

Validation of the electrochemical technology for the regeneration of activated carbon at bench-scale

Validación de la tecnología electroquímica para la regeneración de carbón activado a escala de banco

Borja Ferrández Gómez^a, Diego Cazorla Amorós^b, Emilia Morallón^{a,*}

^a Instituto Universitario de Materiales de Alicante (IUMA) and Department of Physical Chemistry, University of Alicante, 03080 - Alicante, Spain. borja.ferrandez@ua.es, morallon@ua.es

^b Instituto Universitario de Materiales de Alicante (IUMA) and Department of Inorganic Chemistry, University of Alicante, 03080 - Alicante, Spain. cazorla@ua.es

Abstract

The validation study of the electrochemical regeneration process of activated carbons (AC) used in water treatment plants saturated under real conditions has been carried out. The study has been performed using a bench-scale electrochemical reactor and the recovery of the porous texture has been analysed. Saturated AC from different brands and manufacturing methods have been studied. The results showed that it is easier to recover the porosity of the AC prepared by agglomeration than those produced by direct activation process. In addition, it is shown that the larger the surface area of the spent AC, the better is the regeneration efficiency achieved. Specifically, to reach a good regeneration efficiency, the S_{BET} of the spent sample should be higher than 600 m²/g. This is a similar value as that requested by the thermal regeneration companies for a successful regeneration of the AC.

Resumen

El estudio de validación del método electroquímico a escala de banco para la regeneración de carbones activados (CA) utilizados en condiciones reales en plantas de tratamiento de agua se ha realizado empleando CAs de distinta procedencia y forma de fabricación. Los resultados mostraron que los CAs preparados mediante aglomeración presentaron una mayor facilidad para la recuperación de la textura porosa que los fabricados mediante el proceso de activación directa. Además, se pone de manifiesto que, a mayor área superficial del CA usado, mayor es la eficiencia de la regeneración electroquímica. En concreto, se ha determinado que, para lograr una buena eficiencia de regeneración, el S_{BET} del CA gastado debe ser superior a 600 m²/g. Este valor es el mismo que piden las empresas de regeneración térmica para que la regeneración del CA tenga éxito.

1. Introduction

Adsorption is considered a cost-effective and reliable method for wastewater treatment [1,2], achieving a removal efficiency of 99.9% [1]. Therefore, the United States Environmental Protection Agency declared the adsorption process one of the best techniques for water treatment [1,3]. One of the most used adsorbents is AC due to its lower price, which is 20% lower than zeolite or polymeric-based adsorbents [4].

AC production worldwide is estimated over 300000 tons/year [5], increasing by around 10% each year [6]. The AC are produced from different precursors such as bituminous coal, lignite, peat, coconut and almond husks [5,7]. The synthesis of AC consists of two basic steps: carbonisation and activation [8]. Carbonisation aims to reduce the volatile content of raw materials by pyrolysis of carbon precursors. Regarding activation, a process that is considered more important than carbonisation in terms of the final properties of AC, it is carried out to develop the porosity of the AC by opening closed pores and generating new ones [9].

It is important to highlight that ACs can be classified according to their manufacturing process into agglomerate (also called re-agglomerate) and direct activation. The agglomeration process consists of six steps: 1) pulverisation, 2) addition of binder, 3) re-agglomeration into briquettes, 4) grinding, 5) carbonisation and 6) activation of the carbon material [10]. In direct activation, the first three agglomeration steps are skipped and production starts with the grinding of the initial material [10].

The aim of this work was to validate the electrochemical technology for the regeneration of spent AC. Different ACs saturated in drinking water treatment plants (DWTP) in Portugal and Spain under real conditions were used. The electrochemical reactor used is a parallel plate electrodes reactor at bench-scale with 3.5 kg of AC capacity [11].

2. Experimental

2.1. Materials

The granular AC samples used were collected from different industries in Spain and Portugal saturated during 3-10 years in real conditions. The ACs studied were: AquaSorb®F23 (agglomerated) from Spain; this AC sample was named as F23_S. PQ-0602-04® (direct activation) from Spain; this AC sample was named as PQ. M950® (direct activation) from Spain La Presa; this AC sample was named as M950. AquaSorb®F23 (agglomerated) Portugal; this AC sample was named as F23_P. Carbsorb®30 (agglomerated) from Portugal; this AC sample was named as C30. Filtrasorb®TL820 (agglomerated) from Spain, which was used in the DWTP after a thermal regeneration and a *make-up* treatment with 10% Norit1020® (agglomerated); this AC sample was

named as TL820.

Sulphuric acid (H_2SO_4) was used for preparing all the aqueous electrolyte solutions using tap water. Two commercial electrodes were used, Ti mesh fully platinised (Pt/Ti) as anode and 304-stainless steel (SS) as cathode, both had a thickness of 1.5 mm with a geometrical area of 675 cm².

2.2. Electrochemical regeneration of activated carbon

To validate the electrochemical method at bench-scale, the parallel plate electrodes prototype previously described was used and we applied some of experimental parameters optimised in Ferrández-Gómez et al., (2021) [11,12]. Thus, 3.5 kg of spent AC was located in the cathodic compartment, connected through a cationic membrane and a constant current of 16.9 A, which corresponds to a current density of 250 A/m², was applied during 4 h of regeneration time. The separation between electrodes was set to 10.5 cm and the spent AC was in contact with the cationic membrane and the cathode; the height of the resulting AC bed was 13.5 cm and a volume of 18 L of electrolyte per tank was employed. Table 1 summarises the different operating conditions that have been tested for the AC regeneration at kg-scale using a bench-scale electrochemical reactor. The table also includes the initial and final voltages of the cell.

Table 1. Experimental parameters for the validation process at bench-scale using parallel plate electrodes reactor.

Tabla 1. Parámetros experimentales para el proceso de validación a escala de banco empleando un reactor de electrodos planos paralelos.

Variable	BSV_1	BSV_2	BSV_3	BSV_4	BSV_5	BSV_6	Units
AC sample	F23_S	PQ	M950	F23_P	C30	TL820	
[H ₂ SO ₄]	0.5	0.5	0.5	0.5	0.5	0.5	M
Electrolyte flow	400	400	400	400	400	400	L/h
Cathode	SS	SS	SS	SS	SS	SS	
Anode	Pt/Ti	Pt/Ti	Pt/Ti	Pt/Ti	Pt/Ti	Pt/Ti	
Current	16.9	16.9	16.9	16.9	16.9	16.9	A
V _o -V _f	6.0-5.5	7.5-7.0	6.5-6.0	6.5-6.0	5.5-5.0	5.5-5.0	V

Regenerated AC samples were taken at different times of electrochemical treatment from several points of the AC bed. After each experiment, ACs were rinsed with deionised water until pH 7 and dried at 70 °C overnight.

2.3. Characterisation of the activated carbon samples

The porous texture of pristine, spent, and regenerated AC samples was determined by N₂ adsorption-desorption isotherms at -196 °C using an automatic adsorption system (Autosorb-6B, Quantachrome Corporation, USA). 100 mg of sample was outgassed at 150 °C under vacuum for 8 h. Total volume of micropores (V_{DR,N₂}) was calculated applying the Dubinin-Radushkevich equation, the volume of mesopores (V_{meso}) was calculated by subtraction of

the adsorbed volume at relative pressures of 0.9 and 0.2 [13] and the apparent specific surface area (S_{BET}) was determined by the Brunauer-Emmet-Teller equation [14]. The pore size distribution (PSD) was calculated by applying the bidimensional non-local density functional theory method (2D-NLDFT) to the N₂ adsorption isotherm using SAIEUS software (version 2.0, Micromeritics Instrument Corp. 2000-2015) [15].

2.4. Evaluation of the efficiency of electrochemical regeneration

The percentage of recovery of porosity (%RP) was calculated as the ratio of regenerated to pristine BET surface area according to the equation (1), and it is the parameter used for evaluation of the recovery of porosity in the regeneration treatment:

$$\%RP = \frac{S_{BET \text{ of regenerated AC}}}{S_{BET \text{ of pristine AC}}} \cdot 100 \quad (1)$$

In this study, it has been considered that the AC is regenerated when the %RP is higher or equal to 80%.

3. Results and discussion

Table 2 summarises the main textural properties (S_{BET}, V_{meso} and V_{DR,N₂}), as well as the quantification of the %RP, calculated from the analysis of N₂ adsorption-desorption isotherms at -196 °C for the pristine, spent and regenerated samples between 1-4 h.

The results for the spent ACs show a clear decrease in porosity in comparison to the pristine ACs. It must be noted that the porosity available in the spent ACs is higher than 600 mg/g iodine number [16] (it is also considered BET surface areas higher than 600 m²/g); this is the minimum value set by the companies to be able to carry out the thermal regeneration. Thus, ACs with iodine numbers below this value are not regenerated.

Specifically, for BSV_1, the S_{BET} of the pristine AC sample decreased from 995 to 790 m²/g for the spent

AC, whereas the micropore volume had a reduction from 0.40 to 0.32 cm³. Regarding the changes in BSV_2, the S_{BET} of the pristine AC sample decreased from 960 to 645 m²/g for the spent AC and, accordingly, the micropore volume had an important decrease (from 0.38 to 0.22 cm³/g). For BSV_3 sample, the S_{BET} of the pristine AC sample diminished from 890 to 620 m²/g for the spent AC, whereas the micropore volume decreased from 0.36 to 0.25 cm³. Regarding the characteristics in BSV_4, the S_{BET} of the pristine AC sample changed from 995 to 765 m²/g for the spent AC, while the micropore volume decreased from 0.40 to 0.31 cm³/g. For BSV_5, the initial surface area of 1000 m²/g decreased to 650 m²/g after its use in the DWTP. Finally, for BSV_6 AC, that comes from a thermal regeneration treatment,

the S_{BET} of the pristine AC sample decreased from 945 to 700 m²/g, whereas the micropore volume had a smaller variation from 0.33 to 0.27 cm³/g compared to the other ACs. In all the cases, the change in V_{meso} is very small for the spent AC compared to the pristine material.

Table 2 shows the results obtained for AC obtained after the electrochemical regeneration at different times. Regarding the BSV_1 sample, agglomerated AC, at the end of the 1st h of the experiment, an increase of S_{BET} from 790 to 885 m²/g was achieved. The maximum %RP was reached after 4 h of treatment, reaching a value of 91%. The micropore volume for the regenerated samples was partially recovered (Table 2).

Table 2. Porous texture characterisation of activated carbons by N₂ adsorption-desorption isotherm at -196 °C for validation process of electrochemical regeneration method at bench-scale.

Tabla 2. Caracterización de la textura porosa de los carbones activados mediante isoterma de adsorción-desorción de N₂ a -196 °C para la validación del proceso de regeneración electroquímica a escala de banco.

Sample	S _{BET} (m ² /g)	V _{meso} (cm ³ /g)	V _{DR,N2} (cm ³ /g)	%RP
BSV_1				
Pristine	995	0.04	0.40	
Spent	790	0.03	0.32	
Reg-1h	885	0.03	0.35	89
Reg-2h	890	0.04	0.36	89
Reg-3h	830	0.03	0.33	83
Reg-4h	905	0.04	0.36	91
BSV_2				
Pristine	960	0.06	0.38	
Spent	645	0.05	0.22	
Reg-1h	655	0.05	0.22	68
Reg-2h	680	0.06	0.24	71
Reg-3h	700	0.05	0.24	73
Reg-4h	695	0.05	0.25	72
BSV_3				
Pristine	890	0.05	0.36	
Spent	620	0.06	0.25	
Reg-1h	550	0.05	0.22	-
Reg-2h	600	0.04	0.24	-
Reg-3h	645	0.07	0.26	73
Reg-4h	720	0.07	0.29	81
BSV_4				
Pristine	995	0.04	0.40	
Spent	765	0.05	0.31	
Reg-1h	960	0.06	0.40	97
Reg-2h	955	0.06	0.39	96
Reg-3h	960	0.06	0.40	97
Reg-4h	820	0.05	0.34	82
BSV_5				
Pristine	1000			
Spent	650	0.08	0.26	
Reg-1h	695	0.08	0.28	70
Reg-2h	820	0.10	0.30	82
Reg-3h	710	0.08	0.27	71
Reg-4h	725	0.09	0.27	73
BSV_6				
Pristine	945	0.09	0.33	
Spent	700	0.08	0.27	
Reg-1h	800	0.10	0.28	85
Reg-2h	800	0.08	0.28	85
Reg-3h	805	0.09	0.28	85
Reg-4h	820	0.09	0.30	87

On the other hand, and as can be seen in Table 2, it was not possible to recover the textural properties of the BSV_2 sample, manufactured by direct activation technology. The maximum %RP obtained was 73%, and it was reached after 3 h of electrochemical treatment. Regarding BSV_3 sample, manufactured also by direct activation, some regeneration is not observed until the fourth hour of treatment, where 81% regeneration was reached, with a smooth recovery of the porosity. As shown in Table 2, this increase in porosity seems to be due to both the in the volume of micropores and mesopores. It must be noted that the surface area of both spent AC is very close to the limit imposed by the thermal regeneration companies to assure an efficient regeneration of the AC.

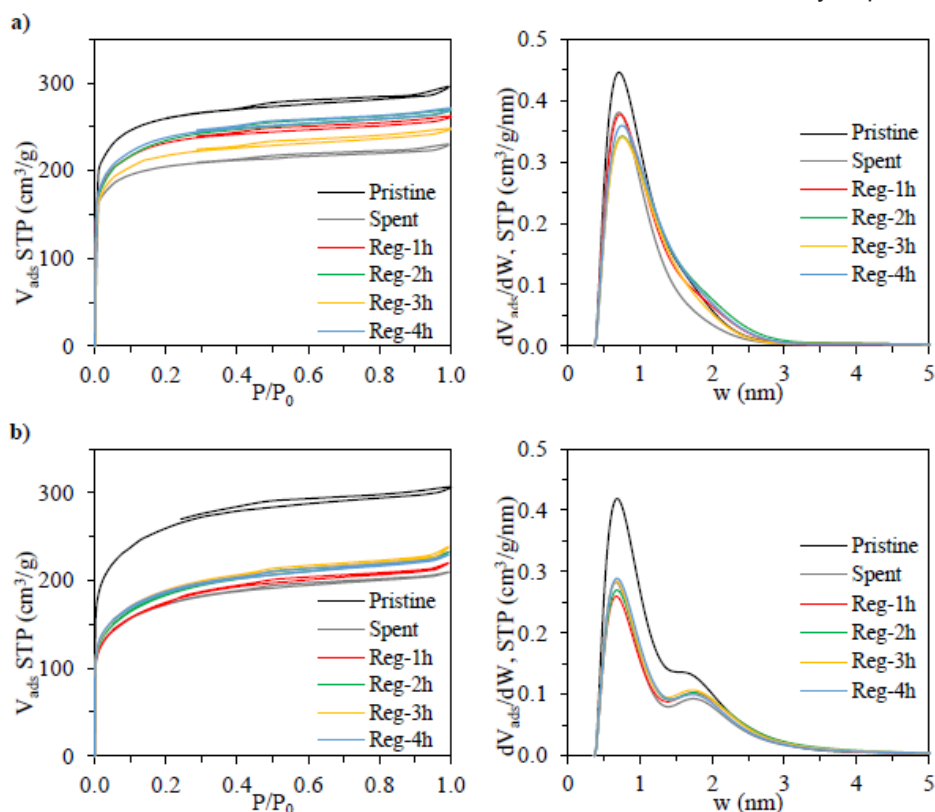
In the case of BSV_4 sample, agglomerated AC, the maximum value of %RP, 97%, is reached after the first hour of treatment and remained constant until the third hour of treatment. It must be noted that the volume of micropores for the regenerated samples reaches the value for the pristine AC. Interestingly, after the fourth hour of treatment the porosity of the AC decreases what can be a consequence of the adsorption of molecules generated during the regeneration treatment due to the long contact time of the experiment. However, some contribution from other mechanisms such as degradation of the AC due to the prolonged electrochemical treatment cannot be discarded. In summary, it should be highlight that the porosity of this AC is fully recovered after 1 h of process.

For the BSV_5 sample, agglomerated AC, an electrochemical regeneration efficiency of 82% was reached in the second hour of the experiment, increasing the S_{BET} from 650 to 820 m^2/g .

In relation to the regeneration attained for BSV_6 sample, which was previously thermally regenerated and after a make-up, it can be seen that, after the 1st h of the treatment, an increase of S_{BET} from 700 to 800 m^2/g was obtained. The maximum %RP was reached after 4 h of electrochemical treatment (%RP= 87% and the micropore volume is close to that of the starting material).

Figure 1 shows the N_2 adsorption-desorption isotherms at -196°C and PSD profiles. All the isotherms were type I [17] corresponding to essentially microporous ACs; the small slope for relative pressures above 0.2 and the small hysteresis, show that the contribution of mesopores is not important, in agreement with data in Table 2. Figure 1 also contains the PSD calculated for each sample.

In all the cases except for sample BSV_4 (Figure 1d), the isotherms for the pristine, spent and regenerated AC had a similar shape, but different adsorption capacities due to the different degree of micropores filling or blockage by adsorbed species. Interestingly, electrochemical regeneration of sample BSV_4 produces materials with similar adsorption capacity but with wider knees and higher slope at relative pressures higher than 0.2 in the N_2 adsorption isotherms. This indicates that the electrochemical regeneration produced some widening of the porosity of the AC. This widening of porosity suggests that some carbon gasification may occur as consequence of the surface oxidation processes that may happen with the oxidising species formed in the cathode from oxygen molecules dissolved in the electrolyte. It seems that this specific AC is the one with the highest reactivity although it cannot be discarded that this mechanism may have a significant contribution in the electrochemical regeneration that is detrimental towards the desired recovery of porosity.



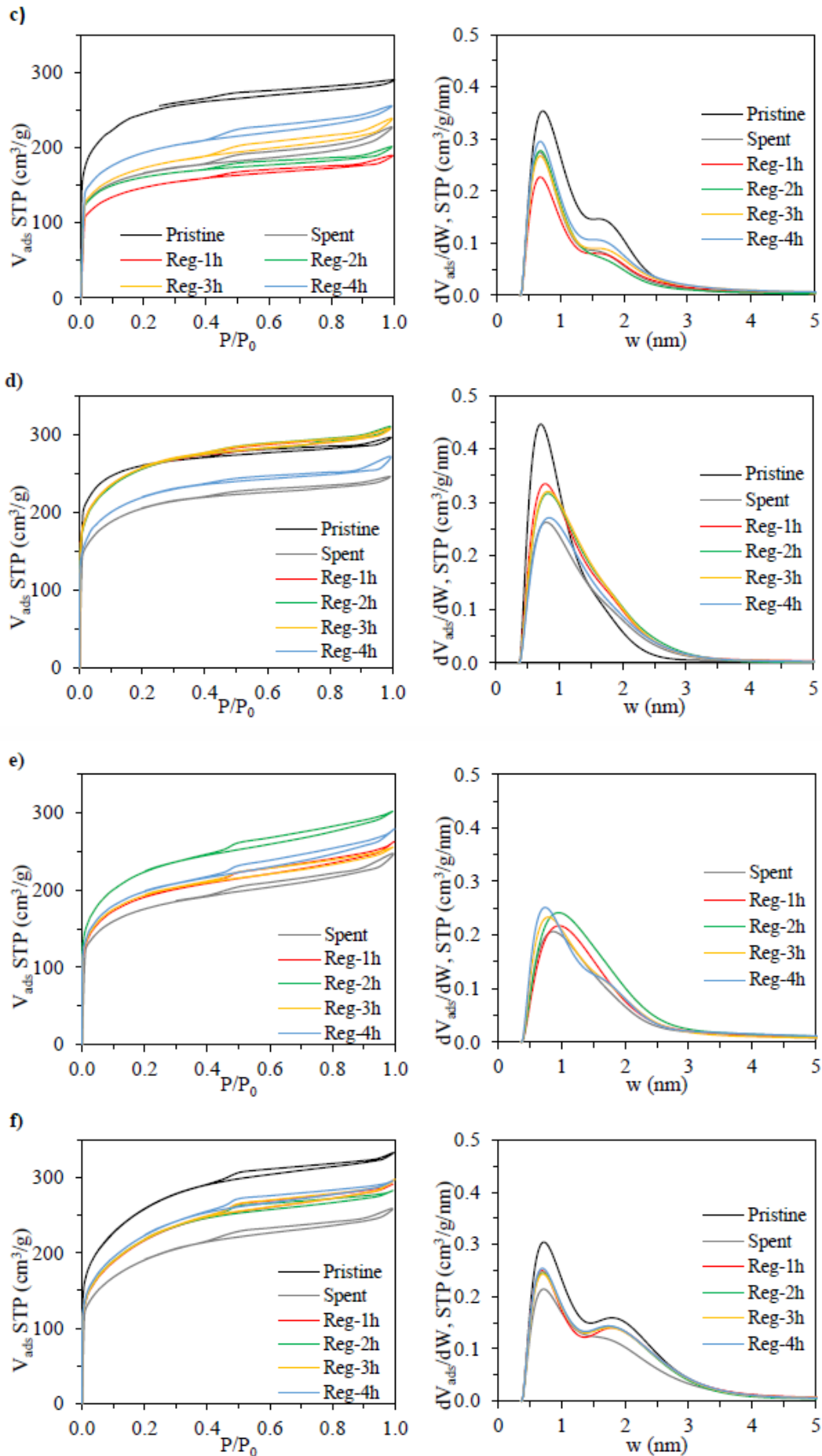


Figure 1. N_2 adsorption-desorption isotherm at $-196^\circ C$ and PSD profile for samples obtained for validation study at bench-scale from: a) BSV_1, b) BSV_2, c) BSV_3, d) BSV_4, e) BSV_5 and f) BSV_6 experiment.

Figura 1. Isoterma de adsorción-desorción de N_2 a $-196^\circ C$ y PSD para las muestras obtenidas en el estudio de validación a escala de banco para los experimentos: a) BSV_1, b) BSV_2, c) BSV_3, d) BSV_4, e) BSV_5 y f) BSV_6.

4. Conclusions

The validation study of the electrochemical regeneration method applied to different spent ACs used in water treatment plants has allowed us to conclude that, in order to achieve a good regeneration efficiency, the S_{BET} of the spent AC should be higher than $600 \text{ m}^2/\text{g}$. This value is the same as that requested by thermal regeneration companies. Regeneration of agglomerated ACs is much more efficient than for AC prepared by direct activation method, reaching recoveries of porosity which, in some cases, is above 90%. However, it must be noted that the porosity of the spent ACs prepared by direct activation used in this study is very close to the limit imposed for the thermal regeneration. To get a conclusion about the feasibility of electrochemical regeneration of AC prepared by direct activation, materials with smaller decrease in porosity should be studied. Each spent AC needs a particular study of the experimental conditions for performing the electrochemical regeneration. Specifically, regeneration time must be controlled to avoid further degradation of the AC.

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