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Development of mesoporous materials from biomass ash with future applications as adsorbent materials

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GRAPHICAL ABSTRACT

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Fig. 1. **Fig. 2.**

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Development of mesoporous materials from biomass ash with future applications as adsorbent materials

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Abstract

This paper proposes the synthesis and functionalization of a low-cost mesoporous material from biomass ashes with the aim of obtaining a new adsorbent material, thereby recycling and transforming an environmental liability into a material with added value. Biomass ashes are an environmental liability, composed mainly of aluminosilicates, which have been modified with the help of a surfactant (Pluronic P-123) to model and modify its porous structure. The functionalization of the synthesized material was carried out with N, N-dimethylacetamide (DMAC) and glycine (GLY) in order to improve the adsorption capacity of the synthesized material. The materials obtained in this article were characterized by adsorption-desorption isotherms of N₂ at 77 K, X-ray fluorescence (XFR), elemental analysis (EA), X-Ray diffraction (XRD), Fourier-transform infrared spectrometry (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoemission spectroscopy (XPS). The adsorption capacity of the synthesized matrices has been tested in batch and electrochemical systems. The surface areas obtained by the BET method were 18.49 m² g⁻¹ for pure ashes (CBT) and 22.84 m² g⁻¹ for modified ashes, and the adsorption capacities of Fe³⁺ ions were of about 80.49% for bare SC1, 83.27% for SC1-GLY and 95.41% for SC1-DMAC.

Keywords: Biomass ashes, recycling, mesoporous materials, functionalization, iron adsorption.

1. Introduction

In recent decades the emergence of mesostructured materials has focused the attention and

study of scientists due to their wide range of applications and versatility, with their capabilities as catalysts and highly efficient adsorbents standing out [1]. It is known that the upgrade of these materials began in 1992 with studies on mesostructures called M41S [2]. This family of mesoporous materials are MCM-48 of cubic mesoporous structure, MCM-50 with laminar mesopores, and MCM-41 of hexagonal mesoporous structure. These materials consist of an ordered structure and pore sizes ranging from 2 to 50 nm. Although the development of mesostructured materials dates back to 1971 [3,4], its massification did not take place until the studies carried out by Mobil and its M41S, thus opening a new field in the study and development of porous structure materials. In the continuous progress in the development of these materials [5], mesostructured materials were obtained using copolymers of three nonionic blocks (EOnPOMeOn), achieving pore sizes between 4.5 and 30 nm, and walls of 3.0 to 7.0 nm, called SBA [5]. Currently, researchers have directed their approach to the synthesis of new mesoporous materials of the M41S and SBA-15 type using alternative sources of precursors and structure supports with and without silica [6-9]. Growing industrialization has produced an overexploitation and contamination of available resources, causing disturbances in the ecosystem that are difficult to reverse [10,11]; for example, the need for energy generation produces large amounts of ash due to the combustion of wood, coal, and biomass residues, among others [12]. Most of this waste is disposed of in landfills, which end up being sources of pollutants for nearby biodiversity. The growing generation and difficulty of disposing of this type of waste suggests the need to seek alternative methods for disposal [13].

Considering these problems, the objective of this study was to develop and study the synthesized mesoporous structure using, as structural precursor, a recycling mass ash of the tree type (mix of Radiata Pine and Eucalyptus tree from a pulp mill) in order to obtain a new sustainable and low-cost mesoporous material, giving an environmental liability an added value towards the remediation of water contaminated with iron. Furthermore, in order to improve the adsorption capacity and give the synthesized material a certain specificity, it has been functionalized with N, N-dimethylacetamide and glycine, increasing the capture synergy by the insertion of extra active functional groups in the mesoporous surface. The synthesized mesoporous matrix was called SC1, the one functionalized with N, N-dimethylacetamide (SC1-DMAC) and that with glycine (SC1-GLY), while the

pristine ash was called CBT. Additionally, an electrochemical characterization of the synthesised mesoporous materials was made for a better understanding of the adsorption mechanism studied.

2. Materials and methods

2.1. Synthesis of the mesoporous material

In a typical synthesis of mesoporous materials use was made of type SBA-15 [14], dissolving 1.0 g of P-123 in 20 mL of absolute ethanol at room temperature with stirring. Subsequently, 1.5 mL of nitric acid (67%) and 2.04 g of ash from tree biomass were added (replacing the synthetic structure precursors and in consideration that more than 90% of its elemental composition consists of mixed oxides, mainly aluminosilicates). The mixture was stirred at room temperature for 5 h, dried in an oven at 60 °C for 48 h and calcined at 550 °C for 5 h for the removal of surfactant (P-123).

2.2. Functionalization of the mesoporous material

For the functionalization of the material with N, N-dimethylacetamide (DMAC), 1.1 g of mesoporous ash, synthesized with an excess of DMAC, were dispersed. This procedure comes from a modification of the method [15], who employed toluene as a solvent and 4.1 mmol of DMAC. The modification of this method was made so that the DMAC acted as a solvent and as a functionalizing molecule. Then, the mixture was refluxed for 12 h, and the reaction products were washed with ethanol and dried at 60 °C for 24 h.

At the same time, the mesoporous materials were functionalized with glycine (GLY) with a weight ratio of 10% of GLY with respect to the mesoporous ash, then the mixture was refluxed in ethanol for 12 h and, finally, the reaction products were filtered, washed with ethanol and dried at 60 °C for 24 h. The proposed mechanism of both functionalizations are shown in Fig. 1.

2.3. Preliminary Fe^{3+} adsorption tests

The Fe^{3+} adsorption tests were performed in batch systems, mixing 0.01 g of adsorbent material (SC1, SC1-DMAC and SC1-GLY) with 5 mL of Fe^{3+} at 50 ppm. The tests were performed for 30 min with constant stirring at 200 rpm, then filtered (pore size of 0.2 μm)

and analyzed in an inductive coupling plasma emission spectrophotometer (ICP-OES) (Perkin Elmer Optima 4300 DV). The Fe^{3+} solutions were prepared from a standard solution of 1000 ppm of $\text{Fe}(\text{NO}_3)_3$ (Merck) and conditioned to pH 2.0, 2.5, and 3.0. The pH was controlled along the test with HNO_3 , 0.1 M and with NaOH , 0.1 M. Removal of the Fe^{3+} ($\%R \text{ Fe}^{3+}$) ion and the equilibrium adsorption amount of Fe^{3+} q_e (mg g^{-1}) were calculated using Equations 1 and 2:

$$\%R_{\text{Fe}^{3+}} = \frac{C_0 - C_e}{C_0} * 100 \quad (1)$$

Adsorption amount of mg Fe^{3+} per gram (g) of adsorbent (mg g^{-1}) is

$$q_e = \frac{(C_0 - C_e) * V}{W} \quad (2)$$

Where C_0 is the initial adsorbate concentration in the solution (mg L^{-1}), C_e is the concentration of adsorbate in the solution at equilibrium (mg L^{-1}), V is the volume of the solution (mL), and W is the mass of adsorbent (g).

2.4. Electrochemical characterization

All electrochemical experiments were performed using a PalmSens electrochemical working station, model PS Trace 4. Cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectrometry (EIS) experiments were performed using one chamber glass cells. The carbon paste electrodes were used as working electrode. Ag/AgCl (CH Instruments) was used as reference electrode. Pt wire (CH Instruments) was used as counter electrode.

2.5. Electrode preparation

Carbon paste electrodes were prepared by mixing a 70 %w/w of graphite powder (Merck), with 30%w/w of paraffin oil (Sigma Aldrich) in agate mortar. Modified electrodes were prepared by mixing 15% w/w of either CBT, SC1, SC1-DMAC or SC1-GLY with 55 %w/w of graphite powder and 30% w/w of paraffin oil.

2.6. Characterization methods

The synthesized matrices were characterized by X-ray fluorescence (XRF) on a Philips Magix Pro model PW2400, equipped with the SuperQ analytical software. The elemental analysis (EA) was performed with the CHNS elementary microanalyzer, which consists of a LECO Micro TruSpec detection system. X-ray powder diffraction (XRD), on a Siemens D500 diffractometer, with CuK α radiation filtered with Ni, at 1.5406 and 1.54184 Å, a time constant of 3 s and angular step speed of 2° per min from 5 to 80° of 2 θ . Nitrogen adsorption and desorption was performed in Quantachrome Autosorb-6B equipment using N₂ as an adsorbate at a temperature of 77 K, from which the specific area was calculated by the BET method applied to the adsorption branch; total pore volume was determined at $p/p_0 = 0.99$ in the adsorption branch, and pore size distribution by the BJH method using Quantachrome software. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed on JEOL JSM-5900-LV ESEM and JEOL JEM-2010 Plus equipment, respectively. In addition, the SEM consists of an Oxford ISIS brand X-ray dispersive energy spectroscopic microanalyzer (EDS). Infrared absorption spectroscopy (FTIR) was performed on a JASCO 4100 FTIR device, in the KM mode from 400 to 4000 cm⁻¹, and X-ray photoemission spectroscopy (XPS) on a VG-Microtech Multilab 3000 device equipped with a hemispherical electron analyzer with 9 channeltrons with step energy of (2-200 eV) and an X-ray radiation source with Mg and Al anodes.

3. Results and discussion

3.1. Synthesis of the mesoporous material (SC1) from biomass ashes (CBT)

Biomass ashes (CBT) were characterized by XRF in order to obtain the elements present. Table 1 summarizes the XRF results. The analysis showed that silica is the phase with the highest presence in the sample, followed by alumina, iron oxides and calcium. The elementary composition of the CBT was compared with a literature result [16] where various biomass ashes were classified; the CBT agrees with two groups classified in that study [16]. The first group corresponds to contaminated biomass ashes, where storage conditions and environmental insulation have modified the pH and composition of the ashes. The second group could be considered as mixed ashes, which do not come from a

single source, due to the use of different woods as combustion material. This categorization is important because it allows one to know which are the present phases in the ashes and their stability, so that a better design of the desired porous structure can be obtained.

Fig. 2 shows XRD results with the modification of the porous structure and surface area of CBT and SC1, which indicate that the CBTs (Fig. 2a) present in their composition phases such as (Q) SiO_2 , (Al) Al_2O_3 , (M) Mullite, (Fe) Fe_2O_3 , and (B) Al (OOH). In the case of SC1 (Fig. 2b), a variation of some of the profiles analyzed in CBTs can be seen. Main phases of mullite and Al (OOH) were modified in the process of synthesis of SC1 due to the use of HNO_3 and Pluronic P-123. At a very acidic pH it is possible to solubilize and hydrolyze some preceding phases in biomass ashes by providing active areas where Pluronic P-123 can interact by modifying and directing the structure of soluble phases. The addition of HNO_3 of 67% purity produces the phase activating effect with the decrease of the synthesis pH, in addition to increasing the synergy of the surfactant-active phase interaction [17]. The coupled FTIR spectra of the CBT and SC1 (see supplementary materials S1) was where the functional groups associated with CBT and SC1 could be identified. The spectra do not suggest substantial losses and/or changes in silanol or aluminol groups during the structural modification of the CBT due to the effect of surfactant extraction (calcination at 550°C), which is ideal when evaluating the active area of the matrices and/or considering the possibility of functionalizing the structure [18-20], because there is no substantial loss of centers or of anchoring groups such as the M-OH matrix. Functionalization can be carried out successfully [18-20]. In the spectra of CBT and SC1, a band in the $3000\text{--}3500\text{ cm}^{-1}$ region can be seen associated with the OH groups belonging to the metal alkoxides present in the sample [21] and to the water physisorbed by the samples [21]; at 1636 cm^{-1} the bending band OH of the same previous species is seen. Between 800 and 1100 cm^{-1} , the Si-O binding signal, attributable to the presence of silica and silicates in pure ash, is seen. Finally, at 400 cm^{-1} and 590 cm^{-1} there are signals associated with the Al-O bonds of alumina and aluminates. On the other hand, the lack of the presence of C-N, C-O, C-H and N-H groups allows it to be stated that the surfactant P-123 had been completely removed from the SC1 by calcination at 550°C .

Supplementary materials S2 (S2a, S2b) shows the N_2 adsorption-desorption isotherms at 77 K of CBT and SC1, respectively. The curves obtained in both cases are of type IV, which is

characteristic of mesoporous solids and low microporosity, and they also have a hysteresis cycle typical of the capillary condensation phenomenon and the percolative properties of the solid [22]. As can also be seen in S2, the hysteresis cycles that were obtained are narrow and without the presence of a plateau at high pressures, indicating that both cycles are type H3. These bonds are produced by the presence of agglomerates of slit-shaped pores [22]. On the other hand, an increase in mesoporosity in SC1 with respect to CBT can be seen, which is reflected in the increase of the hysteresis cycle ('y' axis of the adsorption-desorption isotherms of N₂ at 77 K). Table 2 shows the results obtained by the BET and BJH analysis methods for samples CBT and SC1, where it can be seen how the average pore diameter in the CBT increases from 4 nm to 14 nm with the modification made of the pure ashes. In addition to the increase in pore diameter, it was possible to increase the pore volume and the surface area as shown in Table 2. This makes evident the possibility of modifying the soluble phases of the CBT, achieving a change in their pore structure [14]. Furthermore, comparing the results of the adsorption-desorption of N₂ at 77 K for the SC1 with those of some of the authors cited in this paper, it can be seen that the average BJH pore diameter of the SC1 is greater than that reported [5,14]. The pore volume of the SC1 corresponds to an intermediate range [5,14] and the surface area of the SC1 is similar to that obtained [14].

SEM analyses were performed on the CBT and SC1 samples. Fig. 3 shows the SEM and TEM micrographs obtained for both CBT and SC1. CBTs (Fig. 3a) show particles mixed between spherical particles and agglomerated particles with no defined shape. The SC1 (Fig. 3b) have a larger amount of spherical particles and greater homogeneity. Fig. 3c-e show that CBT presents polycrystallinity without short or long range crystalline ordering with dense and compact polycrystals. There is no presence of porosity on the surface and only interparticle spaces or agglomerates of particles are seen that could suggest a certain porosity of the material, a situation seen in the SEM (Fig. 3a). In Fig. 3d-f, an improvement in the short-range crystalline ordering of SC1 is seen compared to CBT. Furthermore, in this case, the modified material (SC1) has an interparticle porosity with a certain degree of homogeneity, a situation that is not noticeable in CBT. That structural arrangement would be caused by the use of the synthesis method to obtain the modified material.

3.2. SC1 functionalization

The DRIFT spectra of SC1 functionalized with N, N-dimethylacetamide (SC1-DMAC) and glycine (SC1-GLY) are shown in supplementary materials S3. The SC1-DMAC spectrum of S3a shows an OH signal between 3700 and 3000 cm^{-1} , a band that indicates that the amide carbonyl $\text{R}(\text{O})\text{C}-\text{N}$ of the DMAC has been protonated, generating a new group, $2\text{R}-\text{C}-\text{O}-\text{H}$. The signals at 1580 cm^{-1} correspond to C-N bonds, 1470 cm^{-1} to C-C bonds, and 1420 cm^{-1} to CH_3 groups. Subsequently, at 1340 cm^{-1} , the signal of the N, N-dimethylacetamide geminal methyl appears, and between 900 and 1100 cm^{-1} the presence of O-N and O-C-O bonds, showing the functionalization of the material [23,24]. Fig. 4a and Fig. 4b show the X-ray photoemission spectra (XPS) of SC1 and SC1-DMAC, respectively. In the XPS spectrum of SC1 (Fig. 4a) there is no N 1S signal, so it indicates that SC1 does not have a nitrogen present. On the contrary, in the SC1-DMAC (Fig. 4b) a sharp and well-defined N 1S signal appears at 400 eV , indicating the DMAC's nitrogen supply. The deconvolution of the N 1S band shows that the DMAC nitrogen is linked to a hydroxylated carbon $\text{R}(\text{HO})\text{C}-\text{N}$ and to a pair of $\text{N}-(\text{CH}_3)_2$ methyl groups, confirming the functionalization of the CS1 matrix with DMAC [25,26]. The above analyses show that aluminium ions of the CS1 act on the carboxylates of the DMAC as Lewis acids by altering the $\text{C}=\text{O}$ bond of the DMAC carbonyl. This bond is slightly positively charged on the carbon side and negatively on the oxygen side $\text{R}-\text{C}^+(\text{O})-\text{O}^-$. The positively charged carbon (carbocation) attacks an M-O-H hydroxyl of CS1 (with $\text{M} = \text{Si}$ or Al) forming a M-O-CR bond between the DMAC and the SC1. The M-O-H proton released by the SC1 products of the carbocation attack is bonded to the $\text{R}-\text{C}-\text{O}^-$ carboxylate of the DMAC, forming a C-O-H bond in the functionalized DMAC [23], accounting for the disappearance of the $\text{C}=\text{O}$ bond close to 1700 cm^{-1} of the DMAC in the DRIFT (supplementary materials S3a) and XPS spectra of the SC1-DMAC. On the other hand, supplementary materials S3b shows the DRIFT spectrum of the SC1-GLY. The spectrum has a series of signals from approximately 3600 to 3000 cm^{-1} , bands which indicate the presence of primary and secondary amines and hydroxyl groups. The existence of signals at 1642 and 1520 cm^{-1} reveals a GLY-GLY linkage produced by the formation of peptide bonds. This linkage is recurrent in the GLY because it is an amino acid and these types of linkages are typical of amino acids. In turn, the GLY as a zwitterion compound can be linked to another glycine

by both its carboxylic function and its amino function. The splitting of signals located between 1400 and 1300 cm^{-1} of $\text{O}=\text{C}-\text{O}-\text{R}$ bands, at 1200 cm^{-1} of $\text{O}=\text{C}-\text{NH}-\text{R}$ signals, and bands at 900 cm^{-1} of $\text{O}=\text{C}-\text{O}-\text{M}$ groups, confirm the formation of GLY-GLY peptide bonds ($\text{O}=\text{C}-\text{NH}-\text{R}$) and M-GLY binding by esterification of the carboxylic acid of GLY ($\text{O}=\text{C}-\text{OH}$) and the hydrolysed surface of SC1 (MOH), with the result of a $\text{R}(\text{O})\text{C}-\text{O}-\text{M}$ link (with $\text{M} = \text{Si}$ or Al) [27, 28]. The results of the X-ray photoemission spectroscopy (XPS), N 1S of the SC1, and SC1-GLY are presented, comparatively, in Fig. 4c and Fig. 4d, where it can be seen that SC1 does not present N 1S signals at 400 eV . On the other hand, the N 1S spectrum of SC1-GLY presents a signal at 400 eV , showing the functionalization with glycine [26, 29]. Going deeper into the analysis of this spectrum, the deconvolution of the said N 1S band was performed. The deconvolution indicates the presence of two types of N-H bonds; the first deconvolution shows N-H interactions of secondary amines which belong to the GLY-GLY ($\text{R}-\text{NH}-\text{C}(\text{O})-\text{R}$) peptide bond. The second deconvolution indicates N-H interactions of primary amine groups (NH_3), which would confirm the functionalization of glycine with SC1. As already mentioned, the GLY-GLY bonding is caused by the interaction of a carboxylic bond of one GLY (RCOO^-) and the amino part of another GLY (RNH_3^+), resulting in the peptide bond because the glycine at pH between 2 and 11 is a zwitterion. Finally, this GLY-GLY is bonded to SC1 by esterification of the $\text{GLY}(\text{RCOO}^-)$ carboxylic bond with the hydroxyl of the $\text{SC1}(\text{M}-\text{OH})$ [27, 28]. The elementary analyzes (Table 3) indicate the presence of nitrogen in the mesostructures confirming that the functionalization was successful.

3.3. Adsorption tests of Fe^{3+} in aqueous solutions

Table 4 summarizes the results of Fe^{3+} adsorption, tested in batch systems, where Fe^{3+} removal capacity was measured in q_e (mg g^{-1}) and percent adsorption at different pH on SC1, SC1-DMAC and SC1-GLY matrices, respectively. The studied pH range was 2.0, 2.5 and 3.0, with the latter showing the best results, reaching 80.49% removal in SC1, 95.41% in SC1-DMAC and 83.27% in SC1-GLY. It can be seen that the effect of matrix functionalization with both DMAC and GLY brings with it an increase in the removal capacity of the matrices, which is observable even at pH 2.0 and 2.5, where the best removal capacity was obtained by the matrix functionalized with SC1-DMAC. This makes

it clear that the amino groups are species that give the matrices additional active zones to the oxo and hydroxyl groups that make up the mesoporous matrices. It should be mentioned that Fe^{3+} is a rather unstable and complex cation to work with which, at pH above 3.0, precipitates the formation of colloids ($\text{Fe}(\text{OH})^{2+}$; $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}_2(\text{OH})_2^{4+}$) [30] which can alter the removal capacity of Fe^{3+} on the matrices. This alteration is due to the possibility that part of this decrease in the initial concentration of Fe^{3+} post-batch test is associated with the precipitation of Fe^{3+} and not only to the effect of the matrices [30]. To prevent the formation of colloids, the adsorption pH was controlled with 0.1 M NH_3 during the entire adsorption process. On the other hand, in a complementary manner, and with the aim of studying the Fe-matrices interaction sites, XPS analyses of the functionalized matrices were performed. The XPS Spectra of N 1S are presented in Fig. 5a for SC1-DMAC and in Fig. 5b for SC1-GLY. These spectra show the presence of an extra N 1S band with respect to those shown in Fig. 4b and Fig. 4d. This breaking down band, located at approximately 407 eV, indicates the existence of the NO_3^- ion as a counter-ion [27], indicating that the possible adsorption of Fe^{3+} is electrically compensated by the NO_3^- counter-ion. On the other hand, the distortion of the N 1S amine bands at 401 eV would indicate that the functionalized Fe-matrix interactions would possibly be in the electronic pair available in the amine nitrogen of the functionalizing molecules [28, 30], which would be producing this distortion in the amine bands. The XPS spectra of Fig. 5c and Fig. 5d show the Fe $2\text{P}_{3/2}$ bands of the iron adsorbed by SC1-DMAC and SC1-GLY. In both cases, the presence of bands at 711 and 724 eV, which typically belong to Fe^{3+} , with their corresponding satellite bands at 719 and 733 eV, is seen, indicating that iron is captured by the mesoporous matrix and that, in turn, it does not suffer alterations of the 3+ oxidation state [28, 31]. The XPS Fe $2\text{P}_{3/2}$ spectra of the SC1 were not due to the fact that in the composition of the ashes there is the presence of Fe in the form of oxides, which can lead to the making of a slightly assertive analysis of the way in which it can bond with the SC1 matrix.

3.4. Electrochemical characterization

The synthesized mesoporous materials were characterized by electrochemical methods, in order to study their effect into the fabrication of carbon paste electrodes. Cyclic

voltammetry was used to study the difference between the modified carbon paste electrodes, prepared according to the experimental section. Fig. 6 shows the voltammograms obtained with each modified carbon paste electrodes in a KCl 0.1 M solution. Where CPE corresponds to the carbon paste electrode without modification, CBT, SC1, SC1-DMAC and SC1-GLY are related to the electrodes modified with 15%w/w of those materials.

The presence of CBT and SC1 in the electrode produces an increase in the capacitive current, which may be related to an increase in the area of the electrode due to the effect of the porous material [32,33]. Anyway, no further redox processes were registered over the electrochemical window studied for CPE, CBT and SC1 electrodes. On the other hand, SC1-DMAC and SC1-GLY both show redox activity. SC1-GLY shows a quasi-reversible redox couple due to the redox processes of the glycine. The anodic process has an onset potential at 0.4 V and the cathodic process onset at 0.6 V a slightly higher anodic current ($I_{PA} = 4.39 \mu A$), in comparison with the cathodic current ($I_{PC} = 4.15 \mu A$) reduction, in agreement with previous works [34]. SC1-DMAC presents also a quasi-reversible redox process, an anodic process with an onset potential close to 0.7 V and a cathodic process with an onset potential at 0.6 V, consistent with reported electrochemical behaviour of the DMAC [35].

The stability of the modified electrodes was studied by cyclic voltammetry, also the modified electrodes show a similar response to the redox probe $K_3Fe(CN)_6$, (Fig. 7a). All fabricated electrodes showed good stability, losing less than 5% of the current over 20 cycles of cyclic voltammetry (see supplementary materials S4). Linear sweep voltammetry (LSV) was used to perform a scan rate study to determinate the electrochemical properties of the fabricated electrodes. The experiments were carried out in a solution of $K_3Fe(CN)_6$ 5 mM in KCl 0.1 M (Fig. 7b).

The sweeps were made toward the negative potentials to study $Fe(CN)_6^{3-}$ reduction. These experiments were designed to avoid the contribution of the redox couples observed in the cases of SC1-GLY and SC1-DMAC. The cathodic peak current (I_{PC}) values were extracted from the LSV graphic and were plotted against the square root of the scan rate ($v^{1/2}$) obtaining a linear relation, consistent with a diffusion-controlled reaction (see Fig. 7c); this behaviour was observed in each other electrode studied (see supplementary materials S5).

Considering a relative slow scan rate study of the electrodes fabricated, we cannot observe any adsorption process; this may be due to a highly slow mass transport through the mesoporous material, which was impossible to determinate using these techniques. Nevertheless, SC1-GLY and SC1-DMAC modified electrodes show good electrochemical stability, the redox couple that both electrodes presented may be suitable for the fabrication of catalytic electrochemical sensors, enhanced by the redox process of each mesoporous material.

4. Conclusions

The surface of the CBT main phases of mullite and $\text{Al}(\text{OOH})$, that were modified in the process of synthesis of SC1 mass ashes, has been modified successfully by the synthesis method, showing changes in particle morphology, with porosity and some pristine phases of the CBT, the TEM and SEM images, XRD diffractograms and adsorption-desorption isotherms of N_2 at 77 K revealing the aforementioned changes. The modification of CBT biomass ashes with Pluronic P-123 produces changes in both the interparticle and intraparticle porosity of pure ashes. This event is confirmed by the observation of intraparticle mesopores with TEM and in the changes seen in the results of the adsorption-desorption isotherms of N_2 at 77 K. The synthesis method for making mesoporous materials is perfectly replicable in tree biomass ashes (CBT) as they produce a change in the intra- and interparticle porosity, achieving pore sizes of the mesoporous type. Furthermore, it is clear that the modification made to the ashes manages to increase the surface properties from surface areas of $18.49 \text{ m}^2 \text{ g}^{-1}$ to $22.84 \text{ m}^2 \text{ g}^{-1}$. On the other hand, the functionalization of CS1 with DMAC and GLY was successfully achieved by increasing the adsorption capacity of Fe^{3+} of SC1. Electrochemical characterization of the mesoporous materials studied showed the suitable properties for electrode modification of these materials. An increase in the capacitive current of the modified electrodes was associated with enhancement in the surface area, due to the mesoporous materials. On the other hand, SC1-GLY and SC1-DMAC of both modified electrodes show a quasi-reversible redox couple related to the carbonyl moiety of the glycine and the amide moiety of the DMAC, respectively. The presence of these redox couples in the modified electrodes offers new interesting surfaces for metal deposition or catalytic applications. Finally, it can be said that

it is possible to obtain new mesoporous materials from tree biomass ashes and functionalize them, introducing terms like recycling, sustainability, green chemistry and low cost.

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Table 1. Present elements wt. % at CBT obtained by X-ray Fluorescence (XRF).

Phases	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	P _x C	MgO	Na ₂ O	P ₂ O ₅	TiO ₂	MnO
%	47.2	19.5	9.3	8.1	3.9	3.9	2.4	2.1	1.2	0.7

Table 2. Values obtained for the adsorption-desorption isotherm of N₂ at 77 K, predictive models BET and BJH, for CBT and SC1.

	SBET (m ² g ⁻¹)	Vp Total BJH [cm ³ g ⁻¹]	dp Av. BJH [nm]
CBT	18	0.04	3.8
SC1	23	0,1	14

Table 3. C, H, N and S elemental analysis of the synthesized mesoporous SC1, SC1-DMAC, and SC1-GLY.

Elements	SC1	SC1-DMAC	SC1-GLY
%N	0	0.14	0.23
%C	0.17	0.41	0.26
%H	0.1	0.11	0.22
%S	0	0	0

Table 4 Fe³⁺ removal capacity in q_e (mg g⁻¹) and percentage by synthesized matrices.

pH	SC1		SC1-DMAC		SC1-GLY	
	q _e (mg g ⁻¹)	(% Ads.)	q _e (mg g ⁻¹)	(% Ads.)	q _e (mg g ⁻¹)	(% Ads.)
2.0	8.64	44.92	11.67	60.67	10.57	54.97
2.5	9.40	48.88	11.81	61.40	9.40	48.89
3.0	15.48	80.49	18.35	95.41	16.01	83.27

Highlights

- **Synthesis and functionalization of a low-cost mesoporous material from biomass ashes**
- **The functionalization of the synthesized material was carried out with N, N-dimethylacetamide (DMAC) and glycine (GLY)**
- **The adsorption capacity of the synthesized matrices has been tested in batch and electrochemical systems**

Credit Author Statement

Mauricio Gómez: He wrote the paper

Jaime Pizarro: The study was conducted in his laboratory and participated in the discussion of results.

Ximena Castillo: she contributed to the paper's discussion

Alessio Ghisolfi: He contributed to paper's discussion

Carlos Díaz: He contributed with electrochemical analysis

María de Lourdes Chávez: She contributed to paper's discussion

Diego Cazorla-Amorós: Porosimetry and XPS analysis were analyzed in his laboratory

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Declarations of interest: none