doi:10.20944/preprints201908.0093.v1

Extraction of polyphenols and synthesis of new activated carbon from spent coffee grounds

Marina Ramón Gonçalves[1], Lorena Alcaraz[1], Susana Pérez-Ferreras[2], María Eugenia León-González[3], Noelia Rosales-Conrado[3], Félix A. López[1,*]

[1] Centro Nacional de Investigaciones Metalúrgicas (CENIM). Consejo Superior de Investigaciones Científicas (CSIC). Avda. Gregorio del Amo, 8. 28040 Madrid, Spain.

[2] Instituto de Catálisis y Petroleoquímica (ICP). Consejo Superior de Investigaciones Científicas (CSIC). C/ Marie Curie, 2. 28049 Madrid, Spain.

[3] Departamento de Química Analítica. Facultad de Ciencias Químicas. Universidad Complutense de Madrid, 28040 Madrid, Spain.

[*]**Corresponding Author:** f.lopez@csic.es

ABSTRACT

A valorization process of spent coffee grounds (SCG) was studied. Thus, a two-stage process, a stage of extraction of the polyphenols and a stage of obtaining activated carbon (AC) by a carbonization process, was performed. The extraction was carried out with a hydro-alcoholic solution in a pressure reactor, modifying time and temperature. To optimize the extraction of polyphenols, a two-level factorial design with three replications at the central values was used. The best results were obtained by performing the extraction at 80 ºC during 30 min, using a mixture of EtOH:H_2O 1:1 (v/v) as extraction solution. Caffeine and chlorogenic acid were the most abundant compounds in the analysed extracts, ranging from 0.09 to 4.8 $mg \cdot g^{-1}$ and 0.06 to 9.7 $mg \cdot g^{-1}$, respectively. The precursor obtained in the extraction stage were transformed into AC. An experimental design was realized in order to analyze the influence of different variables in the AC obtained process (reaction time and amount of potassium hydroxide used). Actived carbons with BET specific surface (S_{BET}) comprised between 1600 $m^2 \cdot g^{-1}$ and 2330 $m^2 \cdot g^{-1}$ had a microporous surface. Under the optimum conditions, the obtained AC presented a maximum adsorption capacity of methylene blue (q_m) between 411 $mg \cdot g^{-1}$ and 813 $mg \cdot g^{-1}$.

Keyword: Spent coffee grounds; polyphenols; extraction; activated carbon; methylene blue, adsorption.

Introduction

Coffee is a popular and consumed beverage worldwide and during the last 150 years has grown steadily in commercial importance [1–6]. As reported by the International Coffee Organization (ICO, 2017), coffee production suffered significant increased since 2010 [7,8].

Worldwide, large amounts of coffee waste such as pulp, husk and coffee beans are generated daily. These residues contain substantial amounts of high value-added products for example carbohydrates, proteins, pectins and bioactive compounds as polyphenols, which could be extracted and employed in the cosmetic, pharmaceutical and food industries [1,5].

In the upcoming years, with the high coffee production and the concern about waste management [1,9], it is necessary to find novel applications for reusing coffee residues. One of them could be the efficient extraction of polyphenols and the production of different value-added compounds, leading to better management of these wastes and to reduce the environmental impact that they generate, such as the generation of greenhouse gases [1,10,11]. There are numerous studies focused on the extraction of bioactive compounds from different food by-products. Some potential applications for spent coffee grounds (SCG) are antioxidants, anti-inflammatory additives, for the production of biofuels, as a complement in animal feed or, fertilizers [1,2,10,12].

The polyphenols present in SCG are an group of secondary metabolites of plants, which are the constituents of a great number of fruit and vegetables, and beverages such as tea, coffee and wine and the main antioxidants in the human diet [13]. Caffeic acid is a well-known non-flavonoid phenolic compound abundant in coffee, presenting potent antioxidant and neuroprotective properties [14]. Polyphenols might have different properties as an antioxidant, antiproliferative, anti-allergic, anticarcinogen, antimicrobial, antitumor, anti-inflammatory and neuroprotective activities [8,15], that are of potential attention for the agrifood, cosmetic and pharmaceutical industries [1,16,17].

Otherwise, AC is a porous solid with adsorbent and catalytic properties that is used in many industrial sectors. Their textural properties, including their high specific surface and microporosity, makes it an ideal compound to eliminate contaminants through physical adsorption processes [6]. Commercial ACs are mostly obtained from biomass waste [18,19]. Besides, many researches have been developed on the employ of biomass as a precursor of carbon active such as residues derives form tea, coffee or grapes and olives bones [20–22]. Within its wide variety of applications, the most common is the use of AC to removal several pollutants from wastewater due to its simplicity and low cost [6,9,23–25]. Other applications are the employment as a decolourizer for food industry, catalysis, purification of the chemical and pharmaceutical industry, for the elimination of gases, improving the noble metals or storing energy [26,27].

For all these reasons, the aim of the present work was the reuse and valorization of spent coffee grounds by the recovery, identification and quantification of bioactive polyphenols followed by synthesis of active carbon with high specific surface area. Thus, spent coffee grounds were previously subjected to a hydro-alcoholic extraction process under subcritical conditions to obtain an extract that contains the bioactive compounds and a solid (precursor). Next, the extract containing polyphenols was subjected to an evaporation process at low pressure, which allowed recovering the alcohol and reuses it in the extraction stage, and an aqueous solution in which the polyphenols were concentrated. Finally, the precursor was turned into AC by chemical activation and their morphological and textural properties were studied. Methylene blue (MB) adsorption capacity in solution was studied in the AC that presented the best textural properties. Figure 1 schematically describes the process studied.

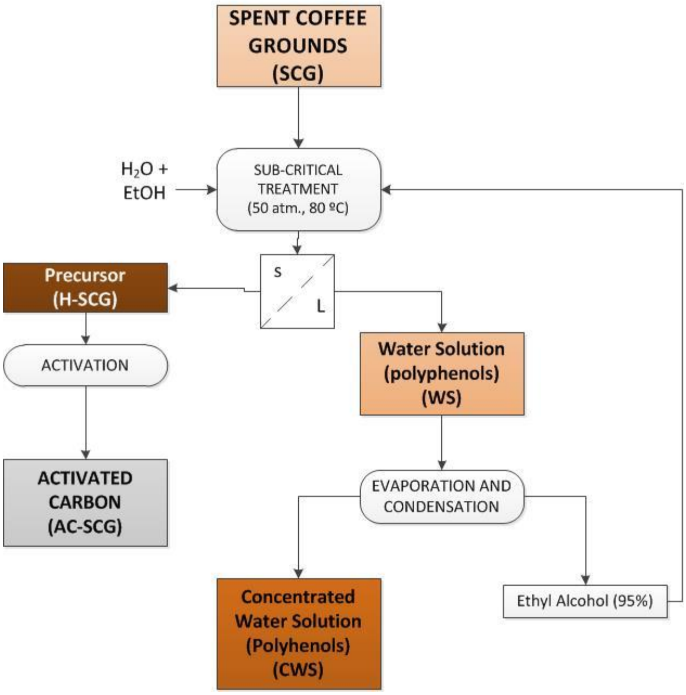

Figure 1. Diagram of the process studied

Results and discussion

Optimization of polyphenol extraction conditions by experimental design

For optimization of the conditions for the extraction of polyphenols from spent coffee ground (SCG) a total of 11 runs were performed. Analysis of the experimental results allowed determining the most favourable experimental extraction conditions for the maximum response. The higher extracted amounts ($mg \cdot g^{-1}$) for caffeine, caffeic acid and *trans*-ferulic acid were obtained with a ratio $EtOH:H_2O$ 30:70 (v/v); a extraction time of 30 min and a temperature of 80 ºC. In the case of rutin and naringin, a ratio $EtOH:H_2O$ 30:70 (v/v); a extraction time of 15 min and a temperature of 80 ºC provided higher contents. For resveratrol, a similar extracted amount was obtained in all the experiments, whereas in the case of kaempferol, it was below its limit of quantification (LOQ) determined by cLC-DAD.

Because of the experimental extraction conditions that provided the maximum responses depending on the analyte, multiple response analysis (MRA) was made. In this way, it is possible determine the combination of the experimental factors which simultaneously optimized the studied responses. So, the desirability function is maximized. As a compromise, the optimum conditions to obtain the maximum responses for the target analytes were 30 min of the extraction time, a temperature of 80 ºC, a mixture of $EtOH:H_2O$ 1:1 (v/v) as extraction solvent, and an extraction pressure of 50 bar. Under these conditions, experimental responses were in agreement with those predicted by means of the experimental design analysis.

Polyphenols determination by cLC-DAD in the extracts from SCG

Individual polyphenols determination in the extracts obtained from SCG, in the extracts from precursor (H-SCG), in the extracts obtained before the evaporation process and the solutions obtained after the evaporation process (the aqueous solution in which the polyphenols are concentrated (CWS) and the organic solution (EtOH)), were performed by cLC-DAD as previously described (section 2.2). The chromatogram of the mixture of the standards used for the identification of the different polyphenols is shown in Figure 2.

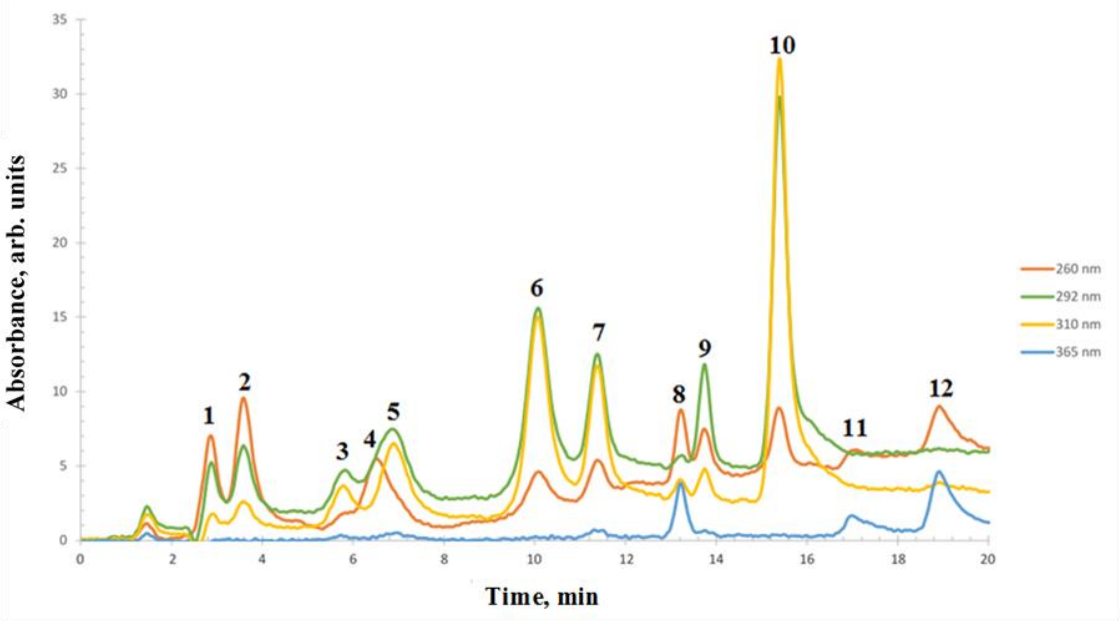

Figure 2. Chromatogram of the standard mixture (80 µg/L) obtained using the cLC-DAD optimized method. **1** Gallic acid; **2** Dihydroxybenzoic acid; **3** Chlorogenic acid; **4** Caffeine; **5** Caffeic acid; **6** *p*-Coumaric acid; **7** *Trans*- Ferulic acid; **8** Rutin; **9** Naringin; **10** Resveratrol; **11** Quercetin; **12** Kaempferol.

Table 1 shows the extracted amount of each analyte in mg per gram of dried sample in the distinct extracts evaluated. As can be observed, CWS presented the highest content of polyphenols and caffeine (except rutin and kaempferol) followed by SCG, while the other extract (WS, H-SCG and EtOH) were found at lower amounts. In addition, it is observed that the evaporation process allows to concentrate polyphenol and caffeine compounds in an aqueous solution, while residual amounts remain in the organic solution.

Estimation of TPC, TFC, and TAA in the extracts obtained from SCG

TFC, TPC and TAA of the obtained extracts from SCF under optimum extractions conditions were evaluated by following the procedures described in Section 2.2. The results obtained in the spectrophotometric methods for WS and CWS were 14 ± 8 mg GAE·g^{-1} DW for TPC, 10.7 ± 0.8 mg QE·g^{-1} DW for TFC, 14.5 ± 0.3 mg GAE·g^{-1} DW for TAA, and 49 ± 1 mg GAE·g^{-1} DW for TPC, 56 ± 7 mg QE·g^{-1} DW for TFC and 23 ± 2 mg GAE·g^{-1} DW for TAA, respectively. As can be observed, after the evaporation process, there was an increase in the TFC and TPC and TAA in the extract obtained.

Optimization of textural and morphological properties by factorial experimental design and characterization of active carbon

For optimization of the textural and morphological properties of AC from precursor (H-SCG) under the optimal conditions, a factorial experimental design was made as described in section 2.4. Once a total of 11 experiments were performed, analysis of the experimental results permitted determining the most favourable obtaining conditions for the maximum response. The results obtained for S_{mi}, S_e and S_{BET} show significant effects for time and temperature factors, and for interaction factors such as temperature and KOH:precursor. Regarding the textural properties of the ACs obtained, they have a microporous microstructure ($S_{mi} \approx S_{BET}$), their volume of micropores (W_o) is similar to the pore volume (V_p). The pore sizes (L_o) are, in all cases, less than 2 nm. The BET surface area varies between 1377-2330 m^2·g^{-1}. According to the International Union of Pure and Applied Chemistry (IUPAC), the shapes of the isotherms are of type I and II. At low relative pressures ($p/p_0 < 0.1$), large volumes of N_2 were adsorbed for both samples [37]. The quantity adsorbed of N_2 at $p/p_0 \sim 1$ varies between 350 and 758 cm^3·g^{-1}.

Moreover, it was necessary to carry out MRA due to the heterogeneity in the experimental conditions. As a compromise, the optimum conditions to obtain the maximum responses were a time of 1 h, a temperature of 850 ºC, and a mixture of KOH:precursor at the ratio 2.5:1. Under these conditions, the experimental responses were in agreement with those predicted by means of the experimental design analysis.

Table 2 shows the variation of the burn-off and yield of the activation process in the assays carried out in the experimental design. As the carbonization temperature increases, the burn-off increases and the recovery in weight of the AC decreases. The burn-off values vary between 82 % and 96 % and the yields between 4 % and 18.5 %.

Finally, Figure 3 shows the morphology of several ACs examined by FE-SEM in which the microporous nature of the carbons can be appreciated.

Adsorption of methylene blue

Thermodynamic adsorption studies

In order to analyzed the possible MB adsorption mechanism different isotherms were assessed at different temperatures. The calculated parameters values for the different isotherms in the linear form, using the equations (2-4), are summarized in Table 3.

The highest obtained R^2 correlation coefficient values were for the Langmuir isotherm. The calculated values q_m increase with the temperature, in accordance to previous studies related to the MB adsorption by ACs obtained from different wastes [38,39]. In addition, the calculated values are similar to the q_m experimental obtained (between 411-813 mg·g^{-1}).

The calculated Langmuir non-dimensional factor (R_L) in all cases were between the range of $0<R_L<1$. These results reveal that the adsorption is a favourable process [33] independently of the temperature of the adsorption experiment.

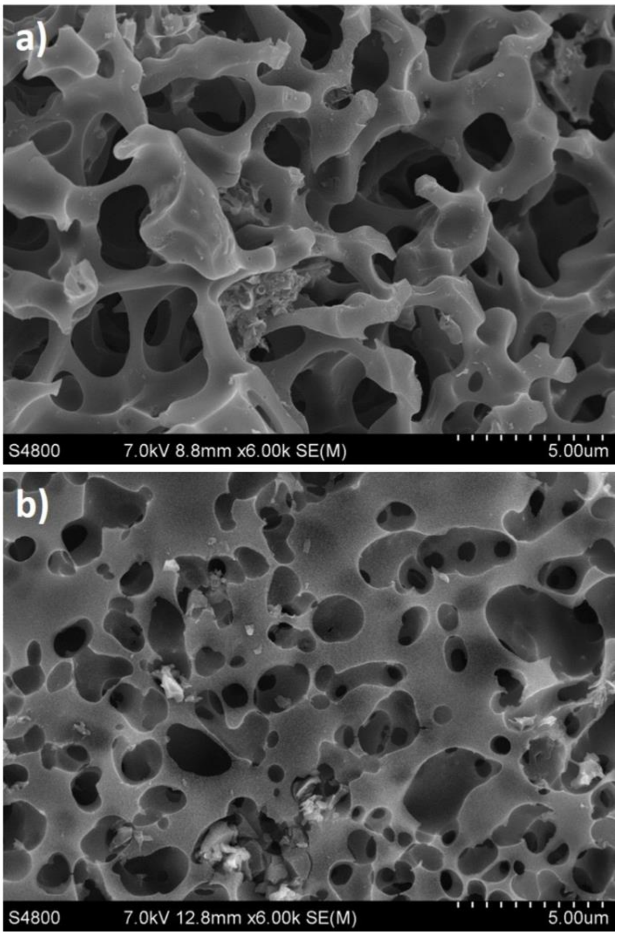

Figure 3. Morphology of several active carbons examined by FE-SEM

Thermodynamic parameters were calculated at different temperatures using equation (10) and equation (11) as previously described in section 2.5. The negative value obtained of enthalpy (ΔH^0) (-77.81 J·mol^{-1}) indicates that the process is exothermic. In addition, the entropy (ΔS^0) was positive, 68.10 J·mol^{-1}·K^{-1}, which indicate the increased disorder at the solid solution interface components. Finally, the free Gibbs energies (ΔG^0) (-205.73 kJ·mol^{-1} at 30 ºC; -226.17 kJ·mol^{-1} at 60 ºC and 239.79 kJ·mol^{-1} at 80 ºC) were also negatives and exhibit that this process is spontaneous and favourable thermodynamically.

Kinetic adsorption studies

The adsorption kinetics experiments of MB were also performed at the different temperatures studied. A pseudo-second-order model was the best fit in all cases. K_2 constant values calculated at different temperatures ($2.85\cdot10^{-3}$ g·min·mg^{-1}, 3.77 g·min·mg^{-1} and 7.60 g·min·mg^{-1} for 30 ºC, 60 ºC and 80 ºC, respectively) increased with temperature, which indicate an enhance of the MB adsorption. The process activation energy (E_a) was calculated fitting the observed kinetics rate constants logarithm (ln $K_{2,obs}$)

versus the inverse of temperature (1/T), where the slope is $-E_a/R$ [40]. This value is used to estimate whether the process is a physical (readily reversible reactions and the energy requirements are small between the range of 5 to 40 kJ·mol^{-1} or chemical adsorption (process that requires higher energies, between 40 to 800 kJ·mol^{-1}, with stronger forces) [40]. The calculated activation energy in the present case was 77.86 kJ·mol^{-1}. The obtained value suggested a chemisorption process.

Isothermal and kinetic models, q_m and the activation agent of various adsorbents are exhibit in Table 4. As can be observed, many cases the KOH is used as an activation agent. In general, a better fit to the Langmuir model were found for the adsorption isotherms. Moreover, the adsorption kinetics fitted a pseudo-second-order model in the majority of the presented cases. In relation to the capacity of adsorption, the spent coffee ground has a wide range together with the residues of the carpets, while the rest of the intervals are smaller. Finally, in the case of the unique values, the q_m presents a value around 400 mg·g^{-1}, with some exception as in the orange peel, wine wastes.

Sample, materials and methods

Obtaining the SCG

The waste recovered after coffee beverage preparation (SCG, spent coffee ground) comes from the canteen of the National Center for Metallurgical Research (Superior Council of Scientific Investigations) in Madrid. The coffee used was a mixture 10 (wt,%) roasted and 90 (wt,%) natural roasted (obtained at 9 bar and 88 ºC). The sample was maintained at -20 ºC until analysis. Moisture content of spent coffee ground was obtained by drying at 80 ºC during 48 h.

Capillary LC-DAD and spectrophotometric analysis

An Agilent cLC instrument Mod. 1100 Series (Agilent Technologies, Madrid, Spain) formed by a G1379A degasser, a G1376A binary capillary pump and a G1315B diode array detector (500 nL, 10 mm pathlength) was used for cLC analysis. A stainless steel loop with a volume of 10 µL was coupled to a Rheodyne® injection valve. The capillary analytical column was a Synergy ™ Fusion 4 µm C18 (150 mm x 0.3 mm I.D.) from Phenomenex (Torrance, CA, USA). Data acquisition and processing were performed with the Agilent Chemstation software package for Microsoft Windows.

The chromatographic method (cLC-DAD) developed by León-González et al., 2018 was employed for caffeine and polyphenols identification. The wavelengths 220, 260, 292, 310 and 365 nm were chosen for the UV-diode array detection. Quantitative analysis was made at 260 nm for 3,4-dihydroxybenzoic, caffeine, rutin and quercetin, 292 nm for both naringin and gallic acid, 310 nm for chlorogenic acid, *trans*-ferulic acid resveratrol and *p*-coumaric acid and 365 nm for kaempferol. For focusing purposes, injections were made in an aqueous solution containing 1 % (v) of ACN and 0.1 % (v) TFA pH 3.24.

The spectrophotometric methods described by Vijayalaxmi *et al.*, 2015 y Shrikanta *et al.*,2015 with some changes were employed for determining total flavonoid (TFC) and total polyphenol content (TPC), and total antioxidant capacity (TAA) [12,29].

Optimization of polyphenols extraction conditions by experimental design

The extraction of polyphenols from spent coffee grounds were done in a Berghof BR3000 reactor at controlled temperature and pressure. An amount of 45 g of spent coffee grounds were added to 600 mL of a hydro-alcoholic solution with different ratios of ethanol (between 30-50 % (v) in water). The extraction time was varied between 15 and 30 min, and the extraction temperature in the range 80-120 ºC. The pressure was kept constant at 50 bar. Once completed the extraction process, the reactor was cooled and the resulting suspension was centrifuged for 1 h. The solid obtained (H-SCG) was separated, and an aliquot of the resulting solution was used to quantify the individual polyphenol and caffeine present in the sample by cLC-DAD.

On the other hand, a two-level factorial design with three replicates at the centre point was planned to maximize the extracted amount of the target polyphenols and caffeine from SCG samples. A previous chromatographic study was carried out for identification of the experimental factors that could most influence the polyphenol extraction: extraction time, extraction temperature, pressure and nature of the extraction solution. As result, nature of the extraction solution, extraction time and extraction temperature were selected as experimental factors and included in the experimental design. Amount extraction ($mg \cdot g^{-1}$) of caffeic acid, rutin, *trans*-ferulic acid, naringin, kaempferol, resveratrol and caffeine were fixed as responses, and the optimization criterion for the analysis of the performed experimental design was the maximization of response values for the analytes evaluated.

Once the extraction process was optimized, the hydro-alcoholic solution obtained under optimum conditions, containing the maximum amounts of the polyphenols extracted (WS), was evaporated in a rotavapor R-100 (Buchi) at 110 mbar pressure and at a temperature of 40 ºC, yielding a concentrated aqueous solution of polyphenols (CWS) and a fraction of ethyl alcohol, which could be reused in the extraction process.

Optimization by factorial experimental design and characterization of active carbon

The precursor obtained under optimum extraction conditions was used to obtain AC by a method of chemical activation with KOH. Thus, 1 g of the carbonaceous precursor was mixed with different amounts of KOH, between 1.5 and 2.5 g. The resulting mixtures were homogenized with a ball mill, placed in alumina crucibles and treated in a Carbolite STF 15 tubular oven at 850 ºC for a variable time between (30-60 min), under a nitrogen carrier ($150\ mL \cdot min^{-1}$). Later cooling to room temperature, the solid was washed with Milli-Q water until neutral pH. After that, it was dried in an oven at 80 ºC for 12 h.

The degree of activation (burn-off) was determined using equation (1):

$$Burn - off\ (wt\%\ daf) = \frac{w_1 - w_2}{w_1}\ x\ 100 \qquad (1)$$

where w_1 and w_2 are the mass (dry ash-free [daf] basis) of carbonaceous material before and after activation.

The yield of the activation process was determined by equation (2):

$$Yield\ (wt, \%) = \frac{w_2}{w_1}\ x\ 100 \qquad (2)$$

The porous structure of the AC was determined by nitrogen adsorption at -196 ºC (77 K) sing the Micromeritics ASAP 2020. The samples were partially degassed at 350 ºC (623 K) for 16 h. The specific surface area was computed using the adsorption isotherm via the BET equation and DFT models, using Micromeritics and Quantachrome software. The surface of ACs was examined by field emission scanning electron microscope (FE-SEM) using a Hitachi S 4800 J microscope.

For optimization of the textural and morphological properties of obtained AC, a two-level factorial design with three replicates at the centre point was employed. Time, temperature and different amounts of KOH were selected as experimental factors. The total volume of pores (V_p), volume of micropores (W_o), the size of the micropores (L_o), the microporous surface (S_{mi}), the non-microporous external surface (S_e) and the specific surface area (S_{BET}) were chosen as responses, and the optimization criterion for the analysis of experimental design was maximization of the response values.

Batch adsorption experiments

The adsorption capacity of MB by the obtained AC was investigated. Different experiments adsorption were carried out. For it, 10 mg of the AC were added to MB solutions of concentration 10 mg·L^{-1}. The mixtures were magnetically stirred at 350 rpm in a thermostatic-controlled bath. Aliquots were extracted every 5 min (up to 30 min), every 10 min (up to 60 min) and finally, every 60 min (until equilibrium is reached). The amount of the MB in solution was calculated by UV-Vis spectroscopy at 610 nm employing a Zuzi spectrophotometer 4101.

The adsorbed MB amount per gram of AC (q_e) was calculated from equation (3):

$$q_e = \frac{(C_0 - C_e)\, V}{m} \qquad (3)$$

where C_o and C_e are the initial and at the equilibrium MB concentration in the solution (mg·L^{-1}), respectively, V is the volume of the solution (L) and m is the mass of the AC (g) employed.

In order to evaluate the thermodynamic study, the linear form of the isotherms of Langmuir [30] (equation (4)), Freundlich [31] (equation (5)) and Temkin [32] (equation (6)) were employed and the AC amount were modify.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} c_e \qquad (4)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \qquad (5)$$

$$q_e = B \cdot \ln A_T + \frac{RT}{b_T} \cdot \ln c_e \qquad (6)$$

where C_e and q_e are the MB concentration (mg·L^{-1}) and the MB amount adsorbed per mass of AC at equilibrium (mg·g^{-1}), respectively; q_m is the maximum adsorption capacity of the AC (mg·g^{-1}) and b is the Langmuir equilibrium constant (L·mg^{-1}); K_F (L·g^{-1}) and n are adsorption constants; A_T is the Temkin isotherm equilibrium binding constant (L·g^{-1}), b_T is the Temkin isotherm constant and R is the universal gas constant (8.314·10^3 kJ·K^{-1}·mol^{-1}).

The non-dimensional Langmuir constant [33] (R_L) was determined using the equation (7):

$$R_L = \frac{1}{1+bC_0} \qquad (7)$$

where C_0 is the initial concentration of MB (mg·L^{-1}).

So, the value of R_L determines if the process is unfavourable (R_L>1), linear (R_L=1), favourable (0<R_L<1) or irreversible (R_L=0) [34].

The kinetic data were evaluated employing a pseudo-first-order (equation (8)) and pseudo-second-order models (equation (9)) [35]:

$$\ln(q_e - q_t) = \ln q_e - K_1 \cdot t \qquad (8)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \cdot t \qquad (9)$$

where K_1 and K_2 are the pseudo-first (min^{-1}) and pseudo-second-order (g·mg^{-1}·min) adsorption constants.

Finally, the thermodynamic equilibrium constant as the Gibbs free energy (ΔG^0) (equation (10)), the standard enthalpy (ΔH^0) and the entropy (ΔS^0) (equation (11)) [36] were determined using:

$$\Delta G^0 = -RT \ln K_a \qquad (10)$$

$$\ln K_a = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (11)$$

where K_a is the thermodynamic equilibrium constant (equation (12)):

$$K_a = \frac{C_s}{C_e} \qquad (12)$$

where C_s and C_e is the solid (mg·g^{-1}) and liquid (mg·L^{-1}) phase concentration at equilibrium.

Conclusions

A hydrothermal treatment was employed to transform spent coffee grounds into AC, previous hydro-alcoholic extraction of the inherent high added value polyphenols. The resulting ACs obtained under different experimental conditions have a microporous structure with specific surfaces greater than 1600 m^2·g^{-1} that gives them excellent adsorption properties. The adsorption capacity of MB on the AC obtained under optimum conditions has been studied. Moreover, evaluated extracts are characterized by high values of both total flavonoid and total polyphenol content, as well as considerable antioxidant activities. All these results give rise to high-quality products, with potential interest for many industries, can be derived from spent coffee grounds, presenting a real alternative for its most common use, organic fertilizer.

References

1. Murthy, P. S. & Madhava Naidu, M. Sustainable management of coffee industry

by-products and value addition—A review. *Resour. Conserv. Recycl.* **66,** 45–58 (2012).

2. Campos-Vega, R., Loarca-Piña, G., Vergara-Castañeda, H. A. & Dave Oomah, B. Spent coffee grounds: A review on current research and future prospects. *Trends Food Sci. Technol.* **45,** 24–36 (2015).
3. Ricciardi, P., Torchia, F., Belloni, E., Lascaro, E. & Buratti, C. Environmental characterisation of coffee chaff, a new recycled material for building applications. *Constr. Build. Mater.* **147,** 185–193 (2017).
4. Dong, W., Hu, R., Chu, Z., Zhao, J. & Tan, L. Effect of different drying techniques on bioactive components, fatty acid composition, and volatile profile of robusta coffee beans. *Food Chem.* **234,** 121–130 (2017).
5. Birkenberg, A. & Birner, R. The world’s first carbon neutral coffee: Lessons on certification and innovation from a pioneer case in Costa Rica. *J. Clean. Prod.* **189,** 485–501 (2018).
6. S., S. & P., S. K. Influence of ultrasonic waves on preparation of active carbon from coffee waste for the reclamation of effluents containing Cr (VI) ions. *J. Ind. Eng. Chem.* **60,** 418–430 (2018).
7. Janissen, B. & Huynh, T. Chemical composition and value-adding applications of coffee industry by-products: A review. *Resour. Conserv. Recycl.* **128,** 110–117 (2018).
8. Iriondo-DeHond, A. *et al.* Validation of coffee by-products as novel food ingredients. *Innov. Food Sci. Emerg. Technol.* 0–1 (2018). doi:10.1016/j.ifset.2018.06.010
9. Franciski, M. A. *et al.* Development of CO_2 activated biochar from solid wastes of a beer industry and its application for methylene blue adsorption. *Waste Manag.* **78,** 630–638 (2018).
10. Kovalcik, A., Obruca, S. & Marova, I. Valorization of Spent Coffee Grounds: A review. *Food Bioprod. Process.* **110,** 104–119 (2018).
11. Du, C. *et al.* Valorization of food waste into biofertiliser and its field application. *J. Clean. Prod.* **187,** 273–284 (2018).

12. Vijayalaxmi, S., Jayalakshmi, S. K. & Sreeramulu, K. Polyphenols from different agricultural residues: extraction, identification and their antioxidant properties. *J. Food Sci. Technol.* **52,** 2761–2769 (2015).

13. Engida, A. M., Faika, S., Nguyen-Thi, B. T. & Ju, Y. H. Analysis of major antioxidants from extracts of Myrmecodia pendans by UV/visible spectrophotometer, liquid chromatography/tandem mass spectrometry, and high-performance liquid chromatography/UV techniques. *J. Food Drug Anal.* **23,** 303–309 (2015).

14. Deshmukh, R., Kaundal, M., Bansal, V. & Samardeep. Caffeic acid attenuates oxidative stress, learning and memory deficit in intra-cerebroventricular streptozotocin induced experimental dementia in rats. *Biomed. Pharmacother.* **81,** 56–62 (2016).

15. García-Blanco, T., Dávalos, A. & Visioli, F. Tea, cocoa, coffee, and affective disorders: vicious or virtuous cycle? *J. Affect. Disord.* **224,** 61–68 (2017).

16. Castro, A. C. C. M. *et al.* Green coffee seed residue: A sustainable source of antioxidant compounds. *Food Chem.* **246,** 48–57 (2018).

17. Rui, L. *et al.* Enhanced solubility and antioxidant activity of chlorogenic acid-chitosan conjugates due to the conjugation of chitosan with chlorogenic acid. *Carbohydr. Polym.* **170,** 206–216 (2017).

18. Amerkhanova, S., Shlyapov, R. & Uali, A. The active carbons modified by industrial wastes in process of sorption concentration of toxic organic compounds and heavy metals ions. *Colloids Surfaces A Physicochem. Eng. Asp.* **532,** 36–40 (2017).

19. Rattanapan, S., Srikram, J. & Kongsune, P. Adsorption of Methyl Orange on Coffee grounds Activated Carbon. *Energy Procedia* **138,** 949–954 (2017).

20. Suganya, S. & P., S. K. Influence of ultrasonic waves on preparation of active carbon from coffee waste for the reclamation of effluents containing Cr (VI) ions. *J. Ind. Eng. Chem.* **60,** 418–430 (2018).

21. Laksaci, H., Khelifi, A., Trari, M. & Addoun, A. Synthesis and characterization of microporous activated carbon from coffee grounds using potassium

hydroxides. *J. Clean. Prod.* **147,** 254–262 (2017).

22. Alcaraz, L., López Fernández, A., García-Díaz, I. & López, F. A. Preparation and characterization of activated carbons from winemaking wastes and their adsorption of methylene blue. *Adsorpt. Sci. Technol.* **36,** 1331–1351 (2018).

23. Ibupoto, A. S. *et al.* Reusable carbon nanofibers for efficient removal of methylene blue from aqueous solution. *Chem. Eng. Res. Des.* **136,** 744–752 (2018).

24. Pawar, R. R. *et al.* Porous synthetic hectorite clay-alginate composite beads for effective adsorption of methylene blue dye from aqueous solution. *Int. J. Biol. Macromol.* **114,** 1315–1324 (2018).

25. Alguacil, F., Alcaraz, L., García-Díaz, I. & López, F. Removal of Pb^{2+} in Wastewater via Adsorption onto an Activated Carbon Produced from Winemaking Waste. *Metals (Basel).* **8,** 697 (2018).

26. Altintig, E. & Kirkil, S. Preparation and properties of Ag-coated activated carbon nanocomposites produced from wild chestnut shell by ZnCl2 activation. *J. Taiwan Inst. Chem. Eng.* **63,** 180–188 (2016).

27. Filippín, A. J., Luna, N. S., Pozzi, M. T. & Pérez, J. D. Obtaining and characterizing of carbon activated from olivic and olive-residues by physical activation. **8,** 59–71 (2017).

28. León-González, M. E., Gómez-Mejía, E., Rosales-Conrado, N. & Madrid-Albarrán, Y. Residual brewing yeast as a source of polyphenols: Extraction, identification and quantification by chromatographic and chemometric tools. *Food Chem.* **267,** 246–254 (2018).

29. Shrikanta, A., Kumar, A. & Govindaswamy, V. Resveratrol content and antioxidant properties of underutilized fruits. *J. Food Sci. Technol.* **52,** 383–390 (2015).

30. Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* **40,** 1361–1403 (1918).

31. Freundlich, H. & Heller, W. The Adsorption of cis - and trans -Azobenzene. *J. Am. Chem. Soc.* **61,** 2228–2230 (1939).

32. Johnson, R. D. & Arnold, F. H. The temkin isotherm describes heterogeneous protein adsorption. *Biochim. Biophys. Acta (BBA)/Protein Struct. Mol.* **1247,** 293–297 (1995).

33. Hall, K. R., Eagleton, L. C., Acrivos, A. & Vermeulen, T. Pore- and Solid-Diffusion Kinetics in Fixed-Bed Adsorption under Constant-Pattern Conditions. *Ind. Eng. Chem. Fundam.* **5,** 212–223 (1966).

34. Adebisi, G. A., Chowdhury, Z. Z. & Alaba, P. A. Equilibrium, kinetic, and thermodynamic studies of lead ion and zinc ion adsorption from aqueous solution onto activated carbon prepared from palm oil mill effluent. *J. Clean. Prod.* **148,** 958–968 (2017).

35. Ho, Y. . & McKay, G. Pseudo-second order model for sorption processes. *Process Biochem.* **34,** 451–465 (1999).

36. El-Aila, H. J., Elsousy, K. M. & Hartany, K. A. Kinetics, equilibrium, and isotherm of the adsorption of cyanide by MDFSD. *Arab. J. Chem.* **9,** S198--S203 (2016).

37. Cheng, S. *et al.* Comparison of activated carbon and iron/cerium modified activated carbon to remove methylene blue from wastewater. *J. Environ. Sci. (China)* (2016). doi:10.1016/j.jes.2016.12.027

38. Alcaraz, L., López Fernández, A., García-Díaz, I. & López, F. A. Preparation and characterization of activated carbons from winemaking wastes and their adsorption of methylene blue. *Adsorpt. Sci. Technol.* **36,** 1331–1351 (2018).

39. Senthil Kumar, P. *et al.* Effect of temperature on the adsorption of methylene blue dye onto sulfuric acid-treated orange peel. *Chem. Eng. Commun.* **201,** 1526–1547 (2014).

40. Boparai, H. K., Joseph, M. & O'Carroll, D. M. Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. *J. Hazard. Mater.* **186,** 458–465 (2011).

Acknowledgements

To the Technical Research Support Unit of the Institute of Catalysis and Petroleum Chemistry (CSIC) for support in the textural characterization of activated carbon.

María Eugenia Léon-González, Noelia Rosales-Conrado and Yolanda Madrid thank the Spanish Commission of Science and Technology (CTQ2017-83569-C2-1-R) and the Comunidad of Madrid and European funding from FSE and FEDER programs for financial support (project S2018/BAA-4393, AVANSECAL-II-CM).

Author contributions statement

M.E.L. and F.A.L. conceived the study; M.R.G., L.A. and S.P.F. carried out the experiments; M.E.L., N.R.C. and F.A.L. helped in the analyses and discussion of the results, M.R.G. and L.A wrote the manuscript; all authors contributed to the review, edit, and approval of the paper.

Competing interests

The authors declare no competing interests

Figure legends

Figure 1. Diagram of the process studied.

Figure 2. Chromatogram of the standard mixture (80 µg/L) obtained using the cLC-DAD optimized method. **1** Gallic acid; **2** Dihydroxybenzoic acid; **3** Chlorogenic acid; **4** Caffeine; **5** Caffeic acid; **6** *p*-Coumaric acid; **7** *Trans*- Ferulic acid; **8** Rutin; **9** Naringin; **10** Resveratrol; **11** Quercetin; **12** Kaempferol.

Figure 3. Morphology of several active carbons examined by FE-SEM.

Tables

	Sample Code				
Compound (mg g^{-1} DW)*	**SCG**	**H-SCG**	**WS**	**CWS**	**Ethanol**
Caffeine	2.476	0.26	0.99	4.833	0.089
Chlorogenic acid	LOD	LOD	n.d	9.689	LOD
p-Coumaric acid	0.155	0.229	n.d	0.348	0.046
trans- Ferulic acid	0.166	0.157	0.110	0.177	0.024
Rutin	0.086	LOD	0.064	LOD	LOD
Naringin	0.214	0.096	0.143	0.423	0.010
Resveratrol	0.071	0.066	0.07	0.093	0.013
Quercetin	0.076	0.073	n.d	0.095	0.015
Kaempferol	0.053	0.098	LOD	0.028	0.014

Table 1. Phenolic compounds and caffeine extracted from different solutions

LOD: determined at the levels of the method detection limit, n.d: no detected, SCG = extract from spent coffee grounds, H-SCG = extract from precursor, WS = extract obtained before the evaporation process, CWS = concentrated extract obtained after the evaporation process, Ethanol = organic solution obtained after the evaporation process.

Experiment	Burn-off (wt,% daf)	Yield (wt,%)
AC-SCG-1	82.0	18.0
AC-SCG-2	82.0	18.0
AC-SCG-3	95.0	5.0
AC-SCG-4	96.0	4.0
AC-SCG-5	81.5	18.5
AC-SCG-6	86.5	13.5
AC-SCG-7	93.0	7.0
AC-SCG-8	96.0	4.0
AC-SCG-9	88.7	12.0

Table 2. The variation of the burn-off and yield of the activation process

T (ºC)	**Langmuir**				**Freundlich**				**Temkin**		
	q_m (mg·g^{-1})	**B (mg^{-1})**	**R_L**	**R^2**	**K_f (g^{-1})**	**n**	**1/n**	**R^2**	**A_t**	**b_T**	**R^2**
30	411,5	18,7	0,003	0,999	340,8	6,4	0,2	0,972	4011,9	60,3	0,962
60	775,2	8,9	0,006	0,999	567,2	3,6	0,3	0,819	224,5	24,9	0,921
80	813,1	3,7	0,013	0,993	510,9	3,9	0,3	0,988	400,3	31,5	0,905

Table 3. Langmuir, Freundlich and Temkin parameters calculated for MB adsorption

Precursor of activated carbon	Activation agent	Maximum monolayer adsorption capacity (q_m) ($mg \cdot g^{-1}$)	Isothermal model	Kinetic model	References
Spent coffee grounds†	KOH	411-813	Langmuir	Pseudo-second order	This work
Wine wastes†	KOH	714 - 847	Langmuir	Pseudo-second-order	(Alcaraz et al. 2018)
Wastes carpets	H_3PO_4	403-769.2	Langmuir	Pseudo-second-order	(Hassan & Elhadidy 2017)
Date stones	$ZnCl_2$	398.2	Langmuir	Pseudo-second-order	(Ahmed & Dhedan 2012)
Bamboo	KOH	454.2	Langmuir	Pseudo-second-order	(HAMEED et al. 2007)
Coconut husk	KOH	437.8	Langmuir	Pseudo-second-order	(Tan et al. 2008)
Vetiver roots	H_3PO_4	423	Langmuir	Pseudo-second-order	(Altenor et al. 2009)
Acorn shell	$ZnCl_2$	312.5	Langmuir	-	(Altintig & Kirkil 2016)
Sucrose †	KOH	704.2	Langmuir	Elovich	(Bedin et al. 2016)
Hazelnut shells†	KOH	524	Langmuir	Pseudo-second-order	(Unur 2013)
Posidonia oceanica (L.)	$ZnCl_2$	285.7	Langmuir	Dubinin-Raduchkevich	(Dural et al. 2011)
Orange peel	$ZnCl_2$	150	-	-	(Köseoğlu & Akmil-Başar 2015)
Peach Stones	H_3PO_4	444.3	Tóth and RedlichPeterson	- -	(Álvarez-Torrellas et al. 2015)
Grape waste	$ZnCl_2$	417	Langmuir	-	(Sayğili et al. 2015)
Waste tea	CH_3COOK	554.3	Langmuir	-	(Auta & Hameed 2011)
Phoenix dactylifera fruit pits	NaOH and KOH	104-146	Langmuir	Pseudo-second-order	(Aldawsari et al. 2017)

Table 4. Maximun monolayer adsorption capacity, isothermal and kinetic models of various adsorbents for MB

† Hydrothermal treatment for obtained the precursor.