

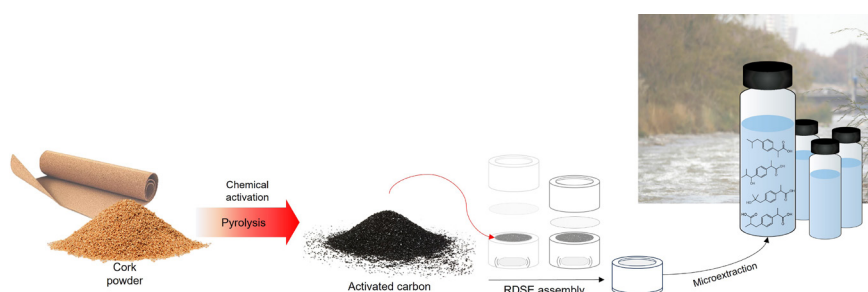
ARTICLE

Cork-Activated Carbon as a Sorptive Phase for Microextraction of Emerging Contaminants in Water Samples

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A novel strategy for microextraction of emerging contaminants was developed by using cork activated carbon (CAC) as the sorbent phase. Carbonization of the natural phase increased the surface area and the porosity of the material, thus improving the extraction efficiency. Moderately polar

compounds, such as ibuprofen and its metabolites, were used as model analytes in water samples. Rotating disk sorptive extraction (RDSE) together with gas chromatography–mass spectrometry (GC–MS) were used for extraction and determination of the analytes, respectively. The optimum conditions for the material synthesis were 600 °C, K₂CO₃ as the activating agent and a mass ratio of 0.8:1 (activating agent:raw material). The optimum values for the RDSE were pH 2, a sample volume of 25 mL and an extraction time of 90 min. The absolute recovery rates for ibuprofen and its metabolites ranged from 19 to 55%, and the relative standard deviations were between 3 and 13%. The proposed method was used to measure the analytes in the influent and effluent from a wastewater treatment plant in Santiago, Chile. The concentrations found for ibuprofen and its metabolites were 0.98–9.8 µg L⁻¹ and 0.8–8.6 µg L⁻¹ in the influent and effluent, respectively. Activation of the cork material enabled the synthesis of a sorbent phase with sorption efficiencies similar to those obtained with the commercial octadecylsilane (C18) phase and superior to that observed for styrene-divinylbenzene (S-DVB). This process is simple and cost-effective.

Keywords: cork activated carbon, ibuprofen, metabolites, RDSE

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INTRODUCTION

As indicated in the literature, sorbents play important roles in sample preparation procedures, since according to their composition, they exhibit selectivity or specificity toward the analytes. The very complex medium in which the molecules under study are found requires an appropriate choice of sorbent, as it defines the selectivity of the extraction method, which in turn influences both the enrichment efficiency and the adsorption capacity.¹ Many commercial synthetic phases, such as polydimethylsiloxane (PDMS), C18, S-DVB, Oasis HLB and others, have proven successful in the determination of various compounds.² However, in recent times, the possibility of working with sustainable raw materials as sorbent phases has been considered since the advantages of biosorbents compared to commercial synthetic phases lie in their origin from renewable sources, their innocuous natures and their capacities for biodegradation. In addition, many of these biomaterials are derived from food and manufacturing waste, which allows recycling and transformation of the waste into biodegradable materials and generation of simpler and more economical alternatives.³⁻⁵

Activated carbon (AC) obtained from agricultural waste has emerged as an option for use as a sustainable sorbent phase. This is a promising strategy because some of the carbon comes from nonrenewable resources, such as petroleum or natural gas.^{6,7} Through the manipulation of experimental pyrolyses and activation conditions, it is feasible to adjust both the porosity and surface polarity of the material and increase the surface area, which improve the extractant properties of the phase.⁸ Typically, there are three types of activations: chemical, physical and physicochemical. Chemical activation is carried out by impregnating the starting material with an activating agent and heating it in a furnace at high temperatures (450–850 °C). A variety of activating agents have been used, including acidic, basic (strong or weak) and neutral salts. The most common are H_3PO_4 , H_2SO_4 , HNO_3 , NaOH , KOH , ZnCl_2 , H_2O_2 , K_2CO_3 and CaCl_2 .^{9,10} In general, this activation method produces AC with a high specific surface area and ample micropores; however, large amounts of the activating agent can lead to pore collapse and reductions in the specific surface area and micropore fraction.¹¹ In this context, it is crucial to manage the ratio between the activating agent and the mass of the raw material, as these factors directly influence the pore sizes and the resulting surface area.⁹⁻¹⁵

Cork is a promising natural sorbent phase, since it comprises suberin, lignin and polysaccharides with a diverse range of functional groups that enable π -stacking interactions, hydrogen bonding and van der Waals forces with different contaminant molecules.^{16,17} Previous work has involved the use of natural cork in microextraction techniques, such as bar adsorptive microextraction (BA μ E) and rotating-disk sorptive extraction (RDSE) with good analytical performance for the determination of parabens and hormones, respectively.^{18,19} However, to take advantage of the material as a sorbent phase, cork activated carbon (CAC) is an alternative form that has been studied as an adsorption material.²⁰ Microextraction-based methodologies have been recognized for their eco-friendliness because they comply with green analytical chemistry (GAC) principles, such as miniaturization of the sample and minimization of the sorbent phase.²¹ The RDSE system is composed of a Teflon disk containing a magnetic stirrer inside, and the sorbent phase can be attached to one of its faces. It is a fast, inexpensive, reusable, simple and easy-to-implement device that also has several advantages, such as a large surface area and high speed.²² Therefore, the joint use of CAC with the RDSE technique gives rise to a green methodology.

Ibuprofen (IBU) has been under study for several years because it was classified as an emerging contaminant. Its ubiquity stems from its ready accessibility and low cost, making it a common medication in many households.²³ Elimination through urine results in the release of IBU and its metabolic products into wastewater and, subsequently, into natural environments. The main metabolites are carboxyibuprofen (COOH-IBU) and 2-hydroxyibuprofen (2-OH-IBU), while to a lesser extent, 1-hydroxyibuprofen (1-OH-IBU) can also be detected.²⁴ Due to their weak acidities (pKa between 3.97 and 5.3), these compounds ionize easily, which allows them to move fluidly in water matrices and undergo incorporation into the trophic chain.²⁵ Therefore, it is of utmost relevance to find efficient methods for their identification in environmental matrices. Previously, various carbon materials derived from *Lantana camara* stems, olive pits, olive

residues, coconut shells and cocoa shells have been documented for the purpose of studying ibuprofen adsorption. Mainly, these materials are applied in the remediation of this contaminant in water sources. However, to date, only the use of cork-derived activated carbon in the microextraction of ibuprofen using BAuE has been reported.²⁶

The main objectives of this work were to develop a novel methodology based on RDSE and use CAC as the sorbent phase for microextraction of ibuprofen and its metabolites from water samples and subsequent detection by gas chromatography–mass spectrometer detector (GC–MS). In the present investigation, several experimental parameters were evaluated and optimized: the CAC synthesis (pyrolysis temperature, nature and amount of the activating agent), as well as some chemical and hydrodynamic variables that describe the microextraction process.

MATERIALS AND METHODS

Reagents and materials

Agglomerated laminar cork, manufactured with 2 mm thick grains and dimensions of 1 m x 1 m, was supplied by Corchos Chile (Santiago, Chile). Ibuprofen, 1-hydroxyibuprofen, 2-hydroxyibuprofen and carboxyibuprofen were obtained from Sigma–Aldrich (Milwaukee, United States). All standard solutions were prepared at 1000 mg L⁻¹ in methanol supplied by Merck (Darmstadt, Germany) and stored at 4 °C. HPLC grade methanol (MeOH), ethyl acetate (EtOAc) and acetonitrile (MeCN) were obtained from Merck. ZnCl₂ and K₂CO₃ (from Merck) were alternatively used as activating agents in the synthesis of activated carbon. Deionized water was obtained from a Millipak® Express 20 Filter system from Merck. N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) supplied by Merck was used as a derivatization agent. Nitrogen (purity ≥ 99.999%) and helium (99.9999%), both supplied by Linde (Santiago, Chile), were used for evaporation of the final extract and as the carrier gas in GC–MS, respectively.

Instruments and software

A Thermo Scientific Trace 1300 gas chromatograph (Milan, Italy) coupled to an ISQ single quadrupole mass detector (United States) with a Restek RTX-5MS (30 m x 0.25 mm id, 0.25 µm) fused silica capillary column (United States) was used as the measuring instrument. The chromatographic conditions consisted of a carrier gas (He) flow rate of 1 mL min⁻¹ and an injection volume of 2 µL of the derivatized extract in splitless mode. The injector was maintained at 280 °C, the ionization source at 250 °C and the transfer line at 300 °C. The temperature program was started at 75 °C for 1 min, then increased to 300 °C at a rate of 15 °C min⁻¹ and held for 5 min. The total duration of the analysis was 21 min with a solvent delay of 7 min. The retention times obtained were 10.62, 11.93, 12.51 and 13.43 min for IBU, 1-OH-IBU, 2-OH-IBU and COOH-IBU, respectively. For analyte quantification, selective ion monitoring (SIM) mode was selected. The quantifier and qualifier ions were 160 and 234 *m/z* for IBU, 323 and 324 *m/z* for 1-OH-IBU, 131 and 308 *m/z* for 2-OH-IBU and 218 and 336 *m/z* for COOH-IBU, respectively.

A Heraeus M-110/1100 °C muffle furnace (Thermo Scientific, United States) was used for syntheses of the carbons under an inert nitrogen atmosphere. A Thermo Scientific Nicolet iS5 Fourier transform infrared spectrophotometer (FT-IR) connected to an iTX-iD7 attenuated total reflectance (ATR) smart sampling accessory was used to characterize the phases. OMNIC 8.0 software (Thermo Scientific) was used to resolve the spectra in the range of 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹ and a scan number of 16. The morphologies of the materials were studied via high-resolution scanning electron microscopy (SEM) with a Thermo Fisher Scientific (FEI, The Netherlands) INSPECT-F50 model. Images were captured at 16000 x. Contact angle measurements were performed with a Ramé-Hart Instrument Co. Model 200 (F4 series) goniometer with DROPimages Standard v2.4 (States United) to characterize the hydrophobicity of each sorbent material. The textures of the carbonaceous materials were studied with automatic adsorption equipment (Micromeritics, United States) generating N₂ adsorption isotherms (BET analysis). The pH studies were carried out with a WTW pH meter, pMX 3000 (United States). MR 300 multiposition magnetic stirrers (Heidolph Instrument, Germany), a KMC-1300 V vortex stirrer (Vision Scientific Co., Ltd., Korea)

and an analog heat block evaporator (VWR, United States) were used in the RDSE procedure. ICP–MS determinations of the elements in the natural cork were performed with a single quadrupole inductively coupled plasma–mass spectrometry instrument, specifically the iCAP RQ from Thermo Scientific (United States). The chemometric studies were designed with Statgraphics Centurion XV statistical software for Windows (Manugistics, United States).

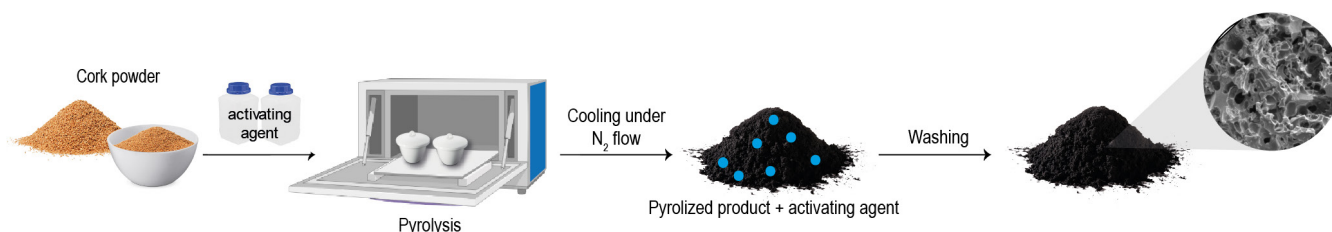


Figure 1. Schematic representation of the CAC synthetic process.

Syntheses of the sorbent phases

Several carbon samples were prepared, including CAC and biochar (BC) from natural cork (NC). The synthesis of CAC was based on previous literature reports with some modifications.²⁷ Figure 1 shows a representation of the synthetic process. Prior to pyrolysis, the laminar cork (granules < 149 μm) was ground. Solutions of the activating agents ZnCl_2 and K_2CO_3 were prepared with different concentrations to reach impregnation ratios of 1.6:1, 0.8:1 and 0.4:1, which were defined as the weight ratio of the activating agent/NC. Each mixture was stirred (150 rpm) at 60 $^\circ\text{C}$ overnight (15 h) to dryness. Then, the homogenized and dried paste in the crucible was capped and placed in the conventional oven. The mixture was saturated inside the furnace with N_2 (1.5 psi) for 20 min to ensure an inert atmosphere. The pyrolysis was started at a temperature of 25 $^\circ\text{C}$ and raised at a rate of 10 $^\circ\text{C min}^{-1}$ until it reached 400 $^\circ\text{C}$, where it was maintained for 30 min. Finally, it was allowed to cool under a N_2 flow to approximately 150 $^\circ\text{C}$. The pyrolyzed material was washed with 5 mol L^{-1} HCl and then with water to neutral pH to remove the ash and excess reagents. It was dried for 24 h at 55 $^\circ\text{C}$, ground in an agate mortar to generate carbon dust and sieved to particle sizes between 75 and 38 μm . The synthesis of the CACs was carried out in the same way but at 600 and 800 $^\circ\text{C}$. In the case of the BC, the cork powder was subjected to pyrolysis under the same conditions in the absence of an activating agent. The optimal phase with the best extraction efficiency of the analytes was selected for the RDSE. The yields of the synthetic procedures were calculated as explained in the Supplementary Material.

Characterization of the sorbent phases

The CAC, BC and NC were characterized by FT-IR, SEM, point of zero charge (PZC), isoelectric point (IEP), contact angle measurements, and BET analysis. For the BET analyses, the sorbent phases were degassed under vacuum for 3 h at 300 $^\circ\text{C}$. Subsequently, the N_2 adsorption isotherms were generated at -196 $^\circ\text{C}$. The Brunauer–Emmett–Teller equation (BET) was employed to calculate the surface area (S_{BET}). The total pore volumes ($V_{\text{pore total}}$) were determined by assessing the liquid volumes of N_2 corresponding to the amount adsorbed at a relatively high pressure of $P/\text{Po} \sim 0.99$. The pore size distribution of the activated carbon produced was characterized with the Barrett–Joyner–Halenda (BJH) method.²⁸ The PZC and IEP of the CAC were determined according to the methodology described in the Supplementary Material. The contact angles were determined with the procedure outlined in the literature.²⁹ Double-sided adhesive tape was applied to glass microscope slides, onto which particles of the sorbent material were deposited. After waiting approximately 20 s, the nonadhered particles were removed. Following this, a water droplet was introduced, and images were captured for up to 4 s. The trace elements of the natural phase measured by ICP–MS were Li, Be, Mg, Al, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Ga, As, Se, Rb, Sr, Mo, and Ag. Cd and Ba (see the methodology in the Supplementary Material).

RDSE Procedure

Preparation

A 30 mg portion of CAC was added to the rotating disk cavity, and then a glass fiber filter was placed on the material and sealed with a Teflon® cover (see Figure S1 in Supplementary Material). The sorbent phase was conditioned in a glass vial with 10 mL of EtOAc, MeOH and deionized water for 5 min rotating at 2000 rpm each.

Extraction

A 25 mL sample aliquot was added to a vial, the pH was adjusted to 2, and NaCl was added at 10% w/v. The extraction process was performed at 2000 rpm for 90 min in a 10-position magnetic stirrer.

Desorption

The disk that contained the analytes was transferred to another vial, where 10 mL of MeCN was added and rotated at 2000 rpm for 20 min. Subsequently, the extract was evaporated to dryness under a N₂ flow at 60 °C. Finally, the extract was derivatized (50 µL of MSTFA and 50 µL of EtOAc were added and shaken for 5 min at room temperature) and injected into the GC–MS.

Optimization of the RDSE method

Optimization studies were carried out with an analyte concentration of 30 µg L⁻¹: (i) Chemical variables; the pH of the aqueous sample was evaluated in a range from 2 to 10, for which different buffer solutions were prepared. The ionic strength (salting-out effect) was studied with different NaCl solutions ranging from 0 to 30% w/v, and both experiments were performed in triplicate. (ii) Hydrodynamic variables; a Doehlert design was applied to analyze the sample volume and extraction time, keeping a high rotation velocity of the disk (2000 rpm), for a total of 9 experiments. Table SIV (see the Supplementary Material) shows the matrix of experiments.

Figures of merit and application of the method in real samples

Matrix-matched calibration was used by considering analyte concentrations from 5 to 100 µg L⁻¹ under the optimized extraction conditions, from which the sensitivity and linearity (R²) were calculated. The limits of detection (LODs) and limits of quantification (LOQs) were determined according to the ICH guidelines: LOD = 3.3S_{x/y}/m and LOQ = 10S_{x/y}/m, and both the slope (m) and deviation standard of the regression line (S_{x/y}) were obtained from the calibration curve. The precision was calculated as a function of the relative standard deviation parameter (RSD) for six replicate samples extracted under the same conditions. Recovery (Re) and matrix effect (ME) were obtained using the following equations:³⁰

$$\text{Re (\%)} = (A_{S4} - A_{S3}) / A_{S2} \quad \text{Equation 1}$$

$$\text{ME (\%)} = (A_{S2} - A_{S3}) / A_{S1} \quad \text{Equation 2}$$

where each term corresponds to the area (A) normalized to an internal standard of S1: 30 µg mL⁻¹ multistandard solution of each analyte; S2: river water extract by RDSE, which was spiked with 30 µg mL⁻¹ of analytes just before injection; S3: extract obtained directly from a river water sample (blank); and S4: extract obtained from a river water sample spiked with 30 µg mL⁻¹ multistandard from the start of extraction.

For the real samples, influent and effluent samples were collected from the wastewater treatment plant (WWTP) *El Trebal* (Metropolitan Region, Chile). The samples were filtered and stored in polypropylene bottles at 4 °C until analysis. The applicability of the proposed method was studied with CAC as the sorbent phase.

RESULTS AND DISCUSSION

Optimization of the CAC preparation

The synthesis of CAC in a conventional horizontal furnace was studied in detail. Several factors were analyzed, including the final pyrolysis temperatures and the nature and proportions of the activating agent. The optimal conditions were selected based on the highest extraction efficiencies of the analytes.

The effects of the two activating agents were studied at 400 °C with different mass ratios. Figure 2 shows the effects of the nature and proportions of the activating agent. The CAC prepared with K_2CO_3 presented better extraction efficiencies for all analytes compared to CAC prepared with $ZnCl_2$. In addition, higher analytical responses were observed for the four analytes when using 0.8 g of K_2CO_3 , which was selected as the optimum amount for material activation. Contradictory to this result, it has been previously reported that porosity development is practically independent of the K_2CO_3 content.³¹ The synthetic yields were quite similar for both activating agents (Table SI, Supplementary Material).

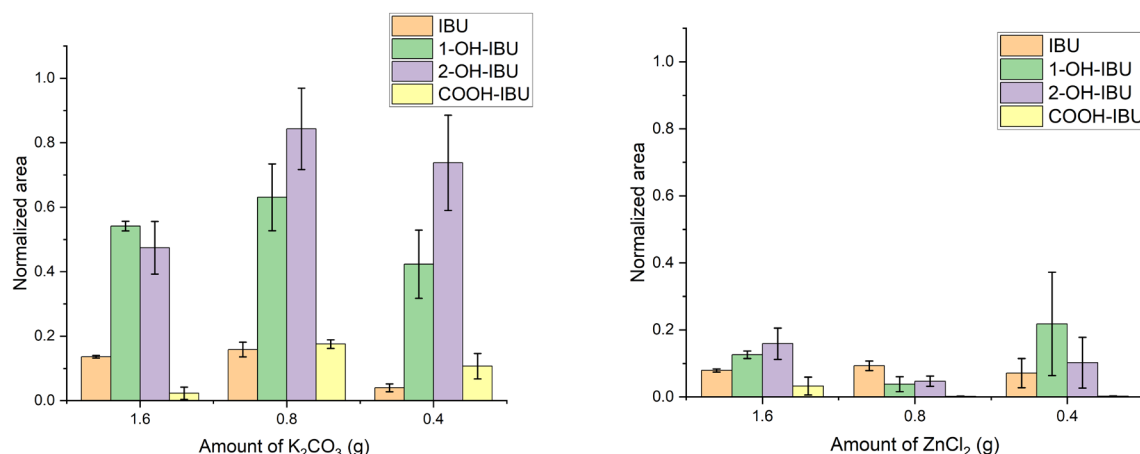
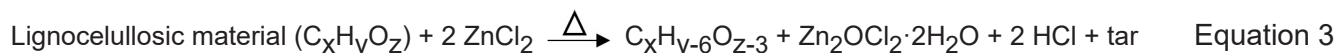


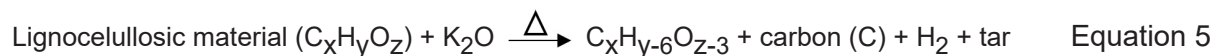
Figure 2. Effects of the amount and nature of the activating agent on the extraction efficiency.

The different behaviors of the materials were probably consequences of the mechanism for reaction of the activating agent with the raw material. $ZnCl_2$ was a neutral activating agent, and its main pore generation process was through the reduction of carbon atoms.⁹ According to the mechanism proposed in the literature (expressed in Equation 3), under thermal conditions, the lignocellulosic composite underwent a dehydration reaction with the activating agent, resulting in the formation of Zn_2OCl_2 .³² Subsequently, the latter compound underwent a new reaction that regenerated the original zinc salt.



K_2CO_3 is a medium alkalinity activating agent.⁹ The mechanism suggested decomposition into K_2O and CO_2 , as expressed in Equation 4.^{32,33} Then, K_2O reacted with the lignocellulosic material, which was dehydrated and lost volatile components, as reflected in Equation 5. An advantage is the production of CO_2 , which served as an oxidizing gas through physical activation.³³ Additionally, metallic potassium was generated during the reaction, and it was shown to react within the carbon atom matrix by inducing a rearrangement process that increased the degree of graphitization and porosity.⁹ Collectively, these factors generated more pronounced activation effects than $ZnCl_2$.





Once the activating agent and its mass ratio were defined, the effect of the pyrolysis temperature was studied. For preparation of the active carbon, the pyrolysis temperature is one of the most relevant factors, followed by the heating rate, a suitable inert atmosphere, and the residence time since all of them influence the structure of the resulting material. For the syntheses of CACs and BCs, three different temperatures were evaluated: 400, 600 and 800 °C. Figure 3 summarizes the carbonization temperatures. It was determined that the optimal option was the use of the CAC prepared at 600 °C since higher extraction efficiencies were obtained. It is important to mention that, although at elevated temperatures the materials resulted in a higher fixed carbon content and a reduction in the contents of volatile compounds, the CAC at 800 °C led to lower yields in carbon production and increased ash content (Table SII, Supplementary Material). Accordingly, 0.8 g of K_2CO_3 and a temperature of 600 °C were selected as the optimal activation conditions.

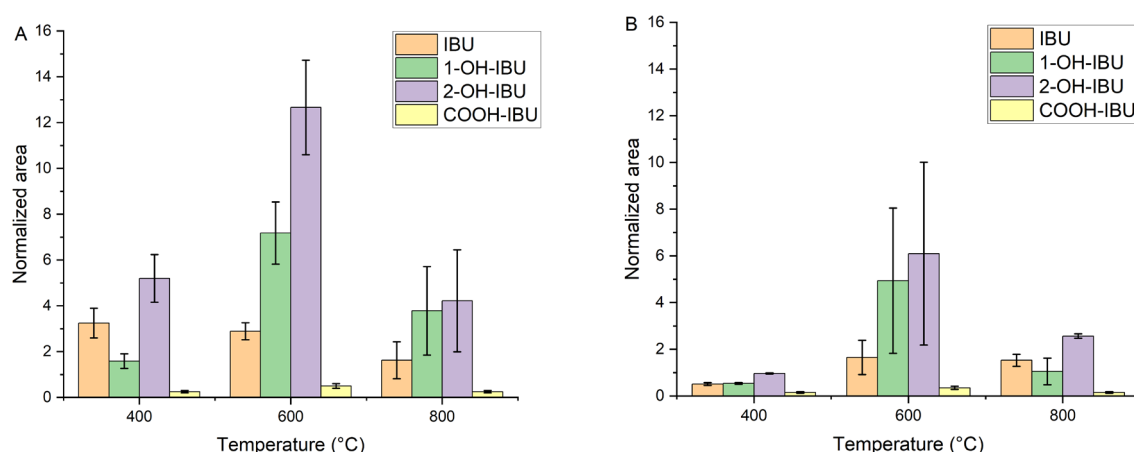


Figure 3. Effect of the pyrolysis temperature on the extraction efficiency; a) CAC and b) BC.

Characterization of the sorbent phase

The morphology of the optimal CAC was studied by establishing comparisons with NC and BC (at 600 °C). The SEM images for the three materials are shown in Figure 4. The NC particles had irregular surfaces and discontinuous structures due to the presence of cracks that passed through the particles. The BC presented a similar structure with sheets or leaves containing cracks and rough surfaces but had small pores. For the CAC, the discontinuous structure was preserved due to the presence of pores on the surface, but it adopted different shapes from both NC and BC. The difference in the numbers of pores was mainly due to the activation process and explains why the extraction efficiencies were higher with CAC.

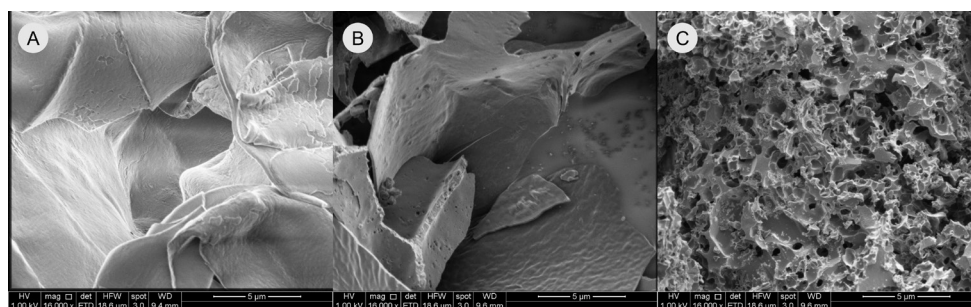


Figure 4. SEM images; a) NC, b) BC at 600 °C and c) CAC (K_2CO_3 0.8 g) at 600 °C.

To observe how the activation process affected the chemical structure, the FT-IR spectra of CAC, NC and BC were compared (Figure 5). The NC spectrum showed a band at 3400 cm^{-1} for OH groups, while the sharp bands between 2800 and 2900 cm^{-1} were associated with the stretching vibrations of aliphatic CH groups. The intense stretching band at 1736 cm^{-1} due to C=O groups. Two weak bands were observed in the aromatic region between 1500 and 1600 cm^{-1} , which are attributed to C=C stretching vibrations. The bands between 1100 and 1300 cm^{-1} were associated with C-O bonds. The spectrum of BC was very similar to that observed for NC. The main functional groups indicated were OH at 3385 cm^{-1} , C=O at 1700 cm^{-1} , C=C at 1600 cm^{-1} and C-O at 1200 cm^{-1} . However, in the case of CAC, no functional groups were indicated by the spectrum, which was relatively flat except for a weak band at approximately 1600 cm^{-1} . It was inferred that the higher extraction efficiency of CAC was caused by a larger and more porous surface area, which supported the interactions between the CAC and analytes via pore filling and chemical adsorption by π -stacking interactions.³⁴ Similar spectra were reported in the literature for NC, BC and CAC.^{16,35,36}

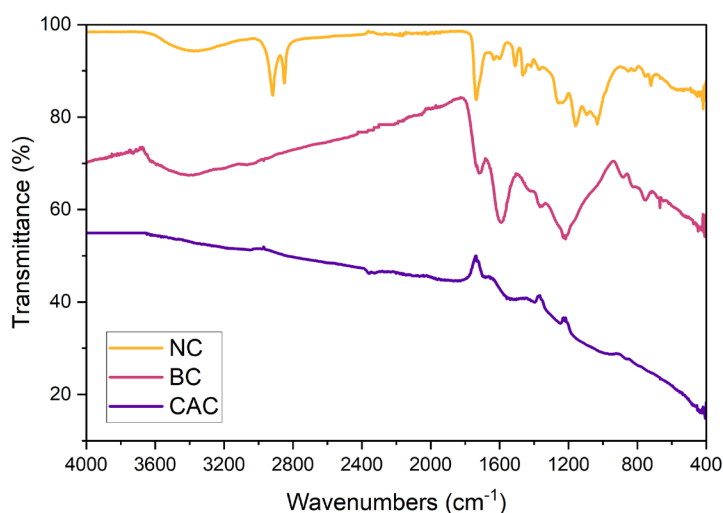


Figure 5. FT-IR spectra for NC, BC at $600\text{ }^{\circ}\text{C}$ and CAC (K_2CO_3 0.8 g) at $600\text{ }^{\circ}\text{C}$.

The contact angle of the optimal CAC was measured and compared with those of the BC and NC to determine the wettabilities of the materials, as the analyte extraction process was performed with water samples. The static analysis employed enabled direct measurement of the contact angle (Θ) between the water droplet and the solid surface of the sorbent material. When the droplet in contact with the surface exhibited high affinity, the angle was less than 90° ; the liquid was attracted by the solid, resulting in elongation in the perpendicular direction, indicating a hydrophilic surface. In the case of very low attractive forces, the solid surface repelled the liquid, and the angle was greater than 90° , signifying a hydrophobic surface.³⁷⁻³⁹ Figure 6 displays images captured for up to 4 s, demonstrating high and similar hydrophobicities for the three materials. The angles recorded at 4 s for NC, BC and CAC were 100° , 100° and 84° , respectively, suggesting that CAC was slightly more hydrophilic.

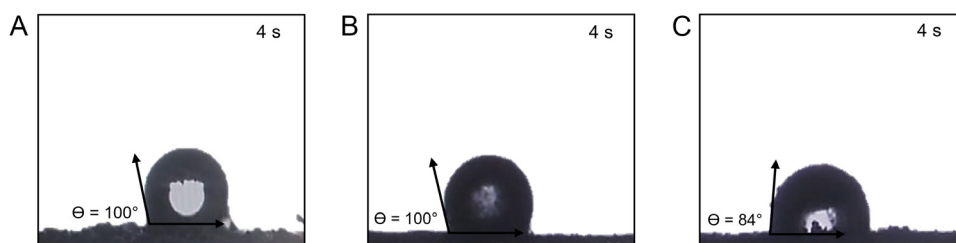


Figure 6. Contact angle measurements; a) NC, b) BC at $600\text{ }^{\circ}\text{C}$ and c) CAC (K_2CO_3 0.8 g) at $600\text{ }^{\circ}\text{C}$.

The element contents were also studied by microwave digestion and quantified with ICP–MS. The elements Mg, Al, V, Mn, Fe, Cu, Ga, As, Rb, Sr and Ba exhibited concentration ranges between 0.58 and 77 $\mu\text{g g}^{-1}$. For more details, see Table SIII in the Supplementary Material.

The N_2 adsorption-desorption isotherms for the optimal CAC are shown in Figure 6. The textural parameters obtained through BET analyses were $S_{\text{BET}} = 524 \text{ m}^2 \text{ g}^{-1}$, $V_{\text{pore total}} = 0.223 \text{ cm}^3 \text{ g}^{-1}$ and an average pore size of 1.7 nm. These values were comparable to those observed previously for the CAC used in BaμE for the extraction of ibuprofen and clofibric acid.^{26,40} Figure 7a shows the N_2 adsorption-desorption isotherm generated at -196°C for the CAC, and Figure 7b shows the pore size distribution. According to the classification ranges established by the International Union of Pure and Applied Chemistry (IUPAC), type I isotherms were observed, and they exhibited horizontal plateaus suggesting microporous structures (pore $< 2 \text{ nm}$) and hysteresis loops.⁴¹ However, the pore sizes were close to 2 nm, which meant the isotherms were combinations of types I and II since at the ends, inflection points were evident at elevated pressures close to saturation. This point was linked to the presence of mesopores (pores with sizes between 2 and 50 nm), which were observed in the SEM analysis.

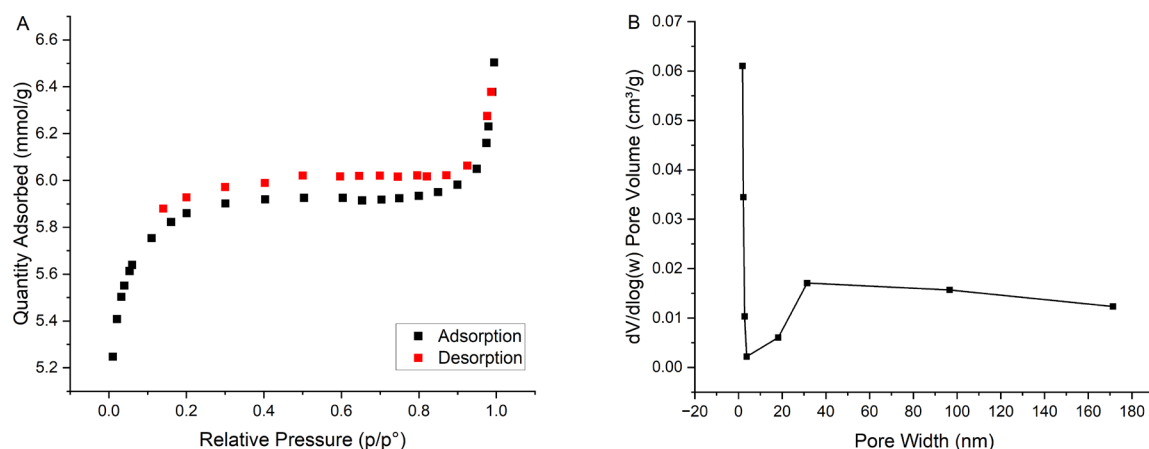


Figure 7. BET analysis of CAC (K_2CO_3 0.8 g); a) N_2 adsorption-desorption isotherms generated at -196°C and b) BJH desorption pore-size distribution.

RDSE Optimization

In RDSE, the disk device is mainly available in two configurations.²² The configuration used in this study consisted of a disk with a 0.1 cm^3 cavity that was loaded with a portion of the particulate extraction phase and then covered with a glass-fiber filter and sealed with a Teflon® cover. The second configuration used in RDSE is a flat disk in which a laminar phase is immobilized. In the current case, we tried to use this second configuration by immobilizing the CAC on a double contact tape; however, unfortunately, this simpler alternative was not feasible because at a high rotational velocity of the disk, the sorbent material was partially removed from the glue. Consequently, the disk containing a cavity for the sorbent was used and optimized.

The various factors that could influence the analyte extraction were optimized by using CAC as the sorbent phase. In this process, the chemical variables such as the pH, salting-out effect and desorption solvent, as well as hydrodynamic variables such as the sample volume and extraction time, were evaluated. These were evaluated to identify the best analytical response for each case.

The pH plays a crucial role in the extractions of acidic compounds. The study was carried out over a pH range of 2 to 10. Figure 8a shows that the best analytical responses of the analytes were obtained at pHs of 2 and 4, and at pH 4, only the IBU showed a larger signal. Otherwise, at pH 7 and 10, significant decreases were observed in the analytical signals. This was explained by the pK_a values of the compounds (between 3.9 and 5.3), indicating that the compounds were preferably extracted in their neutral forms. Consequently, pH 2 was selected as the optimal condition because complete protonation of the analytes was ensured. It

is important to mention that the phase in question exhibited a pH of 4.6 according to the PZC study (see Supplementary Material), which suggested that at pH 2, the interactions between the analytes and the phase were favored.

Since IBU and its metabolites are moderately polar, it is essential to consider the ionic strength. The salting-out effect reduces analyte solubilities in aqueous media and enhances sorption on the sorbent. Figure 8b shows the results for varying the NaCl concentrations between 0 and 30% w/v. This indicated a lower response for the compounds when NaCl was not added. The optimal condition selected was 10% w/v NaCl because it presented the best responses for all analytes with lower dispersions of the data.

Different elution solvents were tested (MeCN, MeOH, CHCl_3 and a MeOH:EtOAc mixture) to identify the best option for desorption of the analytes from the sorbent phase. The results are shown in Figure 8c. The strongest analytical responses for all analytes were obtained with ACN as the elution solvent.

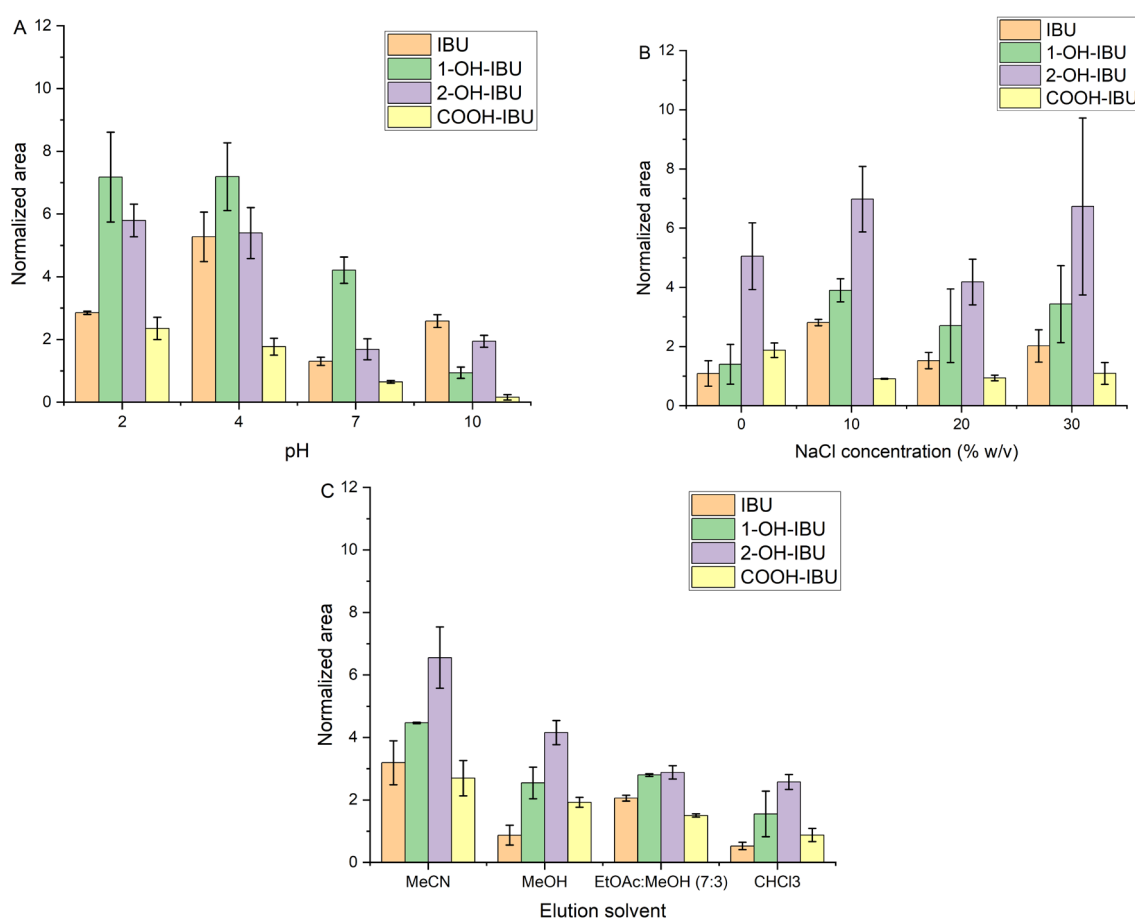


Figure 8. Effects of the different factors on the extraction efficiency; a) pH, b) NaCl concentration (salting out) and c) elution solvent.

Among the hydrodynamic variables, the sample volume and extraction time were investigated simultaneously with a Doehlert experimental design. During this process, the rotational velocity was set at 2000 rpm (maximum value), since it has been reported that an increase in this velocity resulted in better mass transfer.²² Details of the chemometric study are shown in the Supplementary Material (Table SV).

To determine the optimal points for both variables with a multiresponse analysis, the overall desirability function (D) was used and an impact of one was assigned to each factor. Figure 9 shows the estimated response surface for the experiment. A desirability of 0.796609 was obtained. The optimal values for the best analytical response were a sample volume of 25 mL and an extraction time of 90 min.

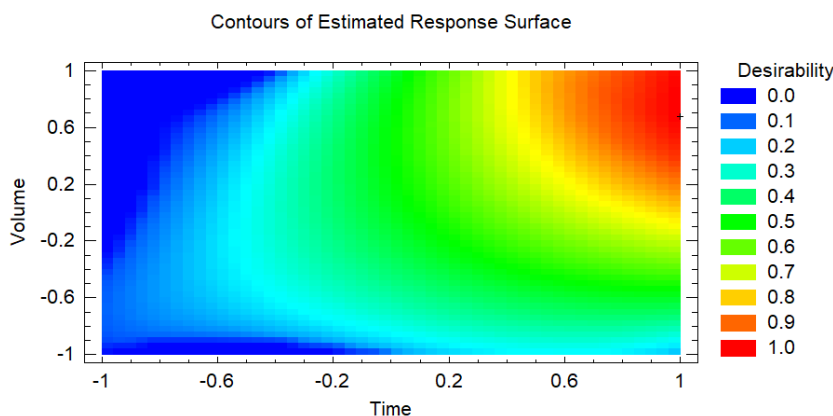


Figure 9. Contour surface for optimization of the hydrodynamic variables.

Determination of figures of merit

River water (Mapocho River, Chile) was used to validate the proposed analytical methodology. The figures of merit for the method are summarized in Table I. The linear equations for each analyte exhibited coefficients of determination (R^2) higher than 0.99, except for COOH-IBU, which exhibited a lower value of 0.96, which was appropriate considering the nature of the matrix analyzed. The LODs and LOQs ranged between 0.17–0.43 and 0.56–1.43 $\mu\text{g L}^{-1}$, respectively, which were consistent with the concentrations of the analytes in wastewaters. The absolute recovery rates ranged from 19 to 55%, and COOH-IBU was extracted most efficiently. In equilibrium techniques, such as RDSE, these recovery values are acceptable. In terms of precision, the relative standard deviations (RSD) remained at values $\leq 13\%$ for the analytes. Finally, the matrix effect was examined, which indicated that COOH-IBU and 2-OH-IBU were most affected by the presence of the matrix. Values close to 100% (for IBU and 1-OH-IBU) indicated a low or almost null matrix effect.

Table I. Figures of merit for the proposed CAC method

Compound	Sensitivity ($\text{L } \mu\text{g}^{-1}$)	R^2	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	%Re	%RSD (n = 6)	%ME
IBU	0.115	0.992	0.43	1.43	21	13	109
1-OH-IBU	0.215	0.991	0.17	0.57	19	13	86
2-OH-IBU	0.197	0.998	0.25	0.85	33	9	70
COOH-IBU	0.043	0.969	0.17	0.56	55	8	180

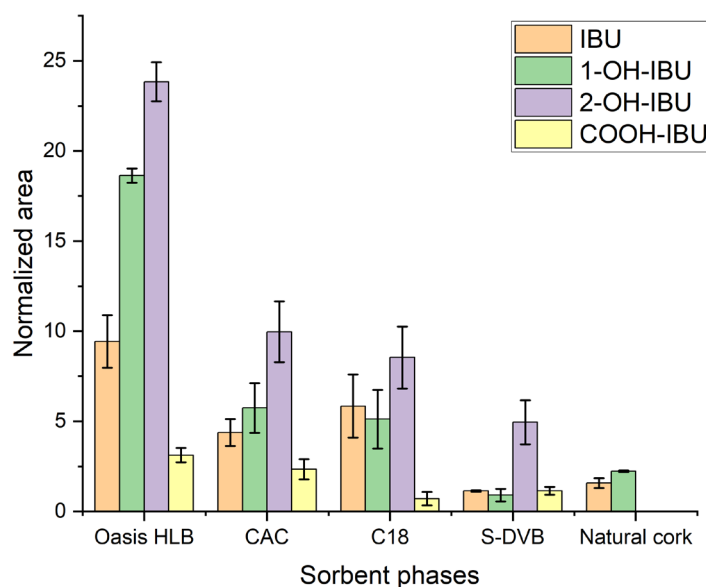
The proposed method was applied to wastewater samples. The resulting analyte concentrations are shown in Table II. The presence of COOH-IBU was found in a higher concentration, which was consistent with the fact that COOH-IBU is one of the main metabolites of IBU and was excreted in greater proportion. The presence of these same analytes has been reported previously, with concentrations ranging of 13.74–94.0 $\mu\text{g L}^{-1}$ for influents and 1.9–10.7 $\mu\text{g L}^{-1}$ for effluents, even though COOH-IBU has been detected in river water samples with a concentration of 3.9 $\mu\text{g L}^{-1}$.⁴² The presence of these compounds in the water samples indicated that the WWTPs do not have effective methods to remove these types of contaminants.

Table II. Concentrations (in $\mu\text{g L}^{-1}$) of the analytes in real water samples

Compound	WWTP	
	Influent	Effluent
IBU	<LOQ	<LOQ
1-OH-IBU	0.98 ± 0.07	0.80 ± 0.02
2-OH-IBU	9 ± 1	<LOQ
COOH-IBU	9.8 ± 0.4	8.6 ± 0.3

Finally, the extraction efficiency of CAC was compared with those of NC and synthetic commercial sorbent phases such as C18, Oasis® HLB and S-DVB. As seen in Figure 10, NC showed no affinity for compounds with higher polarities, such as 2-OH-IBU and COOH-IBU; in contrast, CAC was able to extract the four analytes of interest. The low affinity of NC was associated with its high hydrophobicity ($\Theta = 100^\circ$). The extraction of IBU and 1-OH-IBU with the NC phase in laminar form has been documented,⁴² and efficiencies similar to those of the commercial phases were obtained; however, in the current study, cork was applied in particulate form for comparison with the other phases. Likewise, despite the high analytical efficiency previously reported for the microextraction of parabens and hormone with natural cork,^{18,19} in this case the natural phase did not have affinity for all the compounds under study (IBU and metabolites), which justifies the formation of the CAC to improve its morphological and textural properties.

Regarding the comparison with commercial phases, CAC had a higher extraction efficiency than S-DVB and was statistically similar to C18 (even more effective in the case of COOH-IBU). Likewise, Oasis® HLB had the highest extractant capacity of all phases tested, which was associated with its well-established lipophilic-hydrophilic balance. Nonetheless, it is important to mention that CAC is inexpensive, efficient, easy to synthesize and accessible, and it comes from a natural raw material; therefore, its use advances green analytical chemistry.

**Figure 10.** Extraction efficiencies of different particulate sorbent phases.

CONCLUSIONS

A new material, cork-derived activated carbon, was synthesized and applied as a sorbent phase in the RDSE of IBU and its metabolites. Activation with K_2CO_3 at 600 °C produced a microporous material with a high specific surface area, which extracted the analytes under study from environmental water samples with efficiencies similar to those of C18 and higher than those of S-DVB.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

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SUPPLEMENTARY MATERIAL

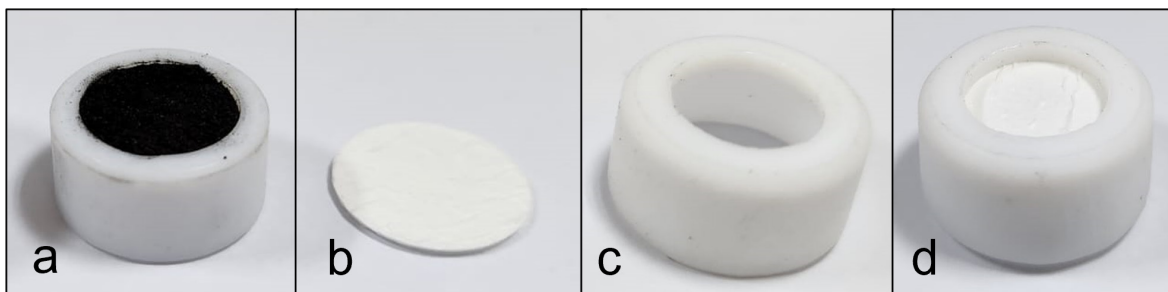
Rotating-Disk System

Figure S1. Rotating disk device used in this study; a) Teflon disk with CAC as the phase sorbent (including the magnet inserted inside), b) glass fiber filter, c) Teflon-cover, and d) assembled rotating system.

Calculation of the CAC and BC synthetic yields

The yields of the synthetic processes were calculated with Equation S1, where m_f is the final mass (dry pyrolyzed material, after washing with acid and water) and m_i is the initial mass of the precursor (before pyrolysis).¹

$$Y (\%) = \frac{m_f}{m_i} \times 100 \quad \text{Equation S1}$$

Table SI. CAC synthetic yields in the study of the amount and nature of the activating agent

Amount of activating agent (g)	Yield _{K₂CO₃} (%)	Yield _{ZnCl₂} (%)
1.6	53	47
0.8	54	60
0.4	50	47

Table SII. CAC synthetic yields in the study of pyrolysis temperatures

Temperature (°C)	Yield _{CAC} (%)	Yield _{BC} (%)
400	53	43
600	32	11
800	23	4

Determination of PZC and IEP

The PZC and IEP methodologies were based on the literature.² For PZC, 20 mL of deionized water was added to different glass vials, and the pH was adjusted within the range 2 to 12 (spanning 9 units). Then, appropriate amounts of acid or base (0.01 mol L^{-1} and 1 mol L^{-1} HCl, and 1 mol L^{-1} , 0.01 mol L^{-1} and 0.05 mol L^{-1} NaOH) were added, and 200 mg of the sorbent phase was introduced. They were stirred for 48 h at room temperature. Once the stirring time was completed, the final pH of the sample was measured. The PZC corresponded to the intersection point of the curve with the diagonal. The IEP was carried out in the same way, but the samples were shaken for 2 h. The IEP value indicates the pH at which the zeta potential is zero.

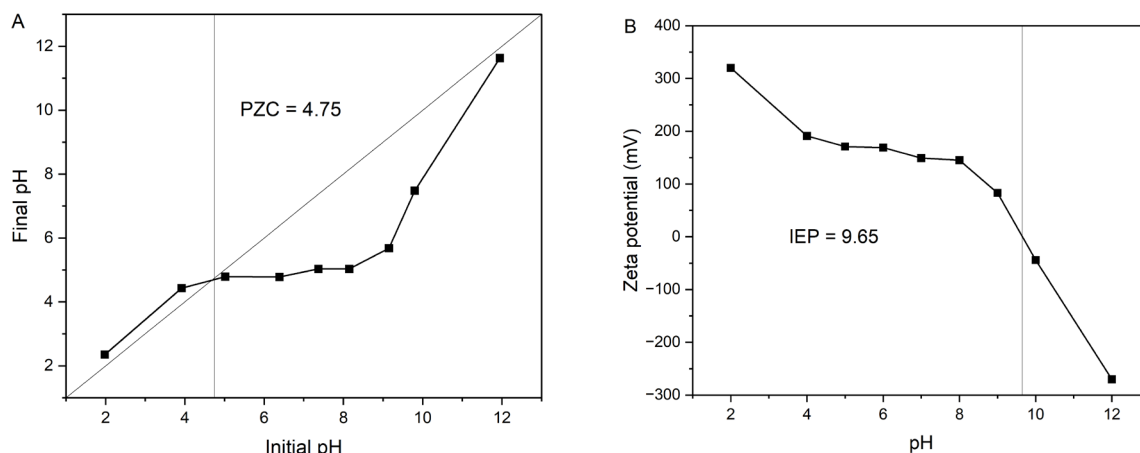


Figure S2. PZC (a) and IEP (b) of the CAC.

Studies of the PZC and the IEP of CAC were carried out. In the case of PZC, constant pH values were observed in the range 4 to 9 (Figure S2a). The PZC was determined to be 4.6, indicating that at this value, both on the surface and inside the material, there were equal amounts of positively and negatively charged sites. This indicated that at pH below the PZC, the positively charged sites would prevail, while at higher pH, the negatively charged sites would predominate. Although the FT-IR spectrum did not reveal the presence of ionizable groups in the structure, it is important to consider that the acidic pH of the phase could modify the pH of the water sample, which should be considered when performing extractions. On the other hand, the IEP provides information about the surface charge of the material. As shown in Figure S2b, a value of 9.65 was obtained for the IEP of the CA. That is, at a pH of 9.5, the zeta potential of the sorbent phase was zero.

Trace element analyses of the natural phase with ICP–MS

Microwave acid digestion (ETHOS Easy Mocrowave MA174 (Milestone)) was performed. For this purpose, 0.5 g of NC, 2 mL of HNO_3 , 7.5 mL of HCl and 0.5 mL of water were used. The digestion process was carried out at 180°C and maintained for 30 min at 1800 W.

The trace element analyses with ICP–MS indicated the concentrations shown in Table SIII.

Table SIII. Mean concentrations ($\mu\text{g g}^{-1}$) of the elements found in NC

Element	Mass	Concentration $\pm$ SD
Mg	24	77 ± 4
Al	27	11 ± 1
V	51	0.6 ± 0.2

(continues on the next page)

Table SIII. Mean concentrations ($\mu\text{g g}^{-1}$) of the elements found in NC (continuation)

Element	Mass	Concentration $\pm$ SD
Mn	55	9.35 ± 0.05
Fe	56	5 ± 1
Cu	63	5.5 ± 0.1
Ga	69	0.58 ± 0.03
As	75	0.70 ± 0.06
Rb	85	1.79 ± 0.07
Sr	88	8 ± 1
Ba	138	9.56 ± 0.03

Li, Be, Cr, Ni, Co, Zn, Se, Mo, Ag and Hg were not found.

Study of the hydrodynamic variables

For the extraction time (denoted X1), five working levels were defined, while for the sample volume (denoted X2), three levels were established. In total, nine experiments were carried out, including three central points. The details of the experimental matrix are presented in Table SIV. To evaluate the quality of the models, ANOVA statistical analyses of the regression were performed. The responses obtained are detailed in Table SV. It was noted that the CAC yielded results with $p < 0.05$ in relation to the model variability and residuals. Likewise, a value of $p > 0.05$ was observed between the lack of fit and the pure error, indicating that the model gave an adequate fit to the data.

Table SIV. Experimental matrix (Doehlert design) for the study of the hydrodynamic variables

Experiments*	Coded values		Real values	
	X1	X2	Time (min)	Volume (mL)
1	0	0	60	20
2	1	0	120	20
3	0.5	0.866	90	30
4	-0.5	0.866	30	30
5	-1	0	0	20
6	-0.5	-0.866	30	10
7	0.5	-0.866	90	10
8	0	0	60	20
9	0	0	60	20

*They were carried out at a rotation of velocity of 2000 rpm.

Table S.V. ANOVA of the regression for the analytes using CAC as the sorbent phase

Compound	p value REG/RE*	p value LOF/EP*	R ² (%)
IBU	0.0258	0.0756	96.05
1-OH-IBU	0.0462	0.1084	91.62
2-OH-IBU	0.0241	0.7734	96.22
COOH-IBU	0.0340	0.4507	74.15

*REG: regression variance (model), RE: residual (total error variance), LOF: lack of fit, EP: pure error.

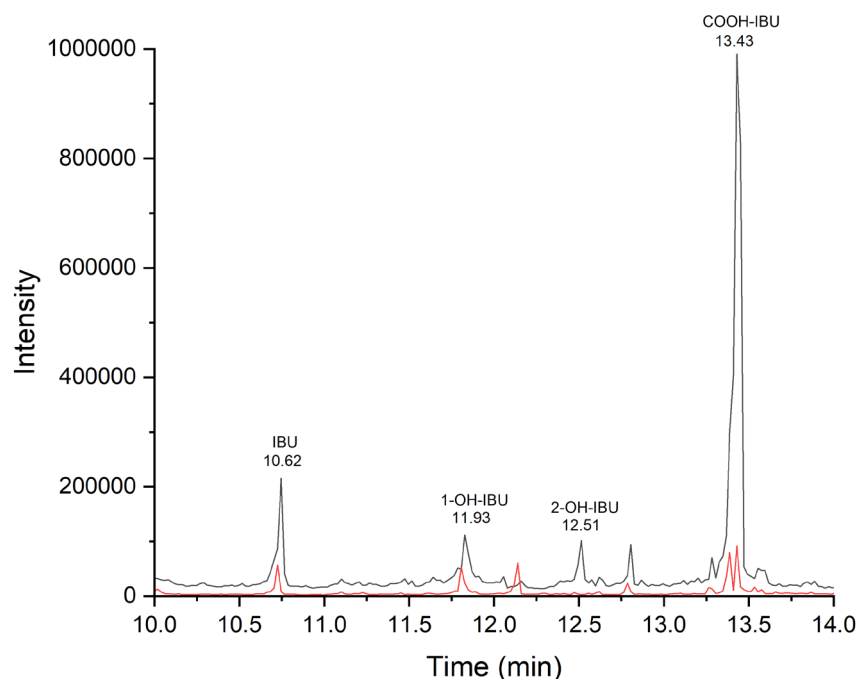


Figure S3. Chromatograms of a blank sample extracted with cork carbon (red line) and of the same sample spiked with a multistandard of the analytes at the LOQ level (black line).

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