.34 M).

During regeneration experiments, small samples of the electrolyte solutions were taken out at different times to measure the phenol concentration/conversion. Phenol concentration was photometrically determined by Phenol Cell Tests (Spectroquant® Nova 60, Merck) .The amount of phenol and some of its derivatives were also followed by UV-Vis Absorption Spectroscopy (Jasco V-670 Uv-vis-NIR spectrometer).

The electrochemically regenerated GAC samples will be referred to in the text as a compound name including the letter W; the letter *p* to indicate phenol pollutant; the letters *c* or *a* referring to the cathodic or anodic regeneration, respectively; a number indicating the applied constant current (0.2, 0.5, 1.0, 1.5 or 2.0 A); and the abbreviations of OH⁻, H⁺ and Cl⁻ referring to the NaOH, H₂SO₄ and NaCl electrolyte solutions, respectively.

2.4. Analysis of the regenerated activated carbon

After regeneration, the regenerated GAC samples were dried in an oven (40 °C) and were used to evaluate the regeneration efficiency and the porous texture, both as described below.

2.4.1. Evaluation of the Regeneration Efficiency

The regenerated GAC samples were used for the readsorption of phenol, under the same previous conditions (see section 2.2.), to determine the percentage of regeneration efficiency, which is defined as the ratio of regenerated to fresh adsorption capacities, according to the following equation (1):

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

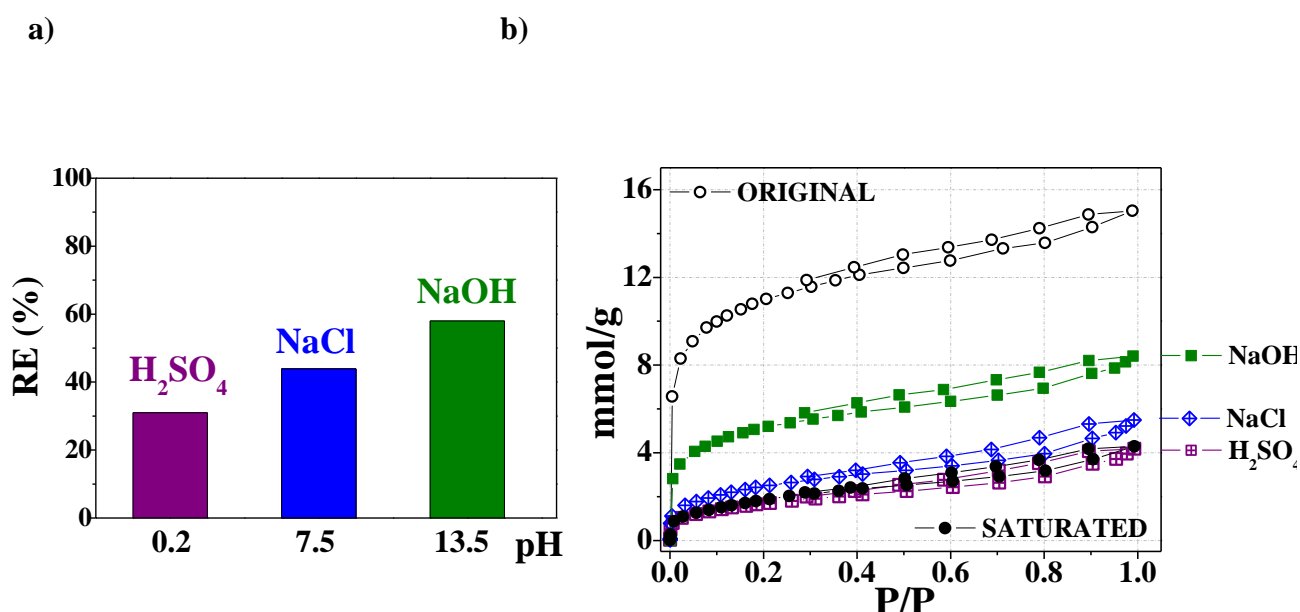
Due to the low amount of regenerated GAC, the batch adsorption experiments in this case were performed using 0.5 g of regenerated AC and 10 ml of phenol concentrated solution (20000 mg/l), keeping constant the mass to volume ratio (1:20).

2.4.2. Porous texture characterization

The porous texture of all samples was determined by physical adsorption of gases (N₂ at 77 K and CO₂ at 273 K) using an automatic adsorption system (Autosorb-6, Quantachrome Corporation) after samples out-gassing at 383 K under vacuum for 4 h. Nitrogen adsorption at 77K has been used for determining the total volume of micropores (V_{DR}(N₂)) (pore size smaller than 2 nm) applying the Dubinin–Radushkevich (DR) equation (range of relative pressures used for the DR analysis was: 0.005 < P/P₀ < 0.17) and for determining the specific surface area by the BET equation (S_{BET}), whereas the adsorption of CO₂ at 273K has been used to assess the narrowest

micropores ($V_{DR}(CO_2)$) (pore size smaller than around 0.7 nm) also by application of the Dubinin–Radushkevich equation for relative pressures below 0.025 [26-28].

Figure 2. Effect of the electrolyte pH on (a) the regeneration efficiencies and (b) on the N_2 isotherms (porosity recovery) for 3-hour regeneration experiments of phenol-saturated AC in the absence of applied current.



3. Results

3.1. Desorption of phenol in absence of current. Influence of the electrolyte pH

In this section, the effect of the electrolyte on the regeneration process without the help of the electrochemistry is analyzed. For this purpose, it was used the same experimental set up than in electrochemically-assisted experiments, but no current was applied. Figure 2(a) shows the regeneration efficiencies obtained for 3-hour experiments in three different electrolytes at different pH. Figure 2(b) and Table 1 present the corresponding N_2 isotherms and textural characterization, respectively, of these samples and those of the original and the phenol-saturated samples. The results show that the adsorption equilibrium of phenol is strongly affected by the pH. REs in alkaline solutions are

higher than in neutral solutions and much higher than in acidic conditions. However, REs in absence of current are no higher than 60%, the porosity recovery is poor and, once desorbed, the adsorbate is not chemically transformed.

Because of the far better behaviour observed in alkaline medium, this work is focused on the study of the electrochemical regeneration of GAC in sodium hydroxide electrolyte.

Table 1. Textural characterization of the original (W), saturated (Wsat) and blank regenerated activated carbon samples, in absence of current, in different electrolytes.

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	146	0.05	0.09
WpbH ⁺	138	0.06	0.06
WpbCl ⁻	205	0.09	0.08
WpOH ⁻	414	0.18	0.16

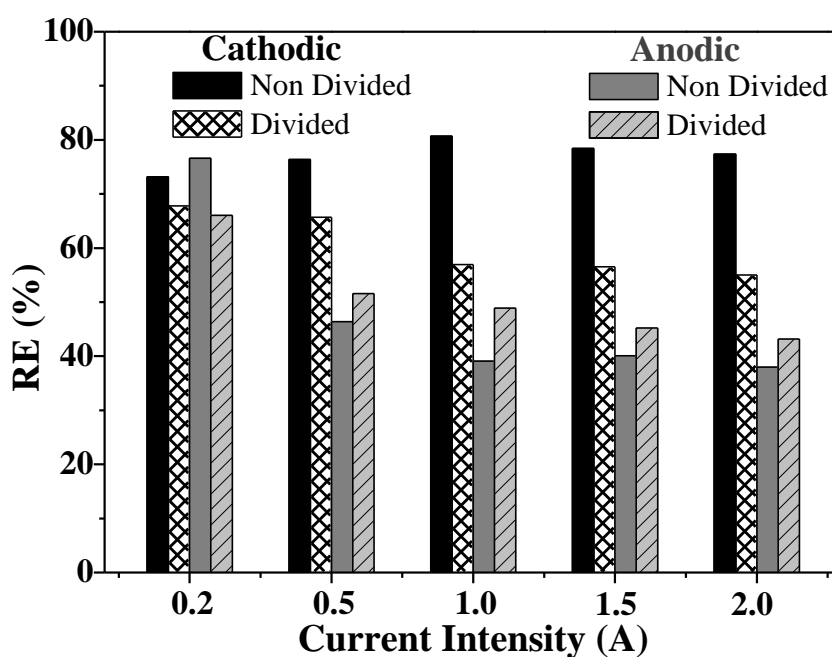
3.2 Electrochemical regeneration in NaOH.

3.2.1 Regeneration efficiency

Figure 3 summarizes the effects of the electrode polarity (whether the treatment is anodic or cathodic), the cell assembly (whether it is divided or undivided) and the applied current on the efficiency of the electrochemical regeneration in alkaline medium. Regarding electrode polarity, the figure shows that, irrespectively of the cell configuration, the RE values achieved by the cathodic regeneration are in general higher than the anodic ones. Moreover, differences between cathodic and anodic treatments

are greater for the undivided cell and at higher currents. An exception occurs at the lowest applied current, at which REs are close to each other, the anodic treatment in an undivided cell showing slightly better yields.

Figure 3. Effect of the applied current, the electrode polarity and the separation of compartments on the regeneration efficiencies for the electrochemical regeneration of phenol-saturated AC in 0.5M NaOH medium.



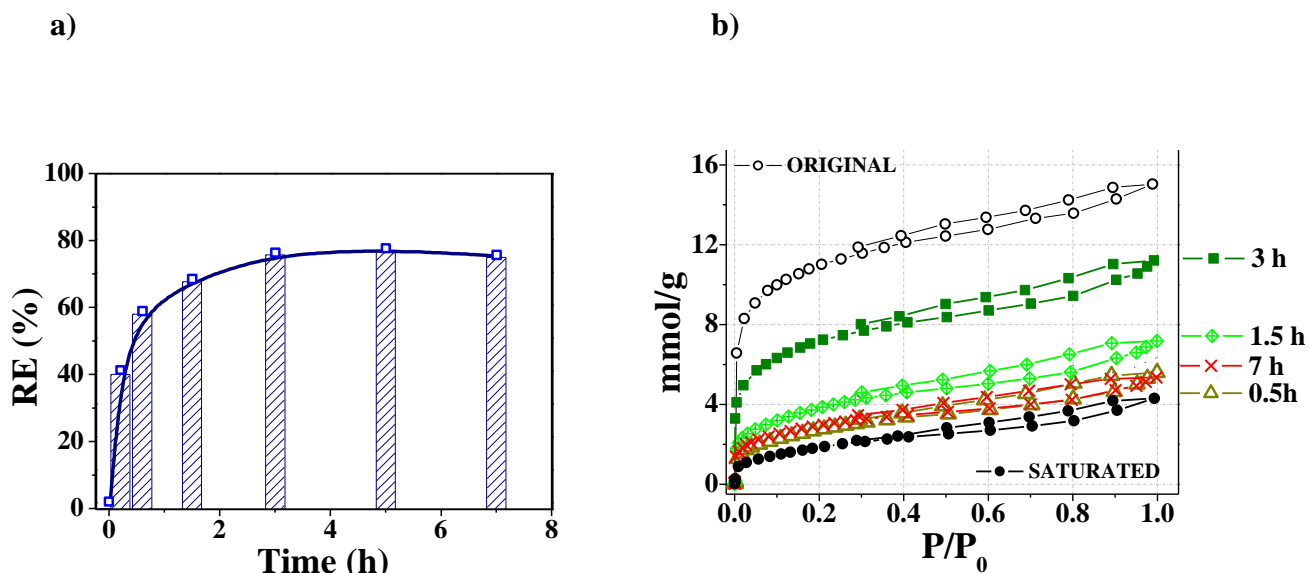
The influence of the compartments separation depends on the previous polarity effect. As observed in Figure 3, the regeneration efficiencies for the cathodic treatment in the undivided cell are better than in the divided case, especially at the higher currents. However, the cell configuration seems not to have a significant effect on the anodic regeneration efficiencies.

The effect of the electrolysis current on the regeneration efficiency can also be analyzed from Figure 3. In most of the regeneration experiments, the highest RE values are

achieved at the lowest current, and then the RE decreases with the increasing current until a constant value is reached. However, the cathodic regeneration in undivided cells does not follow the general tendency. This treatment gives the best yields in a wide range of tested currents. The RE increases with the increasing current to reach the highest value, close to 80 %, at 1.0 A and then it decreases slightly at higher currents. The RE values close to 80% obtained in this work are in agreement with those reported by other authors for electrochemical regeneration of aromatic compounds [18-22].

Prolonged (up to 7 h) electrolytic regeneration experiments were also studied. Figure 4 shows the evolution with time of the RE and the porosity recovery. The regeneration efficiency shows a sharp rise within the 0-3 h timespan, and then it seems to reach a constant value and is not further improved in the investigated time interval. Therefore, all electrolyses were run for three hours, which was considered as the most suitable conditions to achieve the higher regeneration efficiencies.

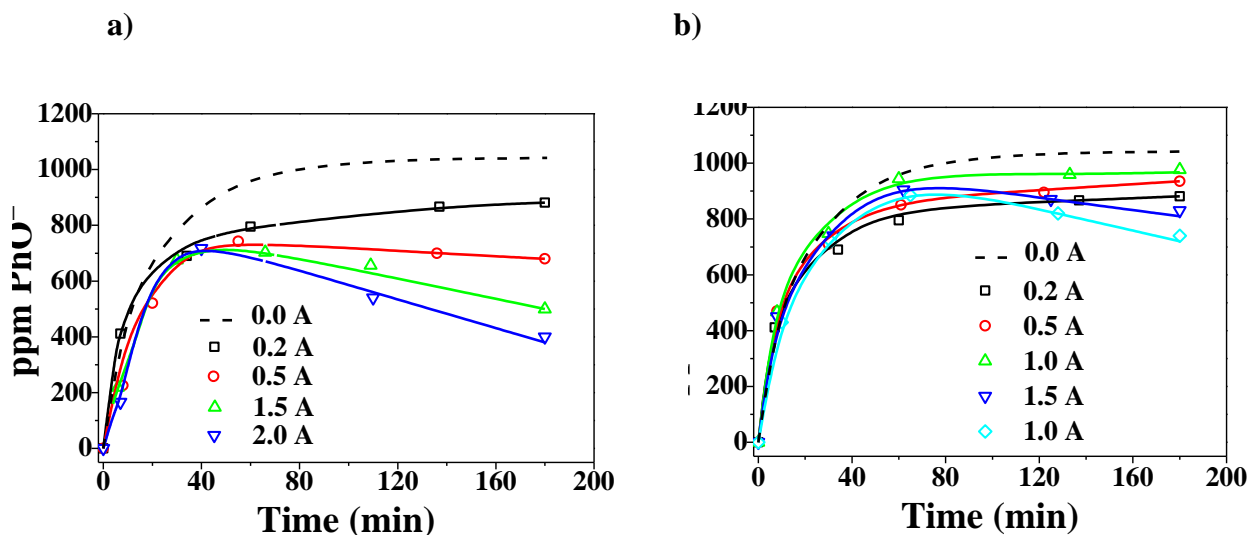
Figure 4. Effect of the regeneration time on (a) the regeneration efficiency and (b) on the N₂ isotherms (porosity recovery) for the cathodic regeneration of phenol-saturated AC in 0.5 M NaOH medium, in an undivided cell, at 0.2 A.



3.2.2 Phenol concentration profile

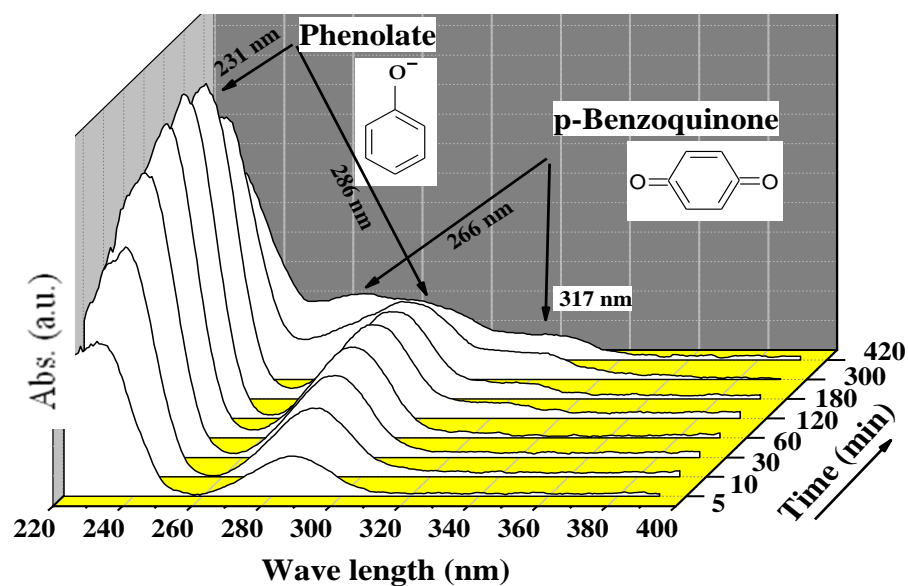
The concentration of phenol in the electrolyte solution was monitored as a function of the electrolysis time; really, the species which is being monitored is phenolate at the pH used. The concentration profiles obtained at different applied currents are compared in Figure 5. For sake of clarity, we only show the results corresponding to the anodic (Fig. 5a) and cathodic (Fig. 5b) regenerations with the best yields (in the divided and undivided assemblies respectively). In both cases, two characteristic regions can be distinguished in the concentration profiles: a region of sharp increase in the phenolate concentration that occurs within the first 40-60 min of electrolysis and is almost independent of the applied current, and a second region at longer times in which the concentration levels off or drops depending on the applied current. Similar phenolate concentration profiles were observed during anodic treatments in undivided cells and cathodic treatment in divided cells.

Figure 5. Effect of the applied current on the phenol concentration-time profile for (a) the anodic treatment in a divided cell and (b) for the cathodic treatment in an undivided cell in 0.5 M NaOH medium.



The decrease in the phenolate concentration at long electrolysis times suggests that, after release from GAC particles, this species is transformed by electrochemical reaction; that is, there is an electrochemical reaction step coupled to the main desorption process. In fact, a detailed analysis of UV-Vis spectra of the electrolyte sampled at selected electrolysis times during a cathodic treatment in an undivided cell (Fig. 6) reveals the presence of p-benzoquinone (with maximum bands at 266 and 317 nm) after 2 h electrolysis. The increase in the area of the quinone spectral features at times longer than 2 h is accompanied by a decrease in the phenolate characteristic bands at 225 and 286 nm. These results indicate that quinone-like molecules are formed by electrochemical oxidation of phenolate.

Figure 6. UV-Vis spectra of the 0.5 M NaOH electrolyte at different regeneration times. Cathodic regeneration in an undivided cell at 0.2 A.



3.2.3 Porosity recovery after electrochemical treatment

The values of the S_{BET} , the total volume of micropores ($V_{\text{DR}}(\text{N}_2)$) and the volume of the narrow micropores ($V_{\text{DR}}(\text{CO}_2)$) of the samples electrochemically regenerated under various experimental conditions are listed in Table 2, in which the percentage of porosity recovery is also presented. The textural characterization reveals that the porosity recovery after electrochemical treatment agrees with the previously observed tendencies of regeneration efficiencies: on the one hand, porosity recoveries for cathodic treatments are higher than those for the anodic ones and, on the other hand, porosity recoveries are much higher in the case of the undivided configuration. The variation in the porosity recovery with the increasing applied current is also in qualitative accordance with the tendency shown by REs. As a general trend, the porosity recovery becomes poorer as the current increases, although this statement does not apply to the cathodic regeneration in undivided cells.

Table 2. Textural characterization of the electrochemically-treated activated carbon samples at different current intensities in 0.5 M NaOH.

Sample	S_{BET} (m^2/g)				$V_{\text{DR}}(\text{N}_2)$ (cm^3/g)				$V_{\text{DR}}(\text{CO}_2)$ (cm^3/g)			
	Div.		Undiv.		Div.		Undiv.		Div.		Undiv.	
	m^2/g	% ^a	m^2/g	% ^a	cm^3/g	% ^b	cm^3/g	% ^b	cm^3/g	% ^c	cm^3/g	% ^c
Wpa0.2OH ⁻	257	30	585	65	0.12	30	0.26	70	0.10	35	0.12	40
Wpa0.5OH ⁻	239	25	224	25	0.11	30	0.08	20	0.10	35	0.13	45
Wpa1.0OH ⁻	247	30	175	20	0.11	30	0.07	20	0.10	35	0.07	25
Wpa1.5OH ⁻	172	20	141	15	0.07	20	0.06	15	0.11	40	0.08	30
Wpa2.0OH ⁻	184	20	109	10	0.09	25	0.04	10	0.10	35	0.06	20
Wpc0.2OH ⁻	450	50	579	65	0.19	50	0.25	70	0.18	60	0.15	50
Wpc0.5OH ⁻	431	50	656	75	0.18	50	0.29	80	0.17	60	0.19	65
Wpc1.0OH ⁻	353	40	734	85	0.14	40	0.32	85	0.16	55	0.19	65
Wpc1.5OH ⁻	406	45	599	70	0.17	45	0.25	70	0.16	55	0.20	70
Wpc2.0OH ⁻	355	40	723	85	0.16	45	0.30	80	0.16	55	0.19	65

^a Percentage of available S_{BET} area relative to the fresh AC (W)

^b Percentage of available total micropore volume relative to the fresh AC(W)

^c Percentage of available narrowest micropore volume relative to the fresh AC(W)

The best porosity recovery values obtained by cathodic regeneration in an undivided cell, agrees with the highest REs. However, the measured porosity recoveries in anodic treatments at the higher current are significantly lower than those that would be expected taking into account the final REs (40-50 %, Fig.3).

4. Discussion

The electrochemically-assisted regeneration of saturated GAC is anticipated to proceed through a very complex mechanism with different coupled and/or parallel steps. Therefore, the overall kinetics of the process and the properties relevant for the feasibility of reuse (regeneration efficiencies and final textural properties) are most likely to be governed by many operational conditions and variables, many often closely related to each other. In this work, we have examined the role of the electrolyte composition and pH, the electrolyzer set up (cathodic or anodic treatment and cell assembly), the applied current and the electrolysis time. The influence of these variables will be discussed separately in order to identify the various steps involved in the process and to propose an overall phenomenological mechanism for the electrochemical regeneration of phenol-saturated GAC.

4.1 Effect of the electrolyte pH

The far better regeneration yield and porosity recovery obtained in alkaline media in absence of current, compared to neutral chloride and acidic sulphuric media, can be explained by three mechanisms acting together: i) at basic conditions phenol ($pK_a=9.89$) is mainly as phenolate and its solubility in water is higher than that of neutral phenol molecule; ii) in NaOH solutions, both the surface oxygen groups of the AC ($pH_{pzc}=9$) and the adsorbed phenol are deprotonated and, because of electrostatic repulsions between phenolate and AC oxygen groups and also between phenolate molecules, phenol is favourably desorbed as phenolate species; and iii) considering the chemical adsorption mechanism of phenol postulated by some authors [29], NaOH solution can hydrolyze some chemical bonds between phenol hydroxyl groups and the surface oxygen groups of the AC.

In H_2SO_4 electrolyte, the adsorbate and the surface oxygen groups of the GAC remain protonated and phenol is adsorbed on the GAC, not only by π - π interactions, but also by extensive hydrogen bonding. In these conditions, the desorption of phenol is unfavoured and the regeneration efficiency is low. In neutral solutions, like NaCl, an intermediate desorption degree is observed.

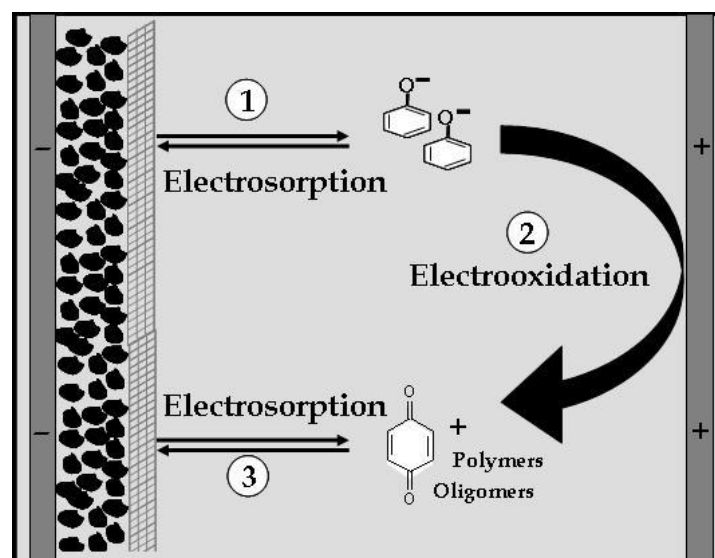
Thus, and before considering any electrochemical variable, the first mechanism involved in the regeneration of GAC is an *adsorption-desorption equilibrium* influenced by the acid-base properties of both the adsorbate and the adsorbent, which are greatly determined by the type of electrolyte and pH.

4.2. Effect of the electrode polarity

The effect of the electrode polarity on the regeneration process (Fig. 3) can be explained by taking into account the sign of the polarization of the GAC and the electric charge of the adsorbate. The positive potential achieved during the anodic regeneration (between +0.9 V and +1.9 V vs Ag/AgCl) produces electrostatic attractive interactions between positively polarized GAC and phenolate species, and keeps a higher concentration of deprotonated species within the double layer region surrounding the anode and the GAC particles. If this occurs, further desorption is hindered and lower REs are obtained. On the contrary, when the regeneration is performed at the cathode, the GAC is subjected to a negative potential which builds up a negative charge on the carbon material. Then, the phenolate species are more easily desorbed from the GAC and removed away by repulsive interactions, thus achieving higher REs.

The results described above suggest that the adsorbate is involved in a new equilibrium of electroadsorption-electrodesorption. We then propose the existence of an *electrosorption step (1)* (Fig. 7) in the mechanism of the electrochemical regeneration of GAC. The electrode polarity is a key factor that may either promote or preclude the shift of the electrosorption equilibrium of phenol to the side of desorption. Also, the current has an indirect impact in the electrosorption process: the higher the applied current, the higher the extent of polarization, this is, the higher the negative charge accumulated on GAC particles in cathodic treatments or the higher the positive charge built up in anodic treatments. However, the role of the electric current is much more complex, because it has an effect on other steps of the mechanism of electrochemical regeneration, as it will be described and discussed below.

Figure 7. General electrochemical regeneration mechanism of phenol-saturated activated carbon. Example of the cathodic regeneration in NaOH in an undivided cell.



The electrode polarity and the resulting imposed electric field may also affect the transport of desorbed phenolate through the GAC pores, which results from the

competition or cooperation of two main mechanisms, namely ionic migration and diffusion. While the phenol concentration gradient always forces phenolate to flow away the pores, the transport of phenol charged species depends on the direction of the electric field. In the cathodic treatment both the concentration gradient and the electric potential gradient are in the same direction and the motion of desorbed phenolate out of the pores is cooperative. Phenol flows easily away into the bulk solution and regeneration is facilitated. On the contrary, in anodic treatments both gradients are opposite and diffusion and migration compete. The flow of phenol into the bulk solution is lowered and regeneration is more difficult. The weight of the migration contribution to the overall transport process within the pores should increase with increasing the applied current (i.e. increasing electric field across the cell) and is another factor that accounts for the drop in anodic REs at high currents. Then, a *migration process* should be also included as an important transport step in the overall mechanism of electrochemical regeneration.

4.3 Effect of the applied current

Desorbed phenolate ions can participate in electrochemical reactions at the electrodes. The anodic electrooxidation of phenol species has been exhaustively investigated at different electrode materials including Pt, Au, glassy carbon and metal oxide electrodes [25,30-36]. Phenol can also be degraded on a cathode via indirect oxidation by electrogenerated hydrogen peroxide [37-40]. The two-electron electroreduction of dissolved oxygen to hydrogen peroxide occurs with acceptable yields in a wide range of pH, from mildly acidic (more adequate for Fenton's reactions) [37,41] to highly alkaline (suitable for paper pulp bleaching [42]) and it has been reported to be favoured on steel [43,44] and carbon electrodes [41,45]. In a previous study [24], fresh activated carbon

was cathodically electrolysed in a filter-press cell under the same conditions used in this work. An increase in the surface oxygen-containing functionalities was found, especially in alkaline media, which was interpreted as an effect of the oxidising power of electrogenerated hydrogen peroxide. Moreover, it has been claimed that AC acts as a catalyst for the decomposition of H_2O_2 into highly oxidizing hydroxyl radicals [46-48].

Then, the involvement of desorbed phenolate in an *electrochemical oxidation step* (2) must be also considered in the overall degradation mechanism, both in cathodic and anodic regeneration treatments (Fig. 7). This step is coupled to the previously mentioned electrosorption equilibrium. When the phenolate concentration decreases by direct electrochemical oxidation at the anode and/or indirect electro-oxidation at the cathode, the electrosorption equilibrium is shifted towards the phenolate desorption and regeneration efficiencies should increase.

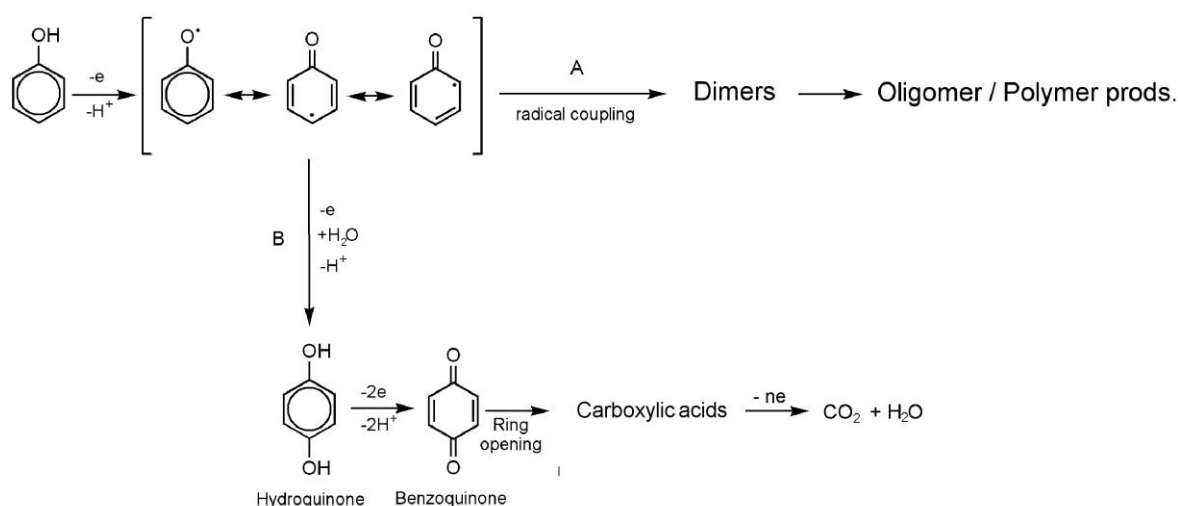
The phenolate concentration profiles recorded as a function of the regeneration times (Fig. 5) can be readily explained by considering the existence of the electrochemical conversion of phenolate. The steep rise in concentration at the beginning of the electrolysis means that phenol desorption is faster than the electrochemical reaction in a wide range of input currents. At longer times, the shape of the phenolate concentration vs. time plot is determined by the relative rates of the desorption and electrochemical reaction steps. At low currents, the rise in phenolate concentration by desorption is counterbalanced by its decay by electrochemical conversion and a stabilized profile results. As the applied current is increased (and so does the anodic or cathodic overvoltage), simple electrode kinetics predict the enhancement of the electrochemical reaction rate and consumption of phenol predominates. In the cathodic treatment (Fig.

5b), a higher current flow compared to the anodic case (fig. 5a) is necessary for the electrochemical degradation to cause a net decay in the phenol concentration. This is probably caused by the enhancement of the phenol release rate by favourable electrodesorption and migration when the GAC is confined near the cathode.

As it can be observed in Fig. 3, the applied current has a marked effect on RE values. However, with the exception of the cathodic treatment in undivided cells, the observed effect is the opposite to the expected one and, although phenol is transformed faster at higher currents, REs are not improved by the electrochemical reactions. These contradictory results indicate that another factor must be taken into account. In fact, the mechanism of the electrochemical reaction of phenol must be carefully considered. It is generally accepted that the oxidation of phenol can proceed through two parallel reaction pathways [32-35], with a first one-electron transfer yielding phenoxy radicals as a common step. This first step can be followed by a radical-radical coupling process to produce a series of phenolic dimers (head-to-head, head-to-tail...), which suffer successive oxidation/radical coupling to yield phenol oligomeric/polymeric fouling products. Alternatively, phenoxy radicals can be involved in a second electron transfer step that leads to phenoxonium ions followed by further oxidation to stable benzoquinone species. Benzoquinone is then degraded with aromatic ring opening to a series of small carboxylic acids, mainly maleic and oxalic acids. These acids are finally mineralised to CO₂ through different intermediate products. A scheme of the reaction pathways of anodic electrochemical degradation of phenol is shown in Figure 8. These reaction pathways apply to both direct electron transfer reactions and indirect oxygen transfer from hydroxyl radicals generated by water electrolysis (typical of metal oxide electrodes). The prevalence of one reaction pathway over the other and the distribution

of intermediates strongly depend on the experimental conditions, such as the type of electrolyte and pH, the electrode potential (applied current) and particularly the anode material. In the peroxide-mediated degradation of phenol compounds, the same kind of oxidized intermediates than in direct anodic electrooxidation were found, i.e., benzoquinone and small organic acids [39,40,46]. In our particular case, UV-Vis spectroscopy (Fig. 6) revealed the occurrence of benzoquinone as intermediate species in the peroxide-mediated electrooxidation of phenol and the coating of the anode surface by black tars pointed to the formation of products of polymeric nature.

Figure 8. Simplified reaction pathways for the electrochemical oxidation of phenol.



Furthermore, it should be emphasized that phenol can also be involved in chemical oxidative coupling reactions with dissolved molecular oxygen to yield phenol oligomeric/polymeric products. It has been shown by others [10,49,50] that chemical oxidative coupling is promoted at high pHs and high concentration of molecular oxygen and is catalysed by carbon surfaces.

Considering this mechanism, it is proposed that the electrooxidation process favours high RE values provided that GAC is not blocked by the electrooxidation products, which can also electroadsorb in the GAC. Among these oxidation intermediates, oligomers, polymeric products and quinones are considered to be the most likely blocking oxidation products. In fact, Zhou and Lei [46] have recently shown that competitive adsorption occurs between phenol degradation products. The activated carbons used by these authors exhibited high adsorption capacities for benzoquinone and hydroquinone and low capacity for organic acids (eg. Fumaric acid). Thus, the *electrosorption of the electrooxidation products* (3), must be also considered in the electrochemical regeneration of the GAC (Fig. 7). According to this view, the poorer regeneration efficiencies achieved in anodic treatments compared to the cathodic ones can also be a consequence of a more severe blocking by phenol oxidation products, especially those of oligomeric nature.

4.4 Effect of the cell assembly

The effect of the cell configuration is closely related to the electrochemical reaction step, since the transport of desorbed phenolate species to the counterelectrode is allowed (undivided cell) or hampered (divided cell), thus enabling or precluding additional electrochemical reaction at the counterelectrode. An extra consumption of phenolate at the counterelectrode would lead to a further shift of the electrosorption equilibrium to the desorption side, thus enhancing REs. The improvement in the efficiency of the cathodic regeneration upon removing the membrane is in full agreement with this argument. However, the effect of the compartment separation on the RE seems not to be particularly important in the case of anodic treatments. If it is assumed that desorbed phenol is converted at the anode mainly in slightly soluble oligomers or polymeric

products which remain attached to GAC, then the amount of phenol and phenol derivatives reaching the cathode for electrochemical reaction would be small. Additionally, peroxide-mediated degradation at the cathode may not be as efficient in the absence of GAC particles, which are catalysts for the decomposition of hydrogen peroxide into stronger oxidizing radicals. Both effects would explain the irrelevance of the compartment separation in the case of anodic treatments.

4.5. Effect of the regeneration time

The steep rise observed in the regeneration efficiency and the porosity recovery within the 0-3 h electrolysis timespan (Fig. 4) is probably a consequence of desorption of phenol adsorbed in the most accessible porosity. The constant RE obtained at longer electrolysis times may be due to a combination of two factors: on the one hand, the sluggish phenolate diffusion through the narrowest micropores and, on the other hand, the increasing amount of blocking oxidation products, whose adsorption on the GAC may also increase with the regeneration time. Longer regeneration times should give phenol/phenolate enough time to diffuse through the pores and higher REs would be expected. Nevertheless, the generation and adsorption of the blocking oxidation products are difficult to avoid. Therefore, the nature of the anode and its electrocatalytic properties towards phenol/phenolate oxidation may play a key role in the regeneration process, since these factors determine the amount and nature of the oxidation products.

4.6. Porosity recovery after electrochemical treatment

The dependence of the textural properties on the electrochemical variables is qualitatively consistent with that exhibited by the regeneration efficiencies. Therefore, the same general arguments developed above are valid to support the observed porosity

recoveries. From Table 2 it follows that the cathodic regeneration in an undivided cell gives rise to the highest porosity recoveries. As discussed in the precedent sections, this may be due to a combination of several factors which, produce enhanced phenolate desorption by favourable electrodesorption and migration conditions, and by the assistance of electrooxidation combined by low readsorption of oxidation blocking products.

However, the low porosity recoveries observed for the anodically-regenerated AC samples at higher currents, which in some cases are as low as that of the phenol-exhausted carbon material, do not seem to agree with their corresponding RE values (40-50 %, see Fig. 3). These results suggest that products blocking the porosity do not hinder and even could participate in the phenol re-adsorption after regeneration. According to different authors [10,49,50], the blocking species which can be involved in phenol adsorption may be phenolic compounds, such as dimers, oligomers, polymers, etc. These products could come from coupling reactions on the AC surface, during regeneration in NaOH and/or during the adsorption process, favoured at high pH and oxic conditions [10,49,50], and/or, they could be produced electrochemically on the electrodes, as we have observed in this work, and then adsorbed on the regenerated AC.

5. Conclusions

The electrochemical regeneration of AC saturated with phenol has been performed in a filter press cell in alkaline medium. A significant influence electrode polarity, compartments separation, applied current and time on regeneration efficiency and porosity recovery of the saturated AC is observed.

The mechanism of the electrochemical regeneration of phenol-saturated activated carbon involves different processes, such as phenol/phenolate sorption and electrosorption equilibria; phenol/phenolate migration and electrochemical oxidation processes; migration, sorption and electrosorption processes of the phenol/phenolate electrooxidation products. All these processes are summarized in Figure 7 and constitute the global electrochemical regeneration mechanism..

The best results in terms of regeneration efficiencies and porosity recoveries in alkaline medium (0.5M NaOH) have been obtained by cathodic regeneration in an undivided cell, at moderate currents and for regeneration times of 3 h. Under these conditions RE values slightly higher than 80 % are achieved. These high efficiencies may be due to a combination of several factors which produce more phenolate desorption, electrooxidation and less readsorption of the blocking products.

The lower RE values obtained in the anodic regeneration can be a consequence of the negative influence of the more positive potential, which favours the electroadsorption of phenolate and the generation of more surface blocking electrooxidation products as the applied current increases.

In order to obtain a better performance of the process, further studies must be carried out and special attention should be paid to the nature of the anode, since it play a key role in the amount and nature of blocking electrooxidation products.

Acknowledgements

Financial support by the Ministerio de Ciencia e Innovación (CTQ2006-08958 and MAT2007-60621) projects and GV (ACOMP/2009/174 and PROMETEO/2009/047) is gratefully acknowledged.

References

- [1] Bansal RC, Donet JB, Stoeckli F. *Active Carbon*. Marcel Dekker, New York. 1988.
- [2] Burchell TD. *Carbon materials for advanced technologies*. Oxford: Elsevier Science Ltd.; 1999.
- [3] Radovic LR, Moreno–Castilla C, Rivera-Utrilla J. Carbon materials as adsorbents in aqueous solutions. In: Radovic LR, editor. *Chemistry and physics of carbon*, Vol. 27, New York; Marcel Dekker; 2001. p. 207–405.
- [4] Derbyshire F, Jagtoyen M, Andrews R, Rao A, Martín-Gullón I, Grulke E. Carbon materials in environmental applications. In: Radovic LR, editor. *Chemistry and physics of carbon*, Vol. 27. New York: Marcel Dekker; 2001. p. 1-66.
- [5] Roskill Consulting Group. *The Economics of Activated Carbon*. 8th Ed. London: Roskill Information Services; 2008.
- [6] Hutchins RA. Economic factors in granular carbon thermal regeneration. *Chem Eng Progr* 1973;69(11):48-55.
- [7] Bercic G, Pintar A, Levec J. Desorption of phenol from activated carbon by hot water regeneration: desorption isotherms. *Ind Eng Chem Res* 1998;35(12):4619–25.
- [8] Álvarez PM, Beltrán FJ, Gómez-Serrano V, Jaramillo J, Rodríguez EM. Comparison between thermal and ozone regenerations of spent activated carbon exhausted with phenol. *Water Res* 2004;38(8):2155-65.
- [9] Sutikno T, Himmelstein KJ. Desorption of phenol from activated carbon by solvent regeneration. *Ind Eng Chem Fund* 1983;22(4):420–6.

- [10] Grant TM, King CJ. (1990). Mechanism of Irreversible Adsorption of Phenolic-Compounds by Activated Carbons. *Ind Eng Chem Res* 1990;29(2):264–71.
- [11] Leng C-C, Pinto NG. An investigation of the mechanisms of chemical regeneration of activated carbon. *Ind Eng Chem Res* 1996;35(6):2024–31.
- [12] Martin RJ, Ng WJ. Chemical regeneration of exhausted activated carbon—I. *Water Res* 1984;18(1):59–73.
- [13] San Miguel G, Lambert SD, Graham NJD. The regeneration of field-spent granular-activated carbons. *Water Res* 2001;35(11):2740-48.
- [14] Ania CO, Menéndez JA, Parra JB, Pis JJ. Microwave-induced regeneration of activated carbons polluted with phenol. A comparison with conventional thermal regeneration. *Carbon* 2004;42(7):1383-87.
- [15] Moreno-Castilla C, Rivera-Utrilla J, Joly JP, López- Ramón MV, Ferro-García MA, Carrasco-Martín F. Thermal regeneration of an activated carbon exhausted with different substituted phenols. *Carbon* 1995;33(10):1417–23.
- [16] Ferro-García MA, Utrera-Hidalgo E, Rivera-Utrilla, J, Moreno-Castilla C, Joly JP. Regeneration of activated carbons exhausted with chlorophenols. *Carbon* 1993;31(6):857-63.
- [17] Schweiger TAJ, Le Van MD. Steam regeneration of solvent adsorbers. *Ind Eng Chem Res* 1993; 32(10):2418-29.
- [18] Cañizares P, Lobato J, García-Gómez J, Rodrigo MA. Combined adsorption and electrochemical processes for the treatment of acidic aqueous phenol wastes. *J Appl Electrochem* 2004;34(1):111-7.
- [19] García-Otón M, Montilla F, Lillo-Ródenas MA, Morallón E, Vázquez JL. Electrochemical regeneration of activated carbon saturated with toluene. *J Appl Electrochem* 2005;35(3):319-25.

- [20] Narbaitz RM, Cen J. Electrochemical regeneration of granular activated carbon. *Water Res* 1994;28(8):1771–78.
- [21] Zhang HP, Ye LY, Zhong H. Regeneration of phenol-saturated activated carbon in an electrochemical reactor. *J Chem Technol Biotechnol* 2002;77(11):1246-50.
- [22] Zhang HP. Regeneration of exhausted activated carbon by electrochemical method. *Chem Eng J* 2002;85(1):81-5.
- [23] Barron MA, Haber L, Maier A, Zhao J, Dourson M. Toxicological review of phenol. CASN° 108-95-2. IRIS. US EPA, 2002.
- [24] Berenguer R, Marco-Lozar, JP, Quijada C, Cazorla-Amorós D, Morallón E. Effect of the electrochemical treatments on the surface chemistry of activated carbon. *Carbon* 2009; 47(4):1018-27.
- [25] Montilla F, Morallón E, Vázquez JL. Evaluation of the electrocatalytic activity of antimony-doped tin dioxide anodes toward the oxidation of phenol in aqueous solutions. *J Electrochem Soc* 2005;152(10):B421-27.
- [26] Lozano-Castelló D, Suárez-García F, Cazorla-Amorós D, Linares-Solano A. Porous texture of carbons. In: Beguin F, Frackowiak E, editors. *Carbons for electrochemical energy storage and conversion systems*. CRC Press; 2009. p. 115-162.
- [27] Cazorla-Amorós D, Alcañiz-Monge J, Linares-Solano A. Characterization of activated carbon fibers by CO₂ adsorption. *Langmuir* 1996;12(11):2820–24.
- [28] Cazorla-Amorós D, Alcañiz-Monge J, de la Casa-Lillo MA, Linares-Solano A. CO₂ as an adsorptive to characterize carbon molecular sieves and activated carbons. *Langmuir* 1998;14(16):4589–96.
- [29] Dabrowski A, Podkościelny P, Hubicki Z, Barczak M. Adsorption of phenolic compounds by activated carbon-a critical review. *Chemosphere* 2005;58(8):1049-70.

- [30] Comninellis C. Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for wastewater treatment, *Electrochim Acta* 1994;39(11-12):1857-62.
- [31] Johnson SK, Houk LL, Feng JR, Johnson DC. Electrochemical incineration of 4-chlorophenol and the identification of products and intermediates by mass spectrometry. *Environ Sci Technol* 1999;33(15):2638-44.
- [32] Feng YJ, Li XY. Electrocatalytic oxidation of phenol on several metal-oxide electrodes in aqueous solutions. *Water Res* 2003;37(10):2399-2407.
- [33] Li XY, Cui YH, Feng YJ, Xie ZM, Gu JD. Reaction pathways and mechanisms of the electrochemical degradation of phenol on different electrodes. *Water Res* 2005;39(10):1972-81.
- [34] Gatrell M, Kirk DW. The electrochemical oxidation of aqueous phenol at a glassy carbon electrode, *Can J Chem Eng* 1990;68(6):997-1003
- [35] Garcés P, Lapuente R, Andión LG, Cases F, Morallón E, Vázquez JL. Electropolymerization of phenol on carbon steel and stainless steel electrodes in carbonate aqueous medium. *Polym J* 2000;32(8):623-28.
- [36] Lapuente R, Cases F, Garcés P, Morallón E, Vázquez JL. A voltammetric and FTIR-ATR study of the electropolymerization of phenol on platinum electrodes in carbonate medium. Influence of sulphide. *J Electroanal Chem* 1998;451(1-2):163-71.
- [37] Hsiao YL, Nobe K. Hydroxylation of chlorobenzene and phenol in a packed bed flow reactor with electrogenerated Fenton's reagent. *J Appl Electrochem* 1993;23(9):943-46.
- [38] Alvarez-Gallegos, A, Pletcher, D. The removal of low level organics via hydrogen peroxide formed in a reticulated vitreous carbon cathode cell. Part 2. the removal of phenols and related compounds from aqueous effluents. *Electrochim Acta* 1999;44(14):2483-92.

- [39] Brillas E, Sauleda R, Casado J. Degradation of 4-chlorophenol by anodic oxidation, electro-Fenton, Photoelectro-Fenton and Peroxi-coagulation Processes. *J Electrochem Soc* 1998;145(3):759-65.
- [40] Wang H, Wang JL. The cooperative electrochemical oxidation of chlorophenols in anode-cathode compartments. *J Hazard Mat* 2008;154(1-3):44-50.
- [41] Alvarez-Gallegos A, Pletcher D. The removal of low level organics via hydrogen peroxide formed in reticulated vitreous carbon cathode cell. Part. 1. The electrosynthesis of hydrogen peroxide in aqueous acidic solutions. *Electrochim Acta* 1998;44(5):853-61.
- [42] Oloman C, Watkinson AP. The electroreduction of oxygen to hydrogen peroxide on fluidized cathodes. *Can J Chem. Eng* 1975;53(2):268-73.
- [43] Jovancicevic V, Bockris JO. The Mechanism of Oxygen Reduction on Iron in Neutral Solutions. *J Electrochem Soc* 1986;133(9):1797-807.
- [44] Wroblowa HS, Qaderi SB. Mechanism and Kinetics of Oxygen Reduction on Steel. *J Electroanal Chem* 1990;279(1-2):231-42.
- [45] Qiang Z, Chang J-H, Huang C-P. Electrochemical generation of hydrogen peroxide from dissolved oxygen in acidic conditions. *Water Res* 2002;36(1):85-94.
- [46] Huang H-H, Lu M-C, Chen JN, Lee CT. Catalytic decomposition of hydrogen peroxide and 4-chlorophenol in the presence of modified activated carbon. *Chemosphere* 2003;51(9):935-43.
- [47] Lücking F, Koser H, Jank M, Ritter A. Iron powder, graphite and activated carbon as catalysts for the oxidation of 4-chlorophenol with hydrogen peroxide in aqueous solutions. *Water Res* 1998;32(9):2607-14.
- [48] Zhou M, Lei L. The role of activated carbon on the removal of p-nitrophenol in an integrated three-phase electrochemical reactor. *Chemosphere* 2006;65(7):1197-203

[49] Vidic R, Suidan MT. Role of dissolved oxygen on the adsorptive capacity of activated carbon for synthetic and natural organic matter. *Environ Sci Technol* 1991;25(9):1612-8.

[50] Pimenta ACO, Kilduff JE. Oxidative coupling and the irreversible adsorption of phenol by graphite. *J Colloid Interface Sci* 2006;293(2):278-89.

FIGURE CAPTIONS

Figure 1. Diagram of the electrochemical filter-press cell: (a) Divided configuration; (b) Undivided configuration.

Figure 2. Effect of the electrolyte pH on (a) the regeneration efficiencies and (b) on the N_2 isotherms (porosity recovery) for 3-hour regeneration experiments of phenol-saturated AC in the absence of applied current.

Figure 3. Effect of the applied current, the electrode polarity and the separation of compartments on the regeneration efficiencies for the electrochemical regeneration of phenol-saturated AC in 0.5M NaOH medium.

Figure 4. Effect of the regeneration time on (a) the regeneration efficiency and (b) on the N_2 isotherms (porosity recovery) for the cathodic regeneration of phenol-saturated AC in 0.5 M NaOH medium, in an undivided cell, at 0.2 A.

Figure 5. Effect of the applied current on the phenol concentration-time profile for (a) the anodic treatment in a divided cell and (b) for the cathodic treatment in an undivided cell in 0.5 M NaOH medium.

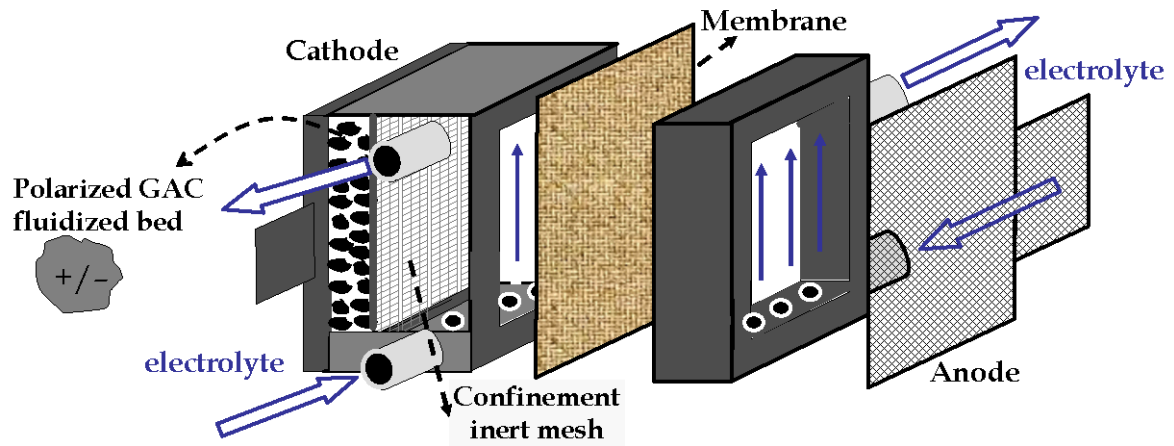
Figure 6. UV-Vis spectra of the 0.5 M NaOH electrolyte at different regeneration times. Cathodic regeneration in an undivided cell at 0.2 A.

Figure 7. General electrochemical regeneration mechanism of phenol-saturated activated carbon. Example of the cathodic regeneration in NaOH in an undivided cell.

Figure 8. Simplified reaction pathways for the electrochemical oxidation of phenol.

Figure 1

a) **DIVIDED**
(2 compartments)



b) **UNDIVIDED**
(1 compartment)

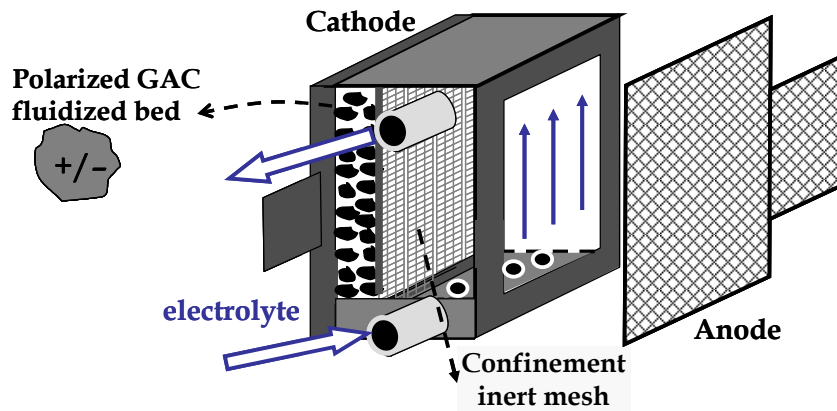
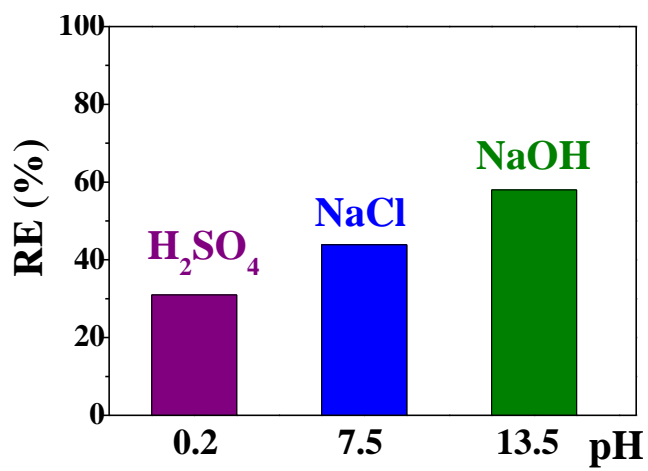


Figure 2

a)



b)

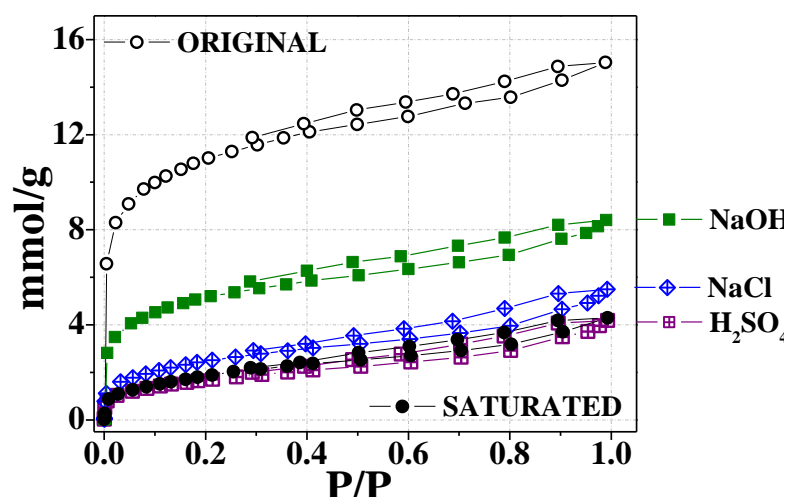


Figure 3

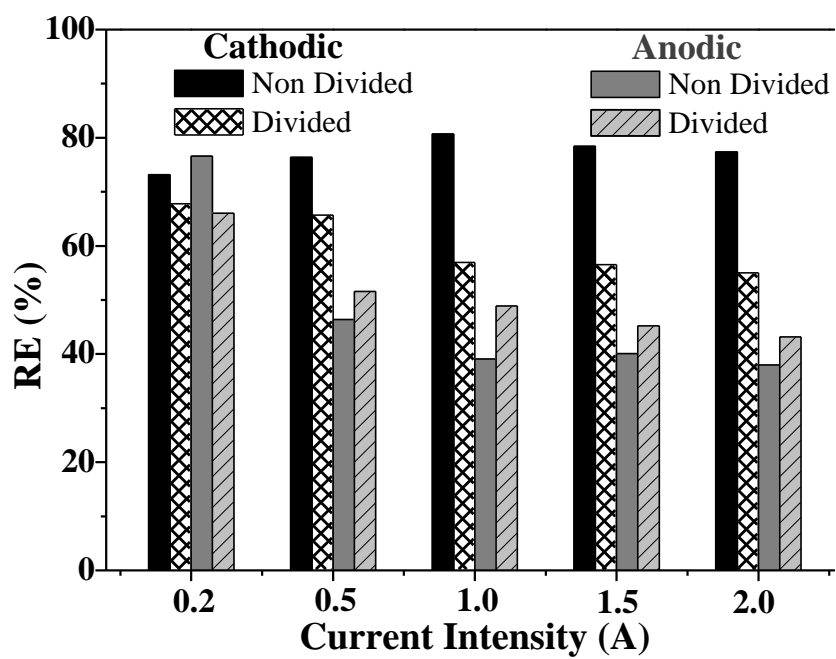


Figure 4

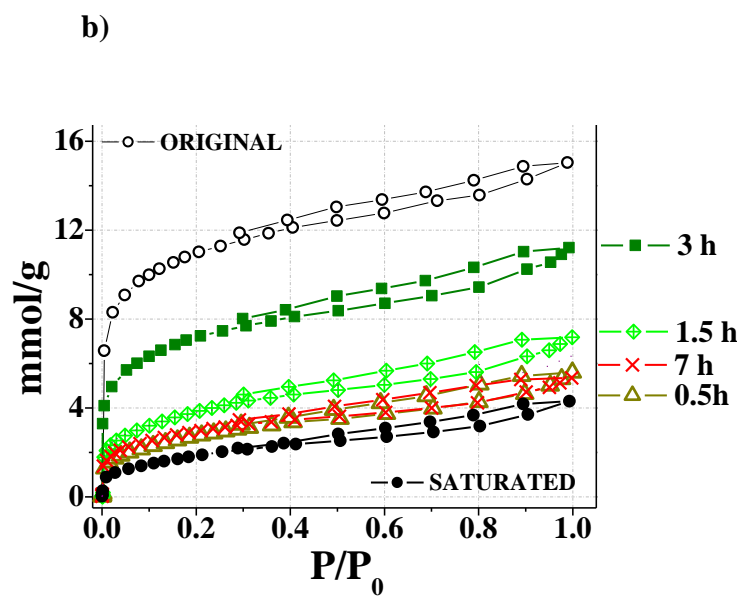
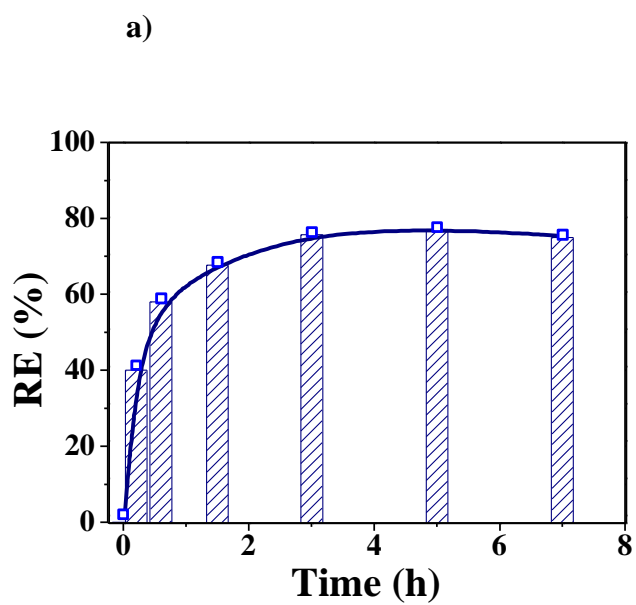
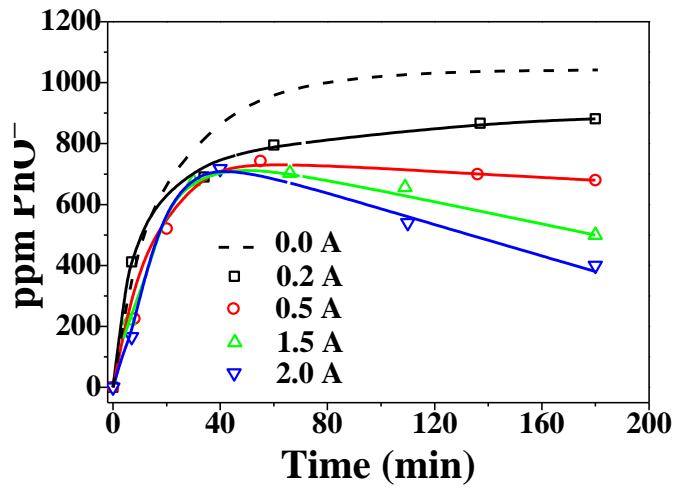


Figure 5

a)



b)

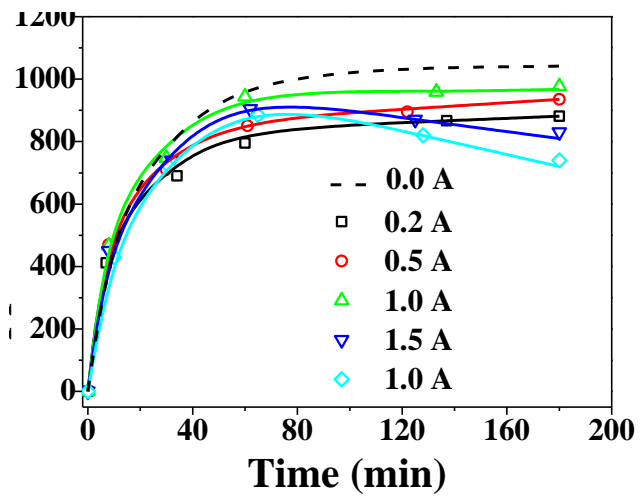


Figure 6

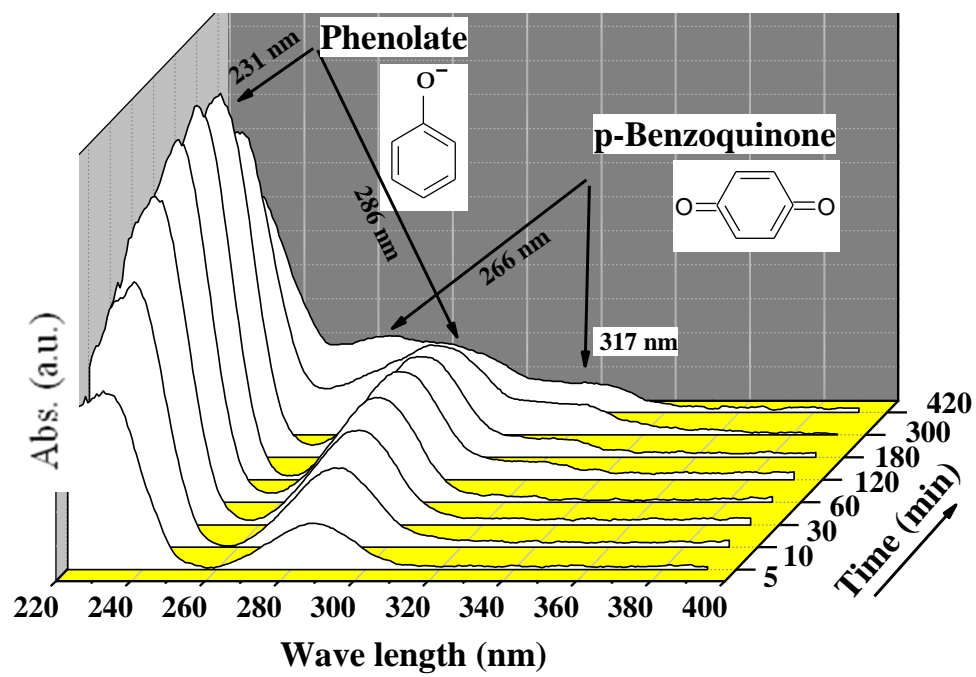


Figure 7

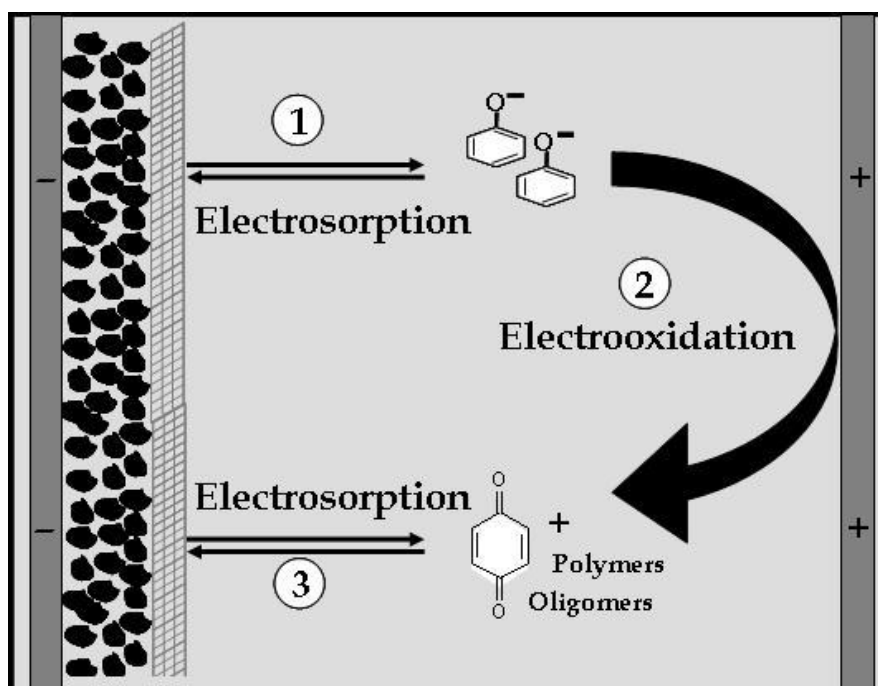


Figure 8

