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Preparation of Activated Carbons from Spent Coffee Grounds and Coffee Parchment and Assessment of Their Adsorbent Efficiency

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Abstract: The valorization of coffee wastes through modification to activated carbon has been considered as a low-cost adsorbent with prospective to compete with commercial carbons. So far, very few studies have referred to the valorization of coffee parchment into activated carbon. Moreover, low-cost and efficient activation methods need to be more investigated. The aim of this work was to prepare activated carbon from spent coffee grounds and parchment, and to assess their adsorption performance. The co-calcination processing with calcium carbonate was used to prepare the activated carbons, and their adsorption capacity for organic acids, phenolic compounds and proteins was evaluated. Both spent coffee grounds and parchment showed yields after the calcination and washing treatments of around 9.0%. The adsorption of lactic acid was found to be optimal at pH 2. The maximum adsorption capacity of lactic acid with standard commercial granular activated carbon was 73.78 mg/g, while the values of 32.33 and 14.73 mg/g were registered for the parchment and spent coffee grounds activated carbons, respectively. The Langmuir isotherm showed that lactic acid was adsorbed as a monolayer and distributed homogeneously on the surface. Around 50% of total phenols and protein content from coffee wastewater were adsorbed after treatment with the prepared activated carbons, while 44, 43, and up to 84% of hydrophobic compounds were removed using parchment, spent coffee grounds and commercial activated carbon, respectively; the adsorption efficiencies of hydrophilic compounds ranged between 13 and 48%. Finally, these results illustrate the potential valorization of coffee by-products parchment and spent coffee grounds into activated carbon and their use as low-cost adsorbent for the removal of organic compounds from aqueous solutions.

Keywords: coffee by-products; spent coffee grounds; parchment; valorization; calcination; activated carbon; organic compounds adsorption

1. Introduction

Coffee is one of the most important traded agricultural products, and a popular beverage consumed worldwide [1]. World production in 2019 was estimated at around 167 million 60 kg bags, with 95 million bags of Arabica (*Coffea arabica*) and 72 million bags of Robusta (*Coffea canephora*) [2]. Ferrão [3] showed that 100 kg of mature coffee cherries were composed of 39 kg of coffee pulp, 22 kg of mucilage, and 39 kg of coffee parchment. From the outside to the inside, the cherry is constituted of the skin, the pulp, the mucilage and the protective bean shell, the parchment [4]. Fresh coffee cherries generally undergo

several processing steps from harvest to final consumption, including hulling, drying, milling, polishing and roasting. The coffee hulling consists of the removal of the parchment skin from the coffee bean and is generally processed in two main different ways: the dry method, also known as the unwashed method, and the wet method, also called the washing method. Two other hybrid methods, namely the pulped natural method and the prime washed method, also exist, but are less common. All these methods involve elimination of the different layers of coffee (coffee pulp, mucilage, and parchment) to produce green coffee beans. The dry method consists of drying the coffee cherries right after harvesting, eliminating the coffee layers in one fraction, called the coffee husk [4]. In the washing method, coffee layers are successively removed through a sequence of steps including pulping (coffee pulp), fermentation (mucilage), washing and drying (coffee parchment) [5].

The coffee produced by the wet method can be processed either in batch or in a continuous system, and both configurations generate large amounts of residues, such as coffee pulp, coffee parchment, spent coffee grounds and wastewater [6].The coffee pulp is generated during the depulping or coffee pulping step, while parchment and spent coffee grounds are produced in the hulling and brewing steps, respectively. It is estimated that about 2 kg of spent coffee grounds are obtained for each kilogram of soluble coffee prepared; the coffee processing generating about 6 million tons of spent coffee grounds each year [7,8]. Coffee wastewater is a complex matrix mainly produced during the fermentation and the washing steps. The fermentation step is carried out mainly by lactic acid bacteria *Enterobacteriaceae* and *Bacillus* species, producing acetic and lactic acids [9,10]. The enzymes produced from fungal and bacterial fermentation trigger the hydrolysis of macromolecules such as protein, carbohydrates, and polyphenols, resulting in simplified products like amino acids and organic acids [9]. These products confer acidity, and a high content of suspended and dissolved organic matter to the wastewater [2].

The recovery of coffee processing by-products for potential uses was investigated. Possible uses in the food sector for the solid coffee wastes are for the production of enzymes and secondary metabolites. The utilization of these in other industry areas has been directed, among others, towards reinforcement of polymer composites [10], in biosorbents [11–14], for cosmetic products [15], cellulose production [16] and application in water treatment [17]. The valorization of coffee wastes through modification to activated carbon has been considered as a low-cost adsorbent. The coffee by-products most evaluated as adsorbents are spent coffee grounds, coffee husk, and coffee pulp. Spent coffee grounds have been investigated for the extraction of secondary plant metabolites [12], removal of organic compounds [11,13], heavy metals [17,18], pesticides [19], as competitors of commercial carbons for water decontamination [14], and as a medium for methane storage [20]. Chemical [21,22] and physical [23,24] activation are the most common methods for activated carbon synthesis using coffee wastes. Direct use of coffee wastes has been recently evaluated for the removal of heavy metals from wastewater [25]. Nevertheless, adsorption of selected organic compounds employing low cost and eco-friendly activation protocols using coffee by-products still needs to be addressed.

Activated carbons are versatile adsorbents; their adsorbent properties lie in the large surface area, area activity, and favorable pore size. Aside from physical characteristics, adsorption capacity is greatly influenced by the chemical structure of the surface, which affects the characteristics of the surface such as polarity, acidity, and hydrophobicity [26]. The surface of the activated carbon is normally modified to change its adsorption properties. The modification is carried out mainly by two manufacturing processes, implicating physical or chemical activation. Physical activation involves heating in the absence of air with steam or other gases like carbon dioxide between 800 and 1000 °C, while chemical activation is commonly performed using several activation agents like potassium hydroxide, zinc chloride, and phosphoric acid [27]. In the chemical activation, removal of the activation agent is required, causing environmental burden and corrosion risks [28], while for the physical activation, steam or carbon dioxide are necessary to oxidize the carbon surface, thereby elevating the production costs. Recently, Kong et al. [29] proposed an acti-

vation step via co-calcination with limestone. This method relies on the fact that limestone is decomposed above 800 °C, producing quicklime (calcium oxide) and resulting in the evolution of carbon dioxide (CO_2). Coffee processing by-products have been transformed into activated carbon using different carbonization and activation protocols. Chemical activation is mainly used to produce activated carbon from coffee wastes; nevertheless, few investigations have addressed the physical activation method using CO_2 and steam mixed with a chemical agent [23]. Characteristics such as contact surface, pore distribution and surface chemistry have been enhanced through activation methods. Adsorbents analyzed by scanning electronic microscopy (SEM) have shown that, after physical activation, a well-developed porosity was obtained; conversely, after chemical activation, disrupted structure was observed [30]. Studies have examined the application of coffee waste activated carbons in the removal of organic molecules (dyes, acids, pesticides), and cationic and anionic components (lead, cadmium, copper, chromium). These have shown that adsorption capacity of the molecules is correlated with the activation protocol, textural properties of the raw material, size of the organic molecule, and charge of the ions of the adsorbate [15,31–34]. Adsorption of gases and vapor phase has been evaluated. Authors have determined that adsorption capacities for methane (CH_4), hydrogen sulfide (H_2S), and CO_2 are due to the high surface area, volume, narrow size of micropores, and chemistry of the adsorbent [20,35,36].

Currently, very few studies have referred to the valorization of coffee parchment into activated carbon using low cost and eco-friendly activation protocols. The aim of this work was then to transform spent coffee grounds and parchment into activated carbon through the co-calcination process. Calcium carbonate ($CaCO_3$) was used to optimize the calcinations of spent coffee grounds or parchment and the performances of the prepared activated carbons were assessed using model lactic acid solution and coffee wastewater. An available commercial activated carbon was used as standard material to compare the performances of the spent coffee grounds and parchment activated carbons.

2. Materials and Methods

2.1. Materials

Spent coffee grounds and parchment used for activated carbon preparation were collected from Deutsche Extrakt Kaffee GmbH (Berlin, Germany) and Rio Colorado coffee company (Palencia, Guatemala), respectively. Commercial carbon Norit®GAC 1240EN with a particle size of 0.42–2.00 mm and moisture content of 5% was obtained from CABOTCORP (Boston, MA, USA). Coffee wastewater was collected at the beginning of the fermentation step from a pilot coffee processing (Santa Sofia Coffee Company, Santa Rosa, Guatemala).

Calcium carbonate fine powder was purchased from VWR International (Radnor, PA, USA) and used to prepare the activated carbon. Citric acid and acetic acid (Carl Roth GmbH, Karlsruhe, Germany), malic acid and propionic acid (Sigma Aldrich, Steinheim, Germany), lactic acid and butyric acid (Alfa Aesar Materials Company, Haverhill, MA, USA), were used as adsorbate matrices. Folin–Ciocalteu reagent was obtained from Sigma-Aldrich Holding AG (Buchs, Switzerland). Gallic acid (Carl Roth GmbH, Karlsruhe, Germany) and Bovine Serum Albumin (Sigma-Aldrich Holding) were used as standards for the determination of phenolic compounds and protein content, respectively.

2.2. Activated Carbon Preparation

The thermal calcination process was used to produce the activated carbons from coffee by-products. Briefly, spent coffee grounds were stirred to obtain a homogeneous particle size of 1.68–2.38 mm and then dried overnight at 110 °C using an oven (Memmert GmbH + Co. KG, Schwabach, Germany). Coffee parchment was first grinded in a ball mill to get particle sizes of about 64 μm. The obtained spent coffee grounds and parchment powders were mixed with calcium carbonate (ratio 1:1, *w/w*) and placed into a quartz tube electric oven (Linn High Therm GmbH, Eschenfelden, Germany) at 850 °C for 1 h, with a heating rate of 5 °C/min under an argon atmosphere. The carbonized samples

were successively washed with 2 M HCl and deionized water on Ø 270 mm filter papers (Macherey-Nagel GmbH & Co., KG, Düren, Germany), to reach near neutral pH. Finally, samples were dried at 110 °C for 24 h and cooled down to room temperature.

2.3. Material Characterization

2.3.1. Infrared Spectroscopy (IR)

Functional groups in activated carbon samples were analyzed by IR spectroscopy. Pulverized samples were placed on the Nicolet iS5 FT-IR spectrometer (Thermo Scientific, Waltham, MA, USA) equipped with a diamond crystal attenuated total reflection unit (iD7 ATR, Thermo Scientific). Spectra were collected from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} by co-adding 32 individual scans.

2.3.2. Thermogravimetric Analysis (TGA)

Changes in the mass as a function of the temperature of the materials were measured as samples were heated and held at a constant temperature in a nitrogen atmosphere. The mass of the samples was analyzed using a Linseis TGA/DTA L81 (Linseis Messgeräte GmbH, Selb, Germany). Temperature was set from 25 to 1000 °C with a heating rate of 10°/min.

2.3.3. Organic Elemental Analysis of Activated Carbon

The carbon, hydrogen, nitrogen, and sulfur amount of the materials were determined using an Elementar Vario EL III (Elementar Analysensysteme GmbH, Langensbold, Germany).

2.3.4. X-ray Powder Diffraction (XRD)

The structure characteristics and phase composition of the samples were analyzed by using an Empyrean powder X-ray diffractometer (Malvern Panalytical, Malvern, UK), in a Bragg–Brentano geometry coupled with a PIXce11D detector, using Cu Kα radiation (λ = 1.5416 Å) operating at 40 kV and 40 mA; θ/θ scans were performed from 4–70° 2θ with a step size of 0.0131° and a sample rotation time of 1 s. The diffractometer was configured with a programmable divergence, anti-scatter slit and a large Ni beta-filter. The detector operated on a continuous mode with an active length of 3.0061°. Data of IR, TGA, and XRD was processed using OriginPro, version 2019b (OriginLab Corporation, Northampton, MA, USA).

2.3.5. Scanning Electron Microscopy (SEM)

SEM was used to analyze the surface properties and morphology of the prepared activated carbons. Samples were loaded onto a double-sided carbon tape attached to SEM tubs and then coated with a gold/palladium using a sputter coater (SC7620 coater, Quorum Technologies, Lewes, UK) for 75 s at 18 mA to avoid charging effects. SEM images were acquired using a JEOL JSM-6510 mode Field Emission Scanning Electron Microscope (JEOL Ltd. Manufacturing Company, Akishima, Tokyo, Japan). The acceleration voltage was set at 15 kV and the images were magnified 4000 times.

2.3.6. Zeta Potential Measurements

Zeta potential measurements were performed to determine electrostatic magnitude between particles of activated carbon samples. Materials were first mixed with 30 mL distilled water and thereafter treated in an ultrasonic bath for 30 min. Samples were then analyzed by using the zeta meter Zetasizer Ultra (Malvern Panalytical, Malvern, UK). Data was calculated using the software ZS XPLORER (Malvern Panalytical)

2.3.7. Specific Surface Area and Porosity by Nitrogen Sorption Analysis

Nitrogen (N_2) sorption isotherms at 77 K were measured on a Micromeritics Gemini VII Surface Area and Porosity Analyzer (Micromeritics, Norcross, GA, USA). The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) equation [31] and

applying the Rouquerol criterion [32]. The pore size distribution and pore volume were calculated using the heterogenous surface non-local density functional theory (HS-NLDFT) with a minimum pore width of 1.47 nm in the SAEIUS software Version 3.0 (Micromeritics, Norcross, GA, USA), as previously described by Maziarka et al. [37]. Prior to N_2 sorption measurements, samples were vacuum dried at room temperature for at least 16 h, followed by degassing under heating and vacuum, using a VacPrep^{TM} 061 Sample Degas System (Micromeritics, Norcross, GA, USA). The spent coffee grounds and parchment (~1 g) were degassed at 80 °C for 16 h, while the activated carbon materials (~250 mg) were degassed at 200 °C for 4 h.

2.4. Adsorption Experiments

The batch equilibrium experiments were conducted in a vertical shaker at 30 rpm. The model of fermentation broth was prepared from an analytical grade 99.5% citric acid, 99.0% L(-)malic acid, 98.0% L-lactic acid, 100% acetic acid, 99.0% propionic acid, 98.0% sodium butyrate stock solution and demineralized water. The initial pH of the bulk solution was adjusted using NaOH or HCl. The batch adsorption experiments were performed in 5 mL microtubes containing 10% w/v as performed by Pradhan et al. [38]. Microtubes were placed in a vertical shaker for 4 h as described by Pradhan et al. [38], with some modifications. Samples were taken at predetermined intervals and further filtered with a 0.22 µm syringe filter. Adsorbents were studied using lactic acid adsorbate at different pH (2–6), and initial concentrations (0.5–25 g/L). The other organic acids were studied using an initial concentration of 20 g/L based on the preliminary studies (data not shown). Finally, adsorbents were studied using wet-coffee processing wastewater collected from the fermentation step. Coffee wastewater was first centrifuged, and the supernatant was filtrated through a 0.22 µm syringe polypropylene filter. All the batch adsorption experiments were performed in triplicate by employing individual microtubes for each data point.

2.5. Batch Adsorption Experiments of Lactic Acid

The effect of pH and initial concentration on the adsorption efficiency of lactic acid was assessed. Different pH (2, 2.85, 3.86, 4 and 6), both above and below the pK_a value (3.86) of lactic acid, were investigated by using an aqueous solution of 2.5 g/L (pH~2.85) lactic acid. The pH scale was selected to represent wet-coffee processing wastewater and literature survey values on lactic acid adsorption [38,39].

The effect of initial concentration of lactic acid on the adsorption efficiency was carried out by changing the initial concentration of lactic acid in the range of 0.5 to 25 g/L (0.5, 1.5, 2.5, 3.0, 3.5, 4.5, 5.5, 6.0, 7.5, 10.0, 15.0, 20.0 and 25 g/L). The pH and initial concentration range were selected to represent the lactic acid production from wet-coffee processing [39] and various heterolactic fermentation processes [40,41]. The effect of main organic acids in wet-coffee processing was tested by using a 200 g/L mixture of organic acids containing citric, malic, lactic, acetic, propionic, and butyric acid. The effect of fermentation of coffee wastewater was tested by using samples from Santa Sofia coffee company located in Palencia, Guatemala.

The adsorption capacity and efficiency, under equilibrium conditions, expressed as mg of adsorbate adsorbed per g of the adsorbent and % adsorbate adsorbed, respectively, were calculated using Equations (1) and (2):

$$q_e = (C_o - C_e) \, V_s / 1000 \times m \tag{1}$$

$$E = (C_o - C_e) / C_n \times 1000 \tag{2}$$

where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), E is organic acid recovery efficiency (%), C_o is the initial concentration of lactic acid (mg/L), C_e is the equilibrium concentration of or lactic acid in the solution (mg/L), V is the volume of the solution (L) and m is the mass of the adsorbent (g).

2.6. Lactic Acid Adsorption Isotherms

Adsorption isotherms are necessary to describe how the adsorbate interacts with the adsorbent surface and essential to understand the adsorption mechanisms. Batch equilibrium results of different initial lactic acid concentration experiments were used for the isotherm study. Two commonly used isotherm models, Langmuir and Freundlich, were selected to characterize the behavior of the lactic acid adsorption on the prepared activated carbons.

The Langmuir adsorption isotherm model assumes homogeneous and monolayer adsorption with no lateral interaction between adjacent adsorbed molecules when a single molecule occupies a single surface site [42]. The non-linearized form of the Langmuir isotherm is expressed as:

$$q_e = q_m \times K_L \times C_e \tag{3}$$

where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), q_m is the maximum adsorption capacity, K_L is the Langmuir isotherm constant (L/mg), C_e is the equilibrium concentration of lactic acid in the solution (mg/L).

On the other hand, the Freundlich isotherm model describes a non-ideal and reversible adsorption process, which is applied to explain the multilayer adsorption onto a heterogenous adsorbent surface. The non-linear form of the Freundlich isotherm model is represented as:

$$q_e = K_f \times C_e^{1/n} \tag{4}$$

where K_f is the Freundlich isotherm constant (mg/g) $(L/g)^n$, n is the adsorption intensity. Adsorption isotherm models are important because they give essential information on how a specific adsorbent will interact with the adsorbent surface. Furthermore, the affinity between absorbent and adsorbate, and maximum adsorption capacity, are elucidated from the isotherm models.

2.7. Analysis

2.7.1. Organic Acid Quantification

An HPLC system (Shimadzu Europa GmbH, Duisburg, Germany) equipped with a UV-Vis Detector SPD-10 AVP (Shimadzu, Kyoto, Japan) was used to analyze the organic acids. A volume of 50 µL of samples untreated and treated with different activated carbons was injected into a SUPELCOGEL^{TM} H, 6% Crosslinked column (250 mm × 4.6 mm, 9 µm; Sigma Aldrich, Steinheim, Germany). The separation was performed at 70 °C under isocratic conditions, using a solution of 0.01 N sulfuric acid as eluent. Flow rate of 0.5 mL/min was applied for a separation time of 15 min.

2.7.2. Total Phenolic Compounds

The Folin–Ciocalteu method was used to determine content of total phenolic compounds as described by Singleton et al. [43], with some modifications using gallic acid as standard. Shortly, 20 µL of standard or sample solutions were mixed with 180 µL of the Folin reagent (mixture of Folin–Ciocalteu and 0.01 M NaOH, 1:1, *v/v*) on the iMark microplates using the corresponding reader (Bio-Rad Laboratories, Hercules, CA, USA). The mixtures were incubated for 30 min at room temperature and absorbance was measured at 750 nm. The results were expressed as mg/L Gallic acid equivalent (GAE).

2.7.3. Protein Content

Protein content was measured by using the method of Lowry et al. [44] with BSA as standard.

2.7.4. Scan Spectra by Liquid Chromatography Mass Spectrometry

Coffee wastewater compounds before and after treatment with the prepared activated carbon materials were measured through an HPLC-MS/MS Agilent 1260 system (Agilent Technologies Sales & Services GmbH & Co. KG, Waldbronn, Germany) with a binary pump,

multicolumn thermostat provided with an Agilent G6470A series triple Quad LC/MS (Agilent Technologies Sales & Services GmbH & Co. KG, Waldbronn, Germany), integrated with an electrospray (ESI) source operating in positive and negative ionization mode. One microlitre of sample was injected into the system through a Kinetex C8 analytical column (150 mm × 4.60 mm, 2.6 μm, 100 A; Phenomenex, Torrance, CA, USA) set at a temperature of 30 °C with a flow rate of 0.5 mL/min. The mobile phase was composed of HPLC grade water containing 0.1% formic acid (eluent A) and 100% LC-MS grade Acetonitrile (eluent B). Mobile phase gradient conditions were set as follows: 100% solvent A from 0 to 5 min, 50–5% solvent A from 20 to 24 min, and 100% solvent A from 25 to 28 min. The desolvation gas temperature in the ionization source was set at 275 °C, gas flow rate of 11 L/min, nebulizer pressure of 35 PSI, fragmentor voltage of 130 V, and dwell time of 20 min. The collision gas used was nitrogen. Determination was performed in the MS2 mode for determination of the mass distribution. The MS-data collection was performed between 2 and 20 min. Mass spectrometric scans were made for the range of 50–1500 m/z. Compounds sorption onto activated carbon was measured considering the total area of all the transitions analyzed.

2.8. Statistical Analysis

All experiments were conducted in triplicate, and data were expressed as mean ± standard deviation. The analysis of the variance (ANOVA) was performed with GraphPad Prism 8[®] (GraphPad Software, Inc., San Diego, CA, USA), and the results were considered statistically significant for $p < 0.05$. Isotherm models were analyzed with OriginPro, version 2019b (OriginLab Corporation, Northampton, MA, USA).

3. Results and Discussion

3.1. Activated Carbon Yield

Initial raw spent coffee grounds and parchment of 20 g were used to perform the calcination process. To optimize the activation, 20 g of calcium carbonate were added prior the treatments and before calcination, washing and drying steps; final masses after calcination of 16.4 and 17 g of activated carbons were obtained for spent coffee grounds and parchment, respectively. These represent yields of 42.5% for parchment and 41.0% for spent coffee grounds. The yield decreased after washing the material with HCl and distilled water to 9.1% for spent coffee grounds and parchment. Decomposition of volatile compounds to residual carbon and breaking down of calcium carbonate to calcium oxide explains the initial weight loss in the carbonization step [45,46]. The low yield after washing step indicates that calcium oxide was removed from activated carbon, losing initial weight on a dry basis.

3.2. Characterization of the Activated Carbon Materials

Zeta potential measurements were performed to determine electrophoretic mobility of activated carbon particles in a diluted suspension. The experiments were conducted in a neutral solution (pH~7) and the zeta potential was measured to be −16.9 ± 3.4, −18.6 ± 1.3, and −24.9 ± 0.23 mV for spent coffee, parchment, and commercial activated carbons, respectively. Zeta potential < ±30 mV indicates that the colloidal system is unstable and particles tend to attract each other [47], whereas the sign of the zeta potential shows that negative charges are predominant at the surface of the activated carbons [48].

SEM was used to determine the microstructure of the prepared activated carbons. Figure 1 shows the SEM images of raw materials, activated carbons obtained from spent coffee grounds, parchment, and the commercially available activated carbon. It is clear from the images that co-calcination with $CaCO_3$ results in the development of a large number of pores on the surfaces of spent coffee grounds and coffee parchment activated carbons (Figure 1b,d) compared to the raw materials (Figure 1a,c). Calcium carbonate is decomposed at temperatures above 800 °C, producing calcium oxide and CO_2. CO_2 is normally used as an oxidation reagent for physical activation. Arenas et al. [49] have

demonstrated that CO_2 steam produces high surface areas due to the steam widened microporosity, which allows carbon dioxide to reach new sites to develop new porosity. The development of pores is also related to yield decline, showing that development progresses from outer to inner structures [50].


(a)

(b)

(c)

(d)

(e)
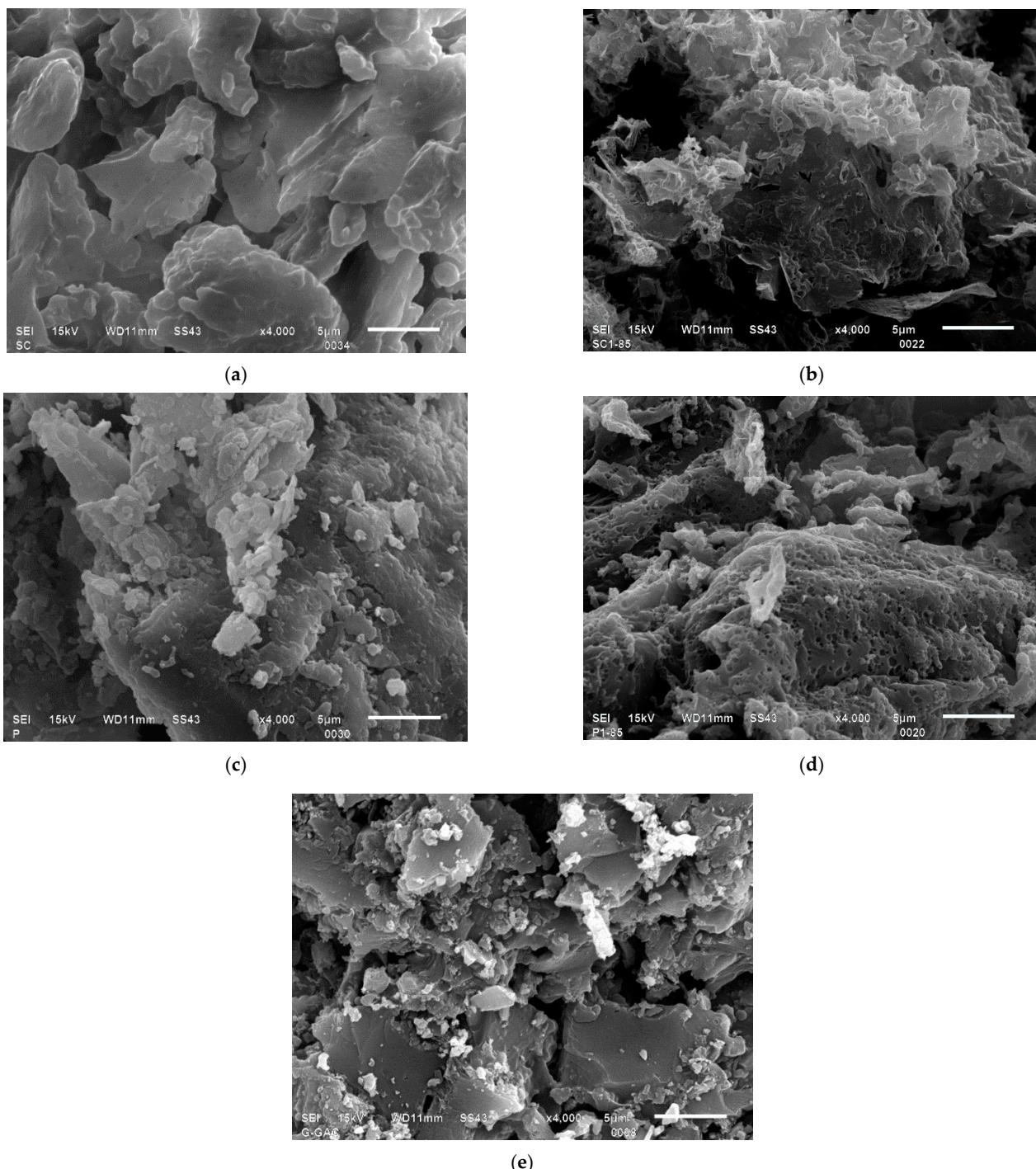
Figure 1. Scanning electron microscope (SEM) images of activated carbon produced from (**a**) raw spent coffee grounds, (**b**) spent coffee grounds, (**c**) raw coffee parchment, (**d**) parchment, and (**e**) commercial activated carbon.

Figure 2a presents the IR spectrums of the materials. Bands from 1500 to 1000 cm^{-1} were obtained for the raw spent coffee and the parchment, while two bands at approximately 2900 cm^{-1} were recorded only for the raw spent coffee grounds. The bands

exhibited by the raw materials are assigned to lignin/cellulose materials [36,51] (Table S1, supplementary data). This is consistent to the composition of spent coffee grounds and parchment rich in cellulose, lignin and hemicellulose [4,52]. For the co-calcinated samples, all the bands exhibited by its corresponding raw materials are no longer detected and spectrums were similar to commercial activated carbon. Elemental analysis data indicates that the raw spent coffee is composed of 56.3% carbon, 7.7% hydrogen, 1.8% nitrogen, and 0.47% sulfur. These values were 46.3, 6.4, 0.4, and 0.7% for parchment. After co-calcination values of 84.0% carbon, 1.38% hydrogen, 2.6% nitrogen and 0.3% sulfur; 91.6% carbon, 0.9% hydrogen, 0.5% nitrogen, and 0.3% sulfur were obtained for the spent coffee and parchment activated carbons, respectively. High temperatures release volatile matter content, removing functional groups; therefore, carbon content in activated carbon samples is higher when compared to those of the raw materials.

(a)

(b)

(c)
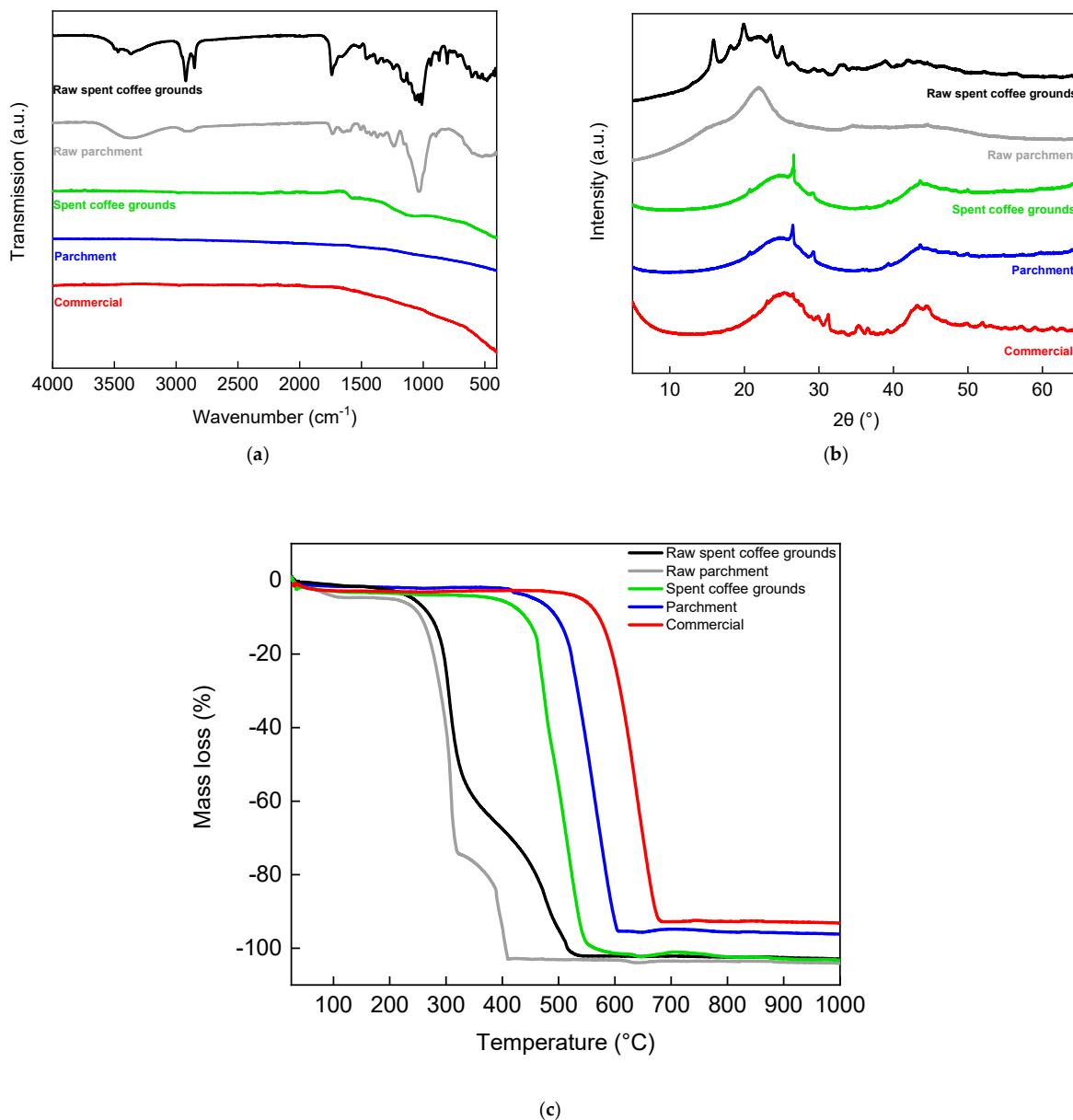
Figure 2. (**a**) IR spectra, (**b**) X-ray diffraction patterns, and (**c**) TGA data of raw spent coffee grounds, raw parchment, spent coffee grounds, parchment, and commercial activated carbons.

Structure of the materials analyzed using the XRD showed one main broad peak at approximately ~20° 2θ for both raw materials (Figure 2b). Those peaks are in agreement

with diffraction peaks of amorphous cellulose-containing material [53]. After co-calcination, the resulting activated carbons exhibited two main peaks at ~25° and ~43° 2θ, showing similar diffractograms compared to commercial activated carbon. Peaks around 20° and 40° correspond to the reflection of the (002) and (100) planes of graphite structure of carbon black, respectively [54].

Thermogravimetric analysis was used to investigate the content of inorganic residues in the materials and results are presented in Figure 2c. The mass losses of raw spent coffee grounds were detected in the temperature range from 282 °C to 324 °C (54% weight loss) and from 438 °C to 520 °C (29% weight loss). These values were in the range from 286 °C to 316 °C (70% weight loss) and from 376 °C to 410 °C (29% weight loss) for raw parchment. Those weight losses were reported to be a thermal decomposition of the amorphous cellulose regions and oxidation of the carbon skeleton [55]. Similar thermogravimetric curves were previously reported from materials with hemicellulose and lignin content [53,56,57]. Weight losses of 98% in the range from 445 °C to 546 °C, and of 93% from 504 °C to 601 °C, were reported for spent coffee grounds and parchment activated carbons, respectively. Commercial activated carbon showed one decrease in sample mass in the temperature range from 582 °C to 674 °C, constituting 90% of the total mass. The results for co-calcinated samples indicate an increase in material crystallinity, therefore causing an improvement in thermal stability.

N_2 sorption measurements were performed to determine the specific surface area and porosity of the activated carbon materials, and the resulting isotherms are presented in Figure 3a. The adsorption branch of the isotherms of the activated carbon materials showed rapid N_2 uptake at low relative pressure ($P/P_0 < 0.1$), followed by a gradual uptake at higher relative pressures. Their sorption behavior indicates that these materials are largely microporous (IUPAC classification Type Ib) [58]. The activated carbon materials from parchment and spent coffee grounds exhibited open hysteresis, as seen from the non-closing of the desorption branch at low P/P_0. The resulting activated carbon from parchment and spent coffee ground exhibited a BET specific surface area (SSA_{BET}) of 416 and 167 m^2/g, respectively, while the commercial activated carbon had the highest SSA_{BET} of 1010 m^2/g (Table 1). The commercial activated carbon also had the highest pore volume of 0.46 cm^3/g, followed by parchment and spent coffee grounds with 0.22 and 0.14 cm^3/g, respectively (Table 1). The pore size distribution (PSD) analysis (Figure 3b) of the adsorption branch using HS-NLDFT calculation revealed that all three materials exhibited a large proportion of micropores (<2 nm pore width), with the commercial activated carbon having only micropores. On the other hand, the activated carbons from parchment and spent coffee grounds also have mesopores (2–30 nm pore width; Figure 3b inset). The parchment activated carbon has a more defined mesopore distribution compared to the spent coffee grounds.
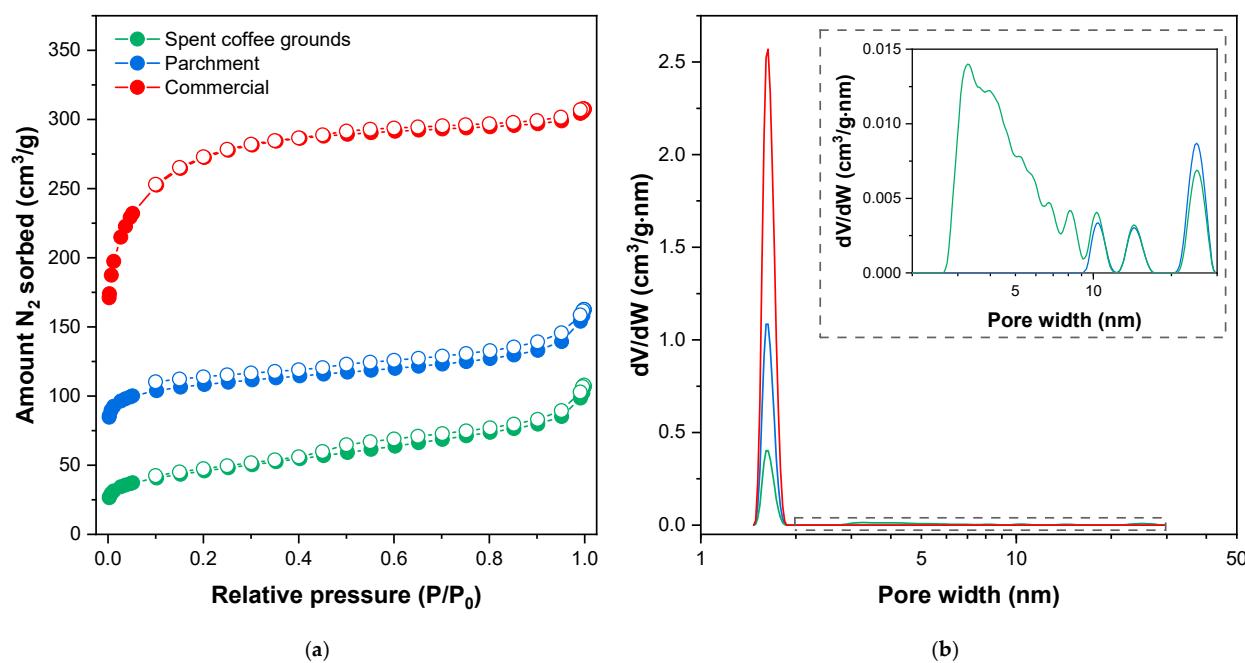
Figure 3. (**a**) N$_2$ sorption isotherms, and (**b**) differential pore size distribution of spent coffee grounds, parchment, and commercial activated carbons (inset comes from the dashed rectangle for pore widths between 2 and 30 nm).

Table 1. Porosity data derived from N$_2$ sorption measurements at 77 K.

Activated Carbon Material	SSA$_{BET}$ [a] (m^2/g)	V$_{pore}$ [b] (cm^3/g)
Parchment	416	0.22
Spent coffee grounds	167	0.14
Commercial	1010	0.46

Note: [a] specific surface area (SSA$_{BET}$) calculated using the BET equation in the adjusted pressure range of 0.05–0.1 based on the Rouquerol criterion; [b] pore volume (V$_{pore}$) calculated using HS-NLDFT with a minimum pore width of 1.47 nm.

3.3. Effect of pH and Concentration on Lactic Acid Adsorption

The effect of pH on the lactic acid adsorption was investigated. Five different initial pH values were tested (pH 2.0, 2.85, 3.86, 4.0 and 6.0), and the results are presented in Figure 4a. The three activated carbons showed greater adsorption selectivity of lactic acid at a pH below pK$_a$ (3.86) of lactic acid. Removal efficiency significantly decreased from 74 ± 0.17 to 14 ± 0.64%), from 33 ± 0.84 to 13 ± 0.26%, and from 75 ± 0.99 to 24% ± 1.10% value for parchment, spent coffee grounds and commercial activated carbon, respectively ($p < 0.001$). Similar values of lactic acid adsorption on different commercial activated carbon were previously reported under comparable experimental conditions [38,59]. Lactic acid adsorption onto activated carbon was reported as physical adsorption which depends on electronic polarization; the decrease of lactic acid at pH above pK$_a$ is owed to fewer dipole-dipole interactions [60]. The results obtained agrees with those mentioned above as the activated carbon samples exhibit adsorption affinity below pK$_a$. Data also showed that lactic acid adsorption is higher for the commercial activated carbon and parchment efficiencies, compared to that of the spent coffee grounds.

(**a**)

(**b**)
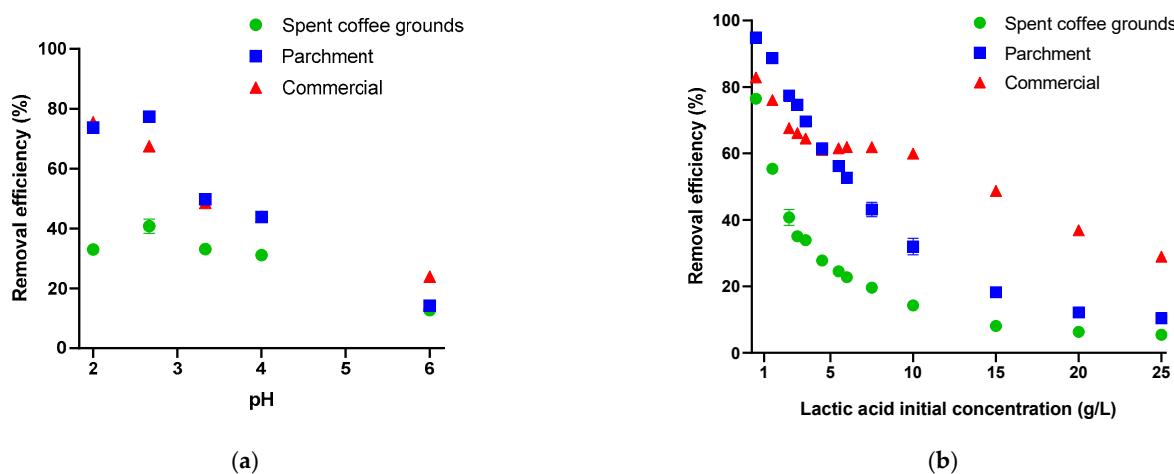
Figure 4. Effect of lactic acid adsorption onto spent coffee grounds, parchment, and commercial activated carbon. (**a**) Different initial pH (2–6) with 2.5 g/L of lactic acid in the bulk solution, adsorbent dose of 10% (*w/v*) and 4 h contact time at room temperature; (**b**) different initial lactic acid concentrations (0.5–25 g/L) without pH correction, adsorbent dose 10% (*w/v*) and 4 h contact time at room temperature. Data are expressed as means $\pm$ standard deviation (*n* = 3). Analysis of the variance two-way ANOVA, *p* < 0.05, Tukey's test.

Adsorption capacity of lactic acid was investigated at different initial lactic acid concentrations within the range of 0.5 to 25 g/L, and the results are presented in Figure 4b. The removal efficiency significantly decreased when the lactic acid increased from 0.5 to 25 g/L. The values ranged from 94.92 ± 0.003 to $10.43 \pm 0.004\%$ (*p* < 0.0001), from 76.46 ± 0.006 to $5.45 \pm 0.002\%$ (*p* < 0.0001), and from 82.88 ± 0.005 to $21.60 \pm 0.018\%$ (*p* < 0.0001) for parchment, spent coffee grounds and commercial activated carbon, respectively. Nevertheless, the adsorption capacity increased until it reached adsorption equilibrium with values ranging from 4.75 ± 0.01 to 26.07 ± 0.94 mg/g, from 3.82 ± 0.03 to 13.62 ± 0.54 mg/g, and from 4.14 ± 0.01 to 72.36 ± 2.61 mg/g for parchment, spent coffee grounds and commercial activated carbon, respectively. The adsorption of lactic acid onto activated carbon was affected by lactic acid initial concentration. Saturation of available pore sites on the adsorbent has been reported as the initial concentration increased [61]. Difference of adsorption efficiencies between activated carbon samples is therefore related to the amount of pore sites available on the adsorbent.

3.4. Lactic Acid Adsorption Isotherm

Langmuir and Freundlich isotherms were performed to find equilibrium adsorption characteristics. Figure 5 shows the non-linear plots for Langmuir and Freundlich isotherms of lactic acid at room temperature. Table S2 (see supplementary data) shows the isotherm parameters and regression coefficients for the two isotherms plots. The maximum adsorption capacity (q_m) was 93.48 ± 5.60, 29.48 ± 1.31, 13.99 ± 0.45 mg/g for commercial activated carbon, parchment, and spent coffee grounds, respectively. Langmuir constant K_L is related to the sorption energy and represents the affinity of the adsorbent to the adsorbate. The values calculated were 3.07×10^{-4} for commercial activated carbon, 4.9×10^{-3} for parchment, and 2.4×10^{-3} for spent coffee grounds. Coefficient of determination (R^2) was compared from the Langmuir and Freundlich isotherms; the Langmuir isotherm was found to be more appropriate in interpreting the adsorption behavior. The shown experimental data agrees with another study where lactic acid adsorption follows the Langmuir isotherm [38]. The Langmuir isotherm model states that the adsorbate was adsorbed as a monolayer and therefore allocated homogeneously on the surface with restricted interaction between adsorbate molecules. The Langmuir constant indicates that parchment has a higher affinity for lactic acid compared to spent coffee grounds and commercial activated carbon.
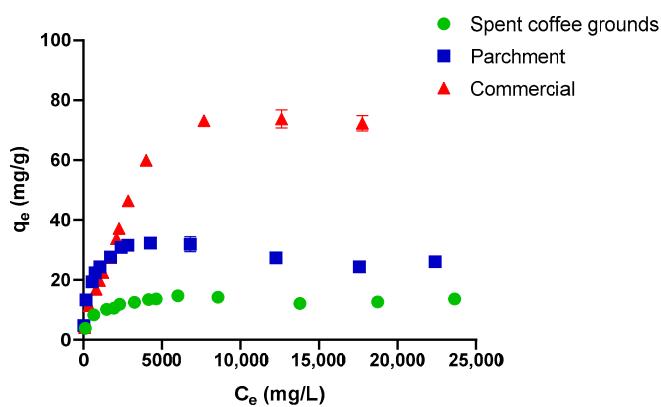
Figure 5. Adsorption capacity (q_e) for lactic acid versus lactic acid concentration at equilibrium in liquid phase (C_e) for spent coffee grounds, parchment, and commercial activated carbons, without pH corrections, adsorbent dose 10% (*w/v*) and 4 h contact time at room temperature.

3.5. Adsorption of Main Organic Acids Present in Wet-Coffee Processing

Organic acids are constituents of importance in wet-coffee processing. During coffee processing, to guarantee the proper drying of green coffee, fermentation takes place so the mucilage layer can be degraded. In previous work, citric acid, malic acid, and lactic acid were found to be present in coffee beans and by-products, while in coffee wastewater, the main organic acids were lactic acid and propionic acid [39]. Adsorption efficiency of citric, malic, lactic, acetic, propionic, and butyric acid was evaluated by preparing a model fermentation broth mixture of 20 g/L containing the six organic acids. The results indicate that all six organic acids were adsorbed onto the three activated carbons (Figure 6). Among the activated carbon samples, parchment showed the highest adsorption removal efficiency for malic acid (73.83 ± 0.065%), lactic acid (52.80 ± 0.063%), acetic acid (85.01 ± 0.002%), propionic acid (96.86 ± 0.001%), and butyric acid (99.52 ± 0.000%), while granular activated carbon exhibited the highest removal efficiency for citric acid (84.69 ± 0.006%). In complex systems, competition between compounds and activated carbon surface takes place, binding compounds with more selectivity and affinity to the adsorbent. Silva et al. [62] reported that adsorption of organic acids onto activated carbon is related to the size of carboxylic acid chain and hydrophobicity of the compounds.
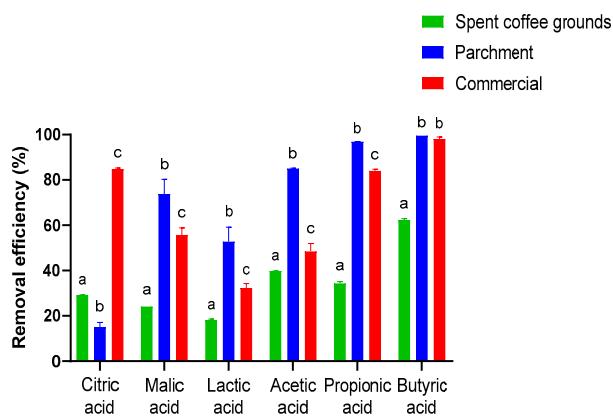

Figure 6. Effect of citric, malic, lactic, acetic, propionic, and butyric acid adsorption on spent coffee grounds, parchment, and commercial activated carbons. An amount of 200 g/L in the bulk solution was used, with an adsorbent dose of 10% (*w/v*) and 4 h contact time at room temperature. Data are expressed as means ± standard deviation (*n* = 3). Different letters indicate significantly different values for each group (different superscript letters indicate a significant difference, *p* < 0.05, two-way ANOVA, Tukey's test).

3.6. Adsorption of Organic Compounds from Wet-Coffee Processing Wastewater

Figure 7 presents the concentration of total phenols and protein content of wastewater before and after treatment with parchment, spent coffee grounds and granular activated carbon. A reduction from 100 to 30%, 100 to 20%, and 100 to 30% of total phenols and protein content can be observed, respectively. Total phenol content in wastewater was 63.63 ± 2.01 mg GAE/L, and after treatment with parchment, spent coffee grounds and granular activated carbon, the values were 17.18 ± 0.81, 15.97 ± 0.42, and 24.68 ± 1.34 mg GAE/L, respectively. These results indicate that up to 60% of total phenols were removed from wastewater after treatment with the three types of activated carbon. The efficiency of polyphenol adsorption onto activated carbon has been reported to be dependent on the type of carbon, carbon surface functionalities, pH of the bulk solution, and oxygen availability [63].

(**a**)

(**b**)
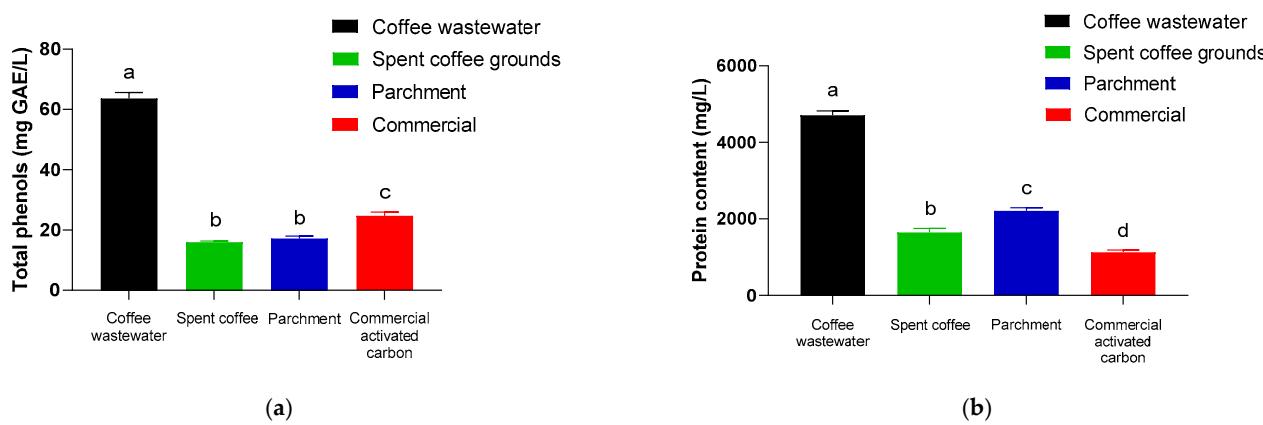
Figure 7. Amount of (**a**) total phenols and (**b**) protein content remaining from the coffee wastewater after their adsorption onto parchment, spent coffee grounds and commercial activated carbons. Adsorbent dose of 10% (*w/v*) and 4 h contact time at room temperature. Data are expressed as means $\pm$ standard deviation (*n* = 3). Different letters indicate significantly different values for each group (different superscript letters indicate a significant difference, *p* < 0.05, one-way ANOVA, Tukey's test).

The results showed that, after treatment, protein content decreased when compared with coffee wastewater. The values of 2212.50 ± 80.57, 1647.5 ± 104.04, and 1127.5 ± 61.31 mg/L were obtained for parchment, spent coffee grounds and granular activated carbon, respectively. It was reported that adsorption of proteins by the activated carbons was more efficient for lower molecular weight proteins (13–66 kDa) when the pH of the bulk solution was close to the protein isoelectric point [64,65]. The overall protein charge is weakened and electrostatic repulsion forces between the adsorbent and protein take place [65]. Moreover, the hydrophobic nature of the activated carbons result in effective adsorption of hydrophobic segments of the protein [66].

The organic acids in coffee wastewater were analyzed by using HPLC. Figure S1 (see supplementary data) shows the chromatograms comparing coffee wastewater before and after treatment with spent coffee grounds (a), parchment (b), and commercial granular activated carbon (c). It appeared that the total area of the coffee wastewater chromatogram decreased after treatment. Removal efficiencies of all adsorbents were up to 50%. Coffee wastewater was also investigated using HPLC-MS/MS. The total ion current spectrum in negative and positive mode from wastewater shows a reduction in compounds after batch experiments. In the ion spectrum from spent coffee grounds and parchment (Figure S2, supplementary data), similar trends can be observed. Adsorption efficiency results indicate that up to 40% of hydrophobic compounds are removed by spent coffee grounds and parchment whereas up to 80% is removed on commercial activated carbon. This percentage decreases with the hydrophilic compounds to a value of $12.45 \pm 3.32\%$, $14.35 \pm 1.44\%$ and $47.90 \pm 1.19\%$ for spent coffee grounds, parchment, and commercial activated carbon,

respectively (Table S3; see supplementary data). Activated carbon is mainly hydrophobic, giving more affinity for nonpolar compounds such as hydrocarbons. Besides this activated carbon property, the presence of micropores facilitate the diffusion process and result in higher adsorption rates [67]. The decrease in removal efficiency on activated carbon surface is associated to the competitive interaction between compounds on the pore structures.

4. Conclusions

In this study, activated carbons were prepared from spent coffee grounds and coffee parchment by co-calcination with calcium carbonate, and their efficiency in absorbing organic compounds was compared to one commercially available activated carbon. Both spent coffee grounds and parchment showed yields of 9.0% after calcination and washing treatments. SEM of the activated carbon materials confirmed that co-calcination with calcium carbonate improved pore structures compared to the raw materials. We found that characteristics of the prepared activated carbon presented similarities to the commercially available form. Further work will be directed towards the optimization of the activation methods to improve the quality of the materials produced. The adsorption of lactic acid occurred via a monolayer, with restricted interaction between adsorbate molecules. Parchment activated carbon showed greater adsorption efficiency for the main monocarboxylic acids present in wet-coffee processing when compared to those of spent coffee and commercial activated carbons. Spent coffee grounds and parchment proved to have similar adsorption efficiency to commercial activated carbon for the removal of total phenols and protein content from coffee wastewater. All adsorbents showed greater affinity to remove hydrophobic than hydrophilic compounds. This study showed that coffee parchment and spent coffee grounds can be valorized via co-calcination with calcium carbonate to produce activated carbons. More studies should be addressed at evaluating the viability of applying such experiments in-situ, thus other valorization opportunities with environmental and economical perspectives can be brought to the coffee producers.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Rivera, X.C.S.; Gallego-Schmid, A.; Najdanovic-Visak, V.; Azapagic, A. Life cycle environmental sustainability of valorisation routes for spent coffee grounds: From waste to resources. *Resour. Conserv. Recy.* **2020**, *157*, 104751. [CrossRef]
2. Rattan, S.; Parande, A.K.; Nagaraju, V.D.; Ghiwari, G.K. A comprehensive review on utilization of wastewater from coffee processing. *Environ. Sci. Pollut. Res. Int.* **2015**, *22*, 6461–6472. [CrossRef] [PubMed]
3. Ferrão, J.E.M. O Café—A Bebida Negra Dos Sonhos Claros. Chaves Ferreira-Publicacoes 2009. Available online: https://acpp.pt/biblio/16-produtos/969-cafe-a-bebida-negra-dos-sonhos-claros-o (accessed on 11 August 2021).
4. Klingel, T.; Kremer, J.I.; Gottstein, V.; de Rezende, T.R.; Schwarz, S.; Lachenmeier, D.W. A review of coffee by-products including leaf, flower, cherry, husk, silver skin, and spent grounds as novel foods within the european union. *Foods* **2020**, *9*, 665. [CrossRef]
5. de Merlo Pereira, G.V.; Thomaz Soccol, V.; Kaur Brar, S.; Neto, E.; Soccol, C.R. Microbial ecology and starter culture technology in coffee processing. *Crit. Rev. Food Sci. Nutr.* **2015**. [CrossRef]
6. Ramalakshmi, K.; Rao, L.J.M.; Takano-Ishikawa, Y.; Goto, M. Bioactivities of low-grade green coffee and spent coffee in different in vitro model systems. *Food Chem.* **2009**, *115*, 79–85. [CrossRef]
7. Mussatto, S.I.; Machado, E.M.S.; Martinis, S.; Teixeira, J.A. Production, composition, and application of coffee and its industrial residues. *Food Bioprocess. Technol.* **2011**, *4*, 661–672. [CrossRef]
8. Dorsey, B.M.; Jones, M.A. *Handbook of Coffee Processing By-Products*; Academic Press: Cambridge, MA, USA, 2017.
9. Avallone, S.B.; Jean, M.; Guyot, B.; Olguin, E.; Guiraud, J.P. Involvemnt of pectolytic micro-organisms in coffee fermentation. *Int. J. Food Sci. Technol.* **2002**, *37*, 191–198. [CrossRef]
10. Obruca, S.; Benesova, P.; Petrik, S.; Oborna, J.; Prikryl, R.; Marova, I. Production of polyhydroxyalkanoates using hydrolysate of spent coffee grounds. *Process. Biochem.* **2014**, *49*, 1409–1414. [CrossRef]
11. Goncalves, M.; Guerreiro, M.C.; Ramos, P.H.; Oliveira, L.C.A.d.; Sapag, K. Activated carbon prepared from coffee pulp: Potential adsorbent of organic contaminants in aqueous solution. *Water Sci. Technol.* **2013**, *68*, 1085–1090. [CrossRef]
12. Ramón-Gonçalves, M.; Alcaraz, L.; Pérez-Ferreras, S.; León-González, M.E.; Rosales-Conrado, N.; López, F.A. Extraction of polyphenols and synthesis of new activated carbon from spent coffee grounds. *Sci. Rep.* **2019**, *9*, 1–11.
13. Iakovleva, E.; Sillanpaa, M.; Maydannik, P.; Liu, J.T.; Allen, S.; Albadarin, A.B.; Mangwandi, C. Manufacturing of novel low-cost adsorbent: Co-granulation of limestone and coffee waste. *J. Environ. Manag.* **2017**, 1–8. [CrossRef]
14. Rosson, E.; Garbo, F.; Marangoni, G.; Bertani, R.; Lavagnolo, M.C.; Moretti, E.; Talon, A.; Mozzon, M.; Sgarbossa, P. Activated carbon from spent coffee grounds: A good competitor of commercial carbons for water decontamination. *Appl. Sci.* **2020**, *10*, 5598. [CrossRef]
15. Ribeiro, H.; Marto, J.; Raposo, S.; Agapito, M.; Isaac, V.; Chiari, B.G. From coffee industry waste materials to skin-friendly products with improved skin fat levels. *Eur. J. Lipid Sci. Technol.* **2013**, *115*, 330–336. [CrossRef]
16. Rani, M.; Appaiah, A. Production of bacterial cellulose by gluconacetobacter hansenii uac09 using coffee cherry husk. *J. Food Sci. Technol.* **2013**, *50*, 755–762. [CrossRef]
17. Chavan, A.A.; Pinto, J.; Liakos, I.; Bayer, I.S.; Lauciello, S.; Athanassiou, A.; Fragouli, D. Spent coffee bioelastomeric composite foams for the removal of pb2+ and hg2+ from water. *ACS Sustain. Chem. Eng.* **2016**, *4*, 5495–5502. [CrossRef]
18. Chwastowski, J.; Bradlo, D.; Zukowski, W. Adsorption of cadmium, manganese and lead ions from aqueous solutions using spent coffee grounds and biochar produced by its pyrolysis in the fluidized bed reactor. *Materials* **2020**, *13*, 2782. [CrossRef]
19. Pavlović, M.D.; Buntić, A.V.; Šiler-Marinković, S.S.; Antonović, D.G.; Milutinović, M.D.; Radovanović, N.R.; Dimitrijević-Branković, S.I. Spent coffee grounds as adsorbents for pesticide paraquat removal from its aqueous solutions. In Proceedings of the International Conference on Civil, Biological and Environmental Engineering (CBEE-2014), Istanbul, Turkey, 27–28 May 2014.
20. Kemp, K.C.; Baek, S.B.; Lee, W.-G.; Meyyappan, M.; Kim, K.S. Activated carbon derived from waste coffee grounds for stable methane storage. *Nanotechnology* **2015**, *26*, 385602. [CrossRef]
21. Ma, X.; Ouyang, F. Adsorption properties of biomass-based activated carbon prepared with spent coffee grounds and pomelo skin by phosphoric acid activation. *Appl. Surf. Sci.* **2013**, *268*, 566–570. [CrossRef]
22. Namane, A.; Mekarzia, A.; Benrachedi, K.; Belhaneche-Bensemra, N.; Hellala, A. Determination of the adsorption capacity of activated carbon made from coffee grounds by chemical activation with $ZnCl_2$ and H_3PO_4. *J. Hazard. Mater.* **2005**, *119*, 189–194. [CrossRef]
23. Boonamnuayvitaya, V.; Sae-ung, S.; Tanthapanichakoon, W. Preparation of activated carbons from coffee residue for the adsorption of formaldehyde. *Sep. Purif. Technol.* **2005**, *42*, 159–168. [CrossRef]
24. Castro, C.S.; Abreu, A.L.; Silva, C.L.T.; Guerreiro, M.C. Phenol adsorption by activated carbon produced from spent coffee grounds. *Water Sci. Technol.* **2011**, *64*, 2059–2065. [CrossRef]
25. Malara, A.; Paone, E.; Frontera, P.; Bonaccorsi, L.; Panzera, G.; Mauriello, F. Sustainable exploitation of coffee silverskin in water remediation. *Sustainability* **2018**, *10*, 3547. [CrossRef]
26. Bernal, V.; Giraldo, L.; Moreno-Piraján, J.C. Physicochemical properties of activated carbon: Their effect on the adsorption of pharmaceutical compounds and adsorbate–adsorbent interactions. *J. Carbon Res.* **2018**, *4*, 62. [CrossRef]
27. Ahmadpour, A.; Do, D.D. The preparation of active carbons from coal by chemical and physcial activation. *Carbon* **1996**, *34*, 471–479. [CrossRef]

28.　Bernardo, M.; Lapa, N.; Matos, I.; Fonseca, I. Critical discussion on activated carbons from bio-wastes-environmental risk assessment. *Bol. Grupo. Esp. Carbon* **2016**, *40*, 18–21.

29.　Kong, L.; Su, M.; Peng, Y.; Hou, L.a.; Liu, J.; Li, H.; Diao, Z.; Shih, K.; Xiong, Y.; Chen, D. Producing sawdust derived activated carbon by co-calcinations with limestone for enhanced acid orange ii adsorption. *J. Clean. Prod.* **2017**, *168*, 22–29. [CrossRef]

30.　Khenniche, L.; Aissani, F. Preparation and characterization of carbons from coffee residue: Adsorption of salicylic acid on the prepared carbons. *J. Chem. Eng. Data* **2010**, *55*, 728–734. [CrossRef]

31.　Brunauer, S.; Emmett, P.H.; Teller, E. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **1938**, *60*, 309–319. [CrossRef]

32.　Rouquerol, J.; Llewellyn, P.; Rouquerol, F. Is the bet equation applicable to microporous adsorbents? *Stud. Surf. Sci. Catal.* **2007**, *160*, 49–56.

33.　Azouaou, N.; Sadaoui, Z.; Djaafri, A.; Mokaddem, H. Adsorption of cadmium from aqueous solution onto untreated coffee grounds: Equilibrium, kinetics and thermodynamics. *J. Haz. Mater.* **2010**, *184*, 129–134. [CrossRef]

34.　Oliveira, L.S.; Franca, A.S.; Alves, T.M.; Rocha, S.D.F. Evaluation of untreated coffee husks as potential biosorbents for treatment of dye contaminated waters. *J. Haz. Mater* **2008**, *155*, 507–512. [CrossRef]

35.　Plaza, M.G.; Gonzáles, A.S.; Pevida, C.; Pis, J.J.; Rubiera, F. Valorisation of spent coffee grounds as CO_2 adsorbents for postcombustion capture applications. *Appl. Energy* **2012**, *99*, 272–279. [CrossRef]

36.　Kante, K.; Nieto-Delgado, C.; Rangel-Mendez, J.R.; Bandosz, T.J. Spent coffee-based activated carbon: Specific surface features and their importance for H_2S separation process. *J. Hazard. Mater.* **2012**, *201–202*, 141–147. [CrossRef]

37.　Maziarka, P.; Wurzer, C.; Arauzo, P.J.; Dieguez-Alonso, A.; Mašek, O.; Ronsse, F. Do you bet on routine? The reliability of N_2 physisorption for the quantitative assessment of biochar's surface area. *Chem. Eng. J.* **2021**, *418*, 129234. [CrossRef]

38.　Pradhan, N.; Rene, E.R.; Lens, P.N.L.; Dipasquale, L.; D'Ippolito, G.; Fontana, A.; Panico, A.; Esposito, G. Adsorption behaviour of lactic acid on granular activated carbon and anionic resins: Thermodynamics, isotherms and kinetic studies. *Energies* **2017**, *10*, 665. [CrossRef]

39.　Figueroa Campos, G.A.; Sagu, S.T.; Saravia Celis, P.; Rawel, H.M. Comparison of batch and continuous wet-processing of coffee: Changes in the main compounds in beans, by-products and wastewater. *Foods* **2020**, *9*, 1135. [CrossRef] [PubMed]

40.　Evangelista, R.L.; Mangold, A.J.; Nikolov, Z.L. Recovery of lactic acid by sorption. *Appl. Biochem. Biotechnol.* **1994**, *45*, 131–144. [CrossRef]

41.　Moldes, A.B.; Alonso, J.L.; Parajó, J.C. Recovery of lactic acid from simultaneous saccharification and fermentation media using anion exchange resins. *Bioprocess Biosyst. Eng.* **2003**, *25*, 357–363.

42.　Swenson, H.; Stadie, N.P. Langmuir's theory of adsorption: A centennial review. *Langmuir* **2019**, *35*, 5409–5426. [CrossRef]

43.　Singleton, V.L.; Orthofer, R.; Lamuela-Raventós, R.M. Analysis of total phenols and other oxidation substrates and antioxidants by means of folin-ciocalteu reagent. *Methods Enzymol.* **1999**, *299*, 152–178.

44.　Lowry, O.H.; Rosebrough, N.J.; Farr, A.L.; Randall, R.J. Protein measurement with the folin phenol reagent. *J. Biol. Chem.* **1951**, *193*, 265–275. [CrossRef]

45.　Gu, X.; Ma, X.; Li, L.; Liu, C.; Cheng, K.; Li, Z. Pyrolysis of poplar wood sawdust by tg-ftir and py–gc/ms. *J. Anal. Appl. Pyrolysis* **2013**, *102*, 16–23. [CrossRef]

46.　Wang, C.B.; Chen, L.; Jia, L.F.; Tan, Y.W. Simultaneous calcination and sulfation of limestone in cfbb. *Appl. Energy* **2015**, *155*, 478–484. [CrossRef]

47.　Sis, H.; Birinci, M. Effect of nonionic and ionic surfactants on zeta potential and dispersion properties of carbon black powders. *Colloids Surf. A Physicochem. Eng. Asp.* **2009**, *341*, 60–67. [CrossRef]

48.　Ridaoui, H.; Jada, A.; Vidal, L.; Donnet, J.-B. Effect of cationic surfactant and block copolymer on carbon black particle surface charge and size. *Colloids Surf. A Physicochem. Eng. Asp.* **2006**, *278*, 149–159. [CrossRef]

49.　Arenas, E.; Chejne, F. The effect of the activating agent and temperature on the porosity development of physically activated coal chars. *Carbon* **2004**, *42*, 2451–2455. [CrossRef]

50.　Baek, J.; Lee, H.-M.; Roh, J.-S.; Lee, H.-S.; Kang, H.-S.; Kim, B.-J. Studies on preparation and applications of polymeric precursor-based activated hard carbons: I. Activation mechanism and microstructure analyses. *Microp. Mesop. Mater.* **2016**, *219*, 258–264. [CrossRef]

51.　Kim, M.S.; Kim, J.G. Adsorption characteristics of spent coffee grounds as an alternative adsorbent for cadmium in solution. *Environments* **2020**, *7*, 24. [CrossRef]

52.　Scully, D.S.; Jaiswal, A.K.; Abu-Ghannam, N. An investigation into spent coffee waste as a renewable source of bioactive compounds and industrially important sugars. *Bioengineering* **2016**, *3*, 33. [CrossRef]

53.　Reis, R.S.; Tienne, L.G.P.; Souza, D.d.H.S.; Marques, M.d.F.V.; Monteiro, S.N. Characterization of coffee parchment and innovative steam explosion treatment to obtain microfibrillated cellulose as potential composite reinforcement. *J. Mater. Res. Technol.* **2020**, *9*, 9412–9421. [CrossRef]

54.　Li, Z.Q.; Lu, C.J.; Xia, Z.P.; Zhou, Y.; Luo, Z. X-ray diffraction patterns of graphite and turbostratic carbon. *Carbon* **2005**, *45*, 1686–1695. [CrossRef]

55.　Biegun, M.; Dymerska, A.; Chen, X.; Mijowska, E. Study of the active carbon from used coffee grounds as the active material for a high-temperature stable supercapacitor with ionic-liquid electrolyte. *Materials* **2020**, *13*, 3919. [CrossRef]

56.　Block, I.; Gunter, C.; Duarte Rodrigues, A.; Paasch, S.; Hesemann, P.; Taubert, A. Carbon adsorbents from spent coffee for removal of methylene blue and methyl orange from water. *Materials* **2021**, *14*, 3996. [CrossRef] [PubMed]

57. Chen, X.L.; Yu, J.; Zhang, Z.B.; Lu, C.H. Study on structure and thermal stability properties of cellulose fibers from rice straw. *Carbohyd Polym.* **2011**, *85*, 245–250. [CrossRef]

58. Thommes, M.; Kaneko, K.; Neimark, A.V.; Olivier, J.P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K.S.W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (iupac technical report). *Pure Appl. Chem.* **2015**, *87*, 1051–1069. [CrossRef]

59. Seankham, S.; Novalin, S.; Pruksasri, S. Kinetics and adsorption isotherm of lactic acid from fermentation broth onto activated choracoal. *Chem. Ind. Chem. Eng. Q.* **2017**, *23*, 515–521. [CrossRef]

60. Gao, M.-T.; Shimamura, T.; Ishida, N.; Takahashi, H. Ph-uncontrolled lactic acid fermentation with activated carbon as an adsorbent. *Enzym. Microb. Technol.* **2011**, *48*, 526–530. [CrossRef] [PubMed]

61. Bayazit, S.S.; Inci, I.; Uslu, H. Adsorption of lactic acid from model fermentation broth onto activated carbon and amberlite ira-67. *J. Chem. Eng. Data* **2011**, *56*, 1751–1754. [CrossRef]

62. Silva, A.H.d.; Miranda, E.A. Adsorption/desorption of organic acids onto different adsorbents for their recovery from fermentation broths. *J. Chem. Eng. Data* **2013**, *58*, 1454–1463. [CrossRef]

63. Dabrowski, A.; Podkoscielny, P.; Hubicki, Z.; Barczak, M. Adsorption of phenolic compounds by activated carbon—A critical review. *Chemosphere* **2003**, *58*, 1049–1070. [CrossRef]

64. Stone, M.T.; Kozlov, M. Separating proteins with activated carbon. *Langmuir* **2014**, *30*, 8046–8055. [CrossRef] [PubMed]

65. Sekaran, G.; Mariappan, M.; Raghavan, K.V. Adsorption of bovine serum albumin from salt solution onto activated carbon. *Bioprocess Eng.* **1996**, *15*, 165–169. [CrossRef]

66. Seredych, M.; Mikhalovska, L.; Mikhalovsky, S.; Gogotsi, Y. Adsorption of bovine serum albumin on carbon-based materials. *J. Carbon Res.* **2017**, *4*, 3. [CrossRef]

67. Piai, L.; Dykstra, J.E.; Adishakti, M.G.; Blokland, M.; Langenhoff, A.A.M.; Wal, A.v.d. Diffusion of hydrophilic organic micropollutants in granular activated carbon with different pore sizes. *Water Res.* **2019**, *162*, 518–527. [CrossRef] [PubMed]