



Whey as a sustainable binder for the production of extruded activated carbon

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ABSTRACT

Whey, the main by-product of the dairy industry, is proposed as a sustainable binder for the production of extruded activated carbon. Coconut shell char was mixed with controlled quantities of either rehydrated whey powders or partially dehydrated liquid whey. After extrusion, extrudates were dried, and carbonised or activated under N₂ or CO₂ atmosphere, respectively. A comprehensive study of the effect of different parameters including binder proportion, coconut shell char particle size and carbonisation temperature was carried out. The composition of whey prompted Maillard reactions boosted with temperature that conferred a resin-like behaviour to the binder. Quality parameters of the resulting extrudates were their ball-mill hardness, real and bulk densities. All whey-bound pellets retained their original shape after the high temperature treatment. The hardness of those whey extrudates was particularly remarkable considering the biomass origin of this binder. The carbonisation temperature had little effect in the hardness or densities of the carbon pellets. The best pellet formulation comprised the use of coconut shell char powders with particle sizes < 212 μm, in mixtures having a 7/3 char/dry whey mass ratio. The properties of the pellets obtained after the activation of such pellets were comparable to those of commercial activated carbon extrudates. The use of partially dehydrated liquid whey rather than re-hydrated dry whey rendered very similar results. The alkalinity of the binder made the resulting activated carbons adequate for H₂S removal at room temperature. An economic estimation of the process placed whey in a practical position within the binder market.

1. Introduction

Activated carbon (AC) is a commodity of widespread use in our society. It is an essential component in a number of gas and water filters, molecular sieves, deodorants, energy storage devices, etc. [1,2]. The key aspects of this material are its high porosity and large surface area, which are attained after the activation of selected precursors including biomass, coal and peat, petroleum coke and polymers [3]. AC is mainly produced as powders, granules and extrudates or pellets, with more sophisticated forms (i.e. activated carbon fibres) having a lower market share [4,5]. Shaping ACs raises their cost. Powdered activated carbon (PAC) is then the cheapest form and it is primarily used in liquid-phase applications. Granules and especially extrudates are required when working with gases because of their low pressure drop when used in fixed beds [6]. In addition, powders are rarely recovered and recycled

whereas the use of pellets allows the recovery of the spent AC for regeneration [7].

The manufacture of AC extrudates comprises a step in which a powdered material is agglomerated with a binder and extruded to form cylinders with 0.8–4 mm diameter. Although there is little information available due to the proprietary process of AC production, there are essentially two practices on hand to prepare extrudates. One possibility is to agglomerate PAC with a binder and to extrude the resulting mixture. Clay binders are preferred in this procedure as the hardening of the pellets requires a heat treatment at mild temperatures (400–600 °C) [8,9]. The other option is to obtain the pellets prior to the activation process [10]. A kneaded mixture of binder and AC precursor is extruded and the pellets are then activated. Binders for this purpose can be either inorganic (clays) or organic (pitches, tars, and resins).

Binders are thus essential in the production of extruded ACs. They

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provide of fluidity to the mixture permitting the extrusion [11,12]. This process is usually carried out by applying pressure and temperature to the mixture, which improves the final quality of the pellets [13]. Both the extrusion process and the raw materials should guarantee a hard extruded AC, i.e. pellets should have a low friability and a high attrition resistance since they are expected to withstand handling and impacts [14,15]. Furthermore, the use of an alien component (binder) when making AC extrudates introduces additional issues related to the porosity and the chemistry of the materials. From that perspective, a good binder should balance the mechanical consistency of the pellets with undesired effects such as porosity reduction or ash content increase [16,17]. Clays, for example, are essentially non-microporous when heated and the resulting pellets will have a significant decrease of the specific surface area compared to that of the PAC, according to the rule of mixtures [8,9,18]. In addition, these inorganic binders contribute to the ash content of the extruded AC, so they are recommended only when such inorganic content is not relevant for a given application. Organic binders, on the other hand, promote pore blockage due to the release of volatiles when heated [19–21]. The eventual pore development of the organic binders during the activation affects not only the porosity of the pellets but also their mechanical properties. Additional aspects such as availability, logistics and, above all, price finally determine the selection of a binder for extruded AC.

The new economic paradigm of the circular economy has prompted chemical industries around the world to implement changes to improve the sustainability of their processes. Using wastes or recycled materials to minimise the depletion of raw materials fits perfectly within this objective [22]. In that scenario, a plethora of research works have explored the possibility of replacing traditional carbon precursors derived from fossil-fuels with sustainable carbon sources including biowastes [23]. The impact of such replacement in the AC industry is somehow limited as far as lignocellulosic precursors (i.e. coconut shells and wood) are currently used [24]. On the other hand, studies that cope with more sustainable binders for the production of AC extrudates are very limited. A possible reason for this could be found in the early work of Prof. Rao that showed the limitations of biomass-derived binders (i.e. molasses and syrups) when compared to binders derived from fossil sources (i.e. coal tars), especially with respect to the brittleness and density of the resulting granular ACs [25].

This paper introduces a novel and sustainable binder, whey, for the manufacture of extruded ACs. Whey is the main residue of the dairy industry, especially in the production of cheese and yogurt [26]. Around 140 million tons of whey are produced annually worldwide [27,28], from which more than 40 million tons come from the European Union [29]. The raw waste is presented as a liquid with a water content of about 94 wt%. The remaining 6 wt% consists of a mixture of sugars (lactose), proteins (lactoglobulins), fats and inorganic matter [26,30]. This composition is responsible of the very high biological oxygen (BOD) and chemical oxygen (COD) demands values of whey, whose disposal is thus a serious burden, especially for small dairies [31]. Significant quantities of whey are dehydrated in big dairy companies, with the resultant powdered whey being marketed mainly as ingredient for animal feed [26,27]. Despite this, at present the industry only manages to use 50% of the total liquid whey [28]. Moreover, important quantities of dehydrated whey end every year as food waste [32]. The use of whey as a binder for the manufacture of extruded AC could then become a large-scale output to mitigate the environmental impact of this waste.

The use of whey as a binder to agglomerate different powders was explored decades ago by Ferretti and Chambers [33,34]. Their seminal work on the subject showed the excellent performance of whey and whey permeates as binders in the preparation of pellets of industrial by-products including coal fines and iron ore/steel powders [33]. They later discovered that the reaction between a glucose-containing reducing sugar and a lysine-containing protein led, in the presence of a basic catalyst (ammonium hydroxide), to a family of Maillard products behaving like a thermosetting resin that outperformed classical

carbohydrate binders such as molasses or lignin [34].

The present paper makes use of this ability of whey and whey derived products to act as thermosetting resins to prepare AC extrudates. This study expands the possible use of whey as a binder for high temperature applications. Whereas the works of Ferretti and Chambers [33,34] showed the performance of whey as a binder at temperatures below 300 °C, the current work explores the possibility of whey binding particles at temperatures up to 1000 °C. The requirements for a binder to be acceptable at such high temperatures are still the same than at lower ones, i.e. that whey-bound pellets preserve their original shape (not size), and that they have acceptable mechanical properties. In that sense, our recent work on whey-derived carbons has prompted this research mainly due to the outstanding mechanical properties of the materials obtained [35]. Thus, the process described herein comprises the steps considered when using organic binders, i.e. kneading of the AC precursor with the binder, extrusion of the mixture and activation of the resulting pellets. Results obtained are presented in two different sections. In the first set of experiments, the whey binder consisted of a mixture of whey powder (dry whey) and water. Coconut shell char (a common AC precursor) particles were then added to the mixture and the pellets obtained were carbonised under a nitrogen atmosphere. This allowed us the tight control of the dough formulation to guarantee the scientific soundness of the study of the different processing variables. Process variables considered in this first study included binder ratio, char particle size and temperature of carbonisation. Two quality parameters (ball mill hardness and density) were obtained for each pellet formulation to evaluate the performance of whey as a binder for high temperature applications. An exploratory study of the physical activation conditions of these pellets was also carried out. Next, a whey binder was obtained by partial dehydration of liquid whey until its dry solids concentration mimicked that of the best formulation obtained when working with dry whey/water admixtures. A final part of the paper sketches the economics of using whey as an alternative binder in the fabrication of AC pellets.

2. Materials and methods

2.1. Materials

Dehydrated (dry) whey (DW) was obtained by spray drying of a sweet whey. The resulting whey powder contains a ca. 3% of moisture, and a grain size distribution between 5 and 200 µm, with a particle size mode of ca. 20 µm. More details about the composition and properties of this whey powder can be found elsewhere [35].

Sweet liquid whey (LW) was collected directly from the manufacturing process of cured cheese by enzymatic coagulation of pasteurised cow milk. The collected whey was stored in a fridge at –20 °C. LW was defrosted at room temperature 24 h before use.

Both LW and DW were supplied by the Spanish dairy company CAPSA-FOOD. DW came from a different batch of liquid whey than LW.

The coconut shell char (CC) was supplied by Carbotecnia (Zapopan, Jalisco, México). CC was provided as pieces with heterogeneous shape and sizes in the centimetre range (see images in Fig. S1, Supplementary Information). A representative fraction (1 kg) of the original char was selected and ground to powder with grain sizes < 212 µm. Parts of this powder were further sieved into different particle size fractions (< 75 µm, 75–150 µm, and 150–212 µm) for different studies.

Three commercial AC extrudates were used as reference materials, a coal-based AC (AC-COAL) from Norit, a coconut-based AC (AC-COCO) supplied by GasN2 company (Barcelona, Spain), and an AC used in wastewater treatment plants for H₂S removal (AC-H2S), supplied by Aqualia (Spain).

2.2. Manufacturing of AC extrudates

The manufacture of the pellets consisted in (i) extrusion of mixtures

of char and binder to obtain the green pellets; and (ii) carbonisation and/or activation of the green pellets to obtain the AC extrudates.

2.2.1. Extrusion

As mentioned in the Introduction, two different studies were carried out using either DW or LW as binders to obtain the green pellets (Fig. 1).

In the first case, the commercial whey powders were partially rehydrated with deionized water and then mixed with the powdered coconut char until a dough with an adequate viscosity to be extruded was obtained.

In the second route, partially dehydrated LW was used as binder to obtain the raw, green pellets. For this purpose, 200 ml of LW were heated at 75 °C under stirring until the solids content was 42 wt%. This solid matter content was found to be the optimum value when using DW as binder (see Results and Discussion).

The char/whey blends were introduced into a manual extruder consisting of a threaded rod that pushes a plunger, which drags the material by pressing it against a nozzle. The outlet diameter of the nozzle, and therefore the diameter of the raw pellets, was 4 mm. The pressure necessary for the dough to be extruded was supplied manually. Once extruded, the pellets were dried for 24 h at room temperature to obtain the raw, green pellets that were kept in polypropylene containers for further use. Pellets were labelled as CCDW or CCLW depending on the use of DW or LW as binder, respectively.

2.2.2. Carbonisation/activation

Carbonisation of batches of 10 g of green pellets were carried out in a

tubular furnace (Carbolite, UK) using 200 ml min⁻¹ of N₂, a heating rate of 10 °C min⁻¹ and a soaking time of 1.5 h at the maximum temperature. Different carbonisation temperatures from 300 to 1000 °C were studied. Activation of the green pellets (batches of 15 g) was carried out in the same tubular furnace under a CO₂ flow, heating the sample at 10 °C min⁻¹ up to 850 °C. CO₂ flow and dwell time at the maximum temperature (850 °C) of the activation process were variables of this study (Tables 1 and 2). Subsequently, the pellets were cooled down to room temperature under the same atmosphere used in the carbonisation/activation treatment.

2.3. Characterisation methods

Thermogravimetric analyses were carried out in a TGA Q5000 device from TA Instruments under N₂ and CO₂ atmospheres using a heating rate of 10 °C min⁻¹ from room temperature to 1000 °C with a sample mass of 25 (± 0.1) mg.

Elemental (CHNSO) analysis of CC, DW and LW was carried out in LECO CHNS-932 and LECO VTF-900 microanalysers.

The point of zero charge (pH_{pzc}) of CC and CCLW A3 was determined as detailed elsewhere [35,36].

N₂ adsorption-desorption isotherms at -196 °C and CO₂ adsorption-desorption isotherms at 0 °C were performed in a Micromeritics Tristar II volumetric adsorption system, after outgassing the samples at 120 °C overnight. Specific surface area (S_{BET}) and micropore volume (V_{DRN2}) have been calculated from the N₂ isotherms using the Brunauer-Emmett-Teller (BET) and Dubinin-Radushkevich (DR) models, respectively. The

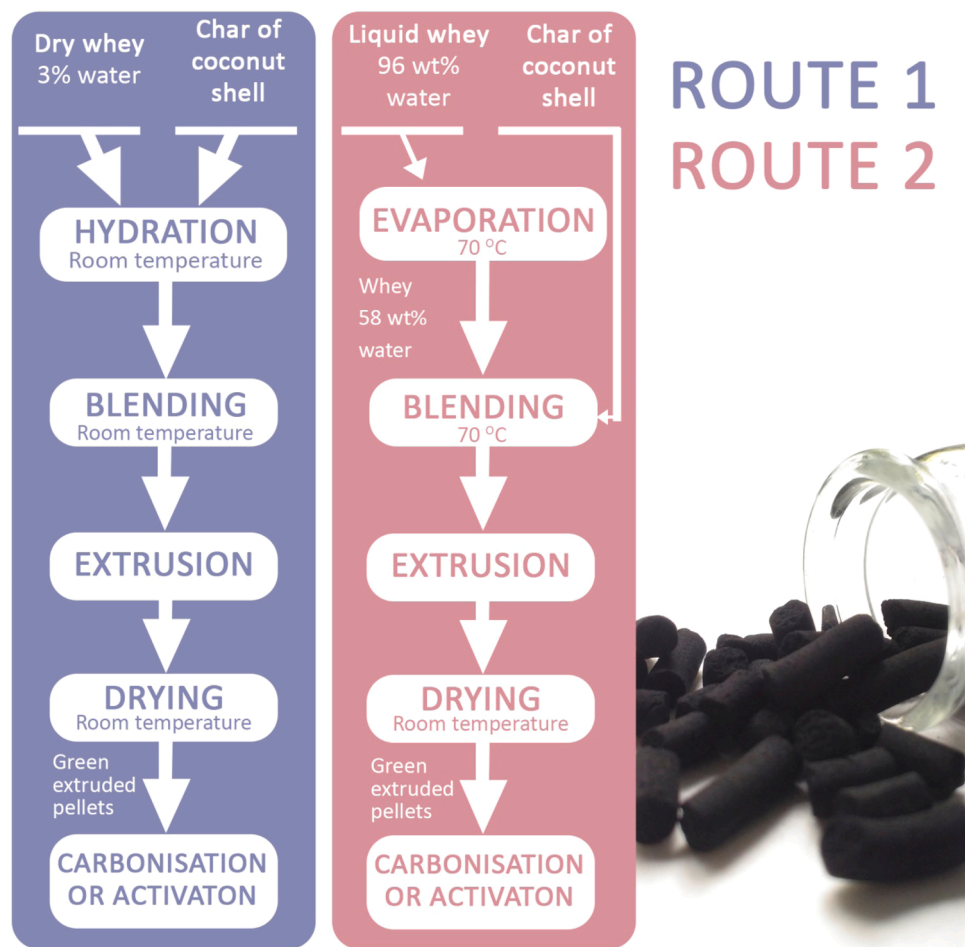


Fig. 1. Schematic of the routes followed to prepare carbonised and activated carbon pellets using whey as a binder. The photograph illustrates the activated carbon pellets obtained.

narrow (< 0.7 nm) micropore volume (V_{DRCO_2}) was obtained from the CO_2 isotherm using also de DR model.

The true density (ρ_{He}) was measured with a Micromeritics AccuPyc 1330 pycnometer, using helium as the probe gas. The bulk density (ρ_{bulk}) was determined with Dry Flo® on a Micromeritics Geopyc 1365 device. In both cases the samples were outgassed at 120 °C overnight before the analysis. Total porosity was determined using the following equation:

$$\text{Porosity}(\%) = [1 - (\rho_{\text{bulk}}/\rho_{\text{He}})] \times 100 \quad (1)$$

Morphology of the pellets was examined using a Quanta FEG 650 (FEI Company, USA) Scanning Electron Microscope (SEM) equipped with an Everhart-Thornley secondary electron detector (ETD). Samples were attached to an aluminium stub using a double-sided conductive adhesive tape without further coating.

A ball mill hardness (I_a) test was carried out to determine the abrasion resistance of the pellets. For this purpose, 2 g of pellets were placed in a stainless-steel cylindrical drum (26 mm diameter x 55 mm length, inner dimensions) containing a stainless-steel ball (14 mm diameter). The drums were shaken at a 10 Hz frequency for 60 s using a RETSCH MM400 ball mill. The I_a of the pellets was then determined by sieving the pieces resulting from the drum test. Specifically, I_a corresponds to the amount of matter (expressed as wt%) passing through the 0.5 mm sieve. All measurements were performed in quadruplicate.

2.4. H_2S removal experiments at room temperature

H_2S dynamic adsorption experiments were carried out on beds of ACs adapting the ASTM D6646 recommendations [37]. Specifically, ca. 4 g of ACs pellets (4 mm diameter) were placed inside a 20 mm (id) glass tubes on top of a ceramic frit. AC pellets were cut to lengths of ca. 1 mm to render pellets with an equivalent spherical diameter of ca. 2 mm. The bed heights were approx. 100 mm. A concentration of 1% H_2S in moist air was obtained by diluting a 2% $\text{H}_2\text{S}/\text{N}_2$ mixture with vapour saturated air. A flow of 100 ml min^{-1} passed through the bed avoiding axial dispersion. Adsorption was carried out at room temperature (22 ± 1 °C) until bed exhaustion, i.e. inlet H_2S concentration = outlet H_2S concentration. The concentration of H_2S was monitored using a Mass Spectrometer (Omnistar®, Pfeiffer Vacuum, Germany). For a given AC, triplicates were carried out to attain statistical soundness.

3. Results and discussion

3.1. Dry whey (DW) as a binder for AC extrudates

3.1.1. Carbonisation of CCDW pellets: thermal analysis

Due to the novelty of this binder for this particular application, it was

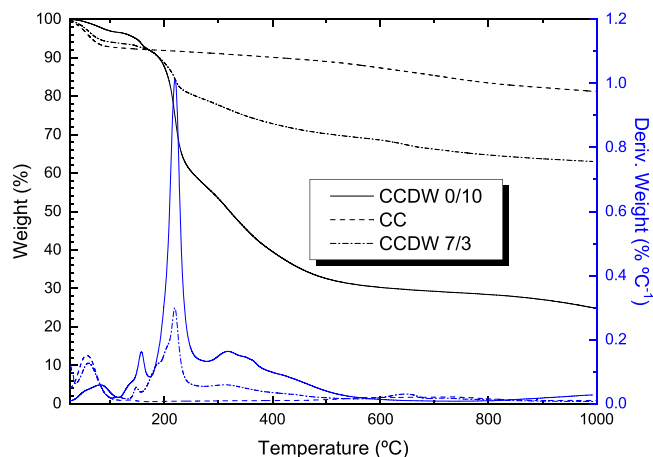


Fig. 2. TG and DTG N_2 profiles of different green CCDW pellets and the CC precursor.

deemed necessary to study first the carbonisation of the raw pellets. Fig. 2 shows the thermal behaviour under a non-oxidising atmosphere of both the AC precursor (CC) and of the binder-only green pellets (labelled as CCDW 0/10, see Table 3 below for nomenclature). The coconut char is very stable in the temperature range studied, with only 17.7% weight loss at 1000 °C, almost half of it (8%) corresponding to the release of moisture (Table 2). This low volatile emission of CC contrasts with the ca. 70% weight loss observed for DW at the same temperature. This means a char yield of ca. 30% for the whey binder at 1000 °C. Most of the volatile emission of the DW pellets takes place at temperatures below 600 °C, with a massive weight loss observed between 175 and 275 °C. This thermal event is absent in the thermal profiles of pure α -lactose or whey proteins obtained under similar conditions [35]. It is speculated that this particular thermal behaviour might be characteristic of Maillard polymers or resins. Other minor events for this new binder are ascribed to the dehydration of crystalline α -lactose (DTG maximum at ca. 150 °C), and to the carbonisation of free carbohydrates, proteins and fats that would most likely be responsible of the wide DTG band from 275 to 600 °C.

The thermal profile of CC/DW 7/3 pellets (see Table 3 below for nomenclature) is also included in Fig. 2. It is a composite profile of the two single components, i.e. CC and DW. Moreover, the profile of CC/DW 7/3 includes all the thermal events characteristic of the DW-only pellets. In other words, the presence of CC does not alter significantly the thermal behaviour of the pure whey pellets. At a given temperature, the carbonisation yield of CCDW 7/3 is thus the sum of yields of the single components CC and DW, according to a simple rule of mixtures. The yield of the CCDW 7/3 pellets ranges from ca. 77% at 300 °C to 66% at 1000 °C.

3.1.2. Carbonisation of CC/DW pellets: effect of the binder proportion, CC particle size and carbonisation temperature

The first screening of the CCDW pellet production was aimed at finding the optimal proportion of binder and CC particle size fraction that would guarantee a good mechanical integrity of the carbonised pellets. Three parameters have been considered to determine the quality of the pellets in this initial screening, namely real and bulk densities (ρ_{He} and ρ_{bulk} , respectively) and ball mill hardness (I_a). It should be pointed out that, in all cases, the carbonised pellets preserved the shape of the green pellets in spite of a contraction of their original dimensions.

Starting with the binder proportion, four CC/DW relative weight proportions were considered, namely, 8/2, 7/3, 6/4 and 5/5 expressed as unit mass of CC per unit mass of DW. Changes in these weight proportions altered the amount of water required to get mixtures with similar viscosity, the higher the amount of CC the higher the mass of water added (Table 3). Carbonisation temperature was set at 450 °C and CC powders with a particle size < 212 μm were selected for the manufacture of pellets to study the effect of the binder proportion. Results obtained are shown in Fig. 3a.

The pellets prepared by extruding DW-only pastes (CCDW 0/10) have an exceptional low abrasiveness (< 1%), as measured by the ball mill test. This would confirm the resin-like carbonisation behaviour of this particular binder [33,35]. The mechanical integrity of the CCDW pellets remains essentially unaltered until a CCDW ratio of 8/2 is reached. A significant increase of the I_a value is observed for this sample thus establishing a limit in the minimum amount of DW that is required

Table 1
Activation conditions of the pellets.

	Temperature (°C)	CO_2 Flow (ml min^{-1})	Heating rate (°C min^{-1})	Dwell time (h)
A1	850	50	10	1.5
A2	850	100	10	1.5
A3	850	100	10	2.0
A4	850	100	10	2.5

Table 2

Elemental analysis, pH, ash and water contents of the whey powder (DW), liquid whey (LW) and coconut shell char (CC).

	DW	LW	CC
C (%) ^a	40.7	40.2	87.2
H (%) ^a	6.3	6.0	2.3
N (%) ^a	2.3	2.2	0.8
O (%) ^a	46.1	44.1	0.1
S (%) ^a	0.2	0.2	6.9
Ash (%) ^b	3.3	n.d.	4.6
Water content (%) ^b	3.6	95.8	7.7
pH	5.1 ^c	6.3	9.7 ^d

^a Dry basis.^b Gravimetric analysis.^c pH of a DW saturated solution.^d pH_{pzc}.**Table 3**

Amounts of char, whey powder and water used in the extrusion of the pellets.

CC/DW mass ratio (g/g)	8/2	7/3	6/4	5/5	0/10
Added water (g)	4.25	4	3.3	2.75	2.5

to bind effectively the char particles. On the other hand, the ρ_{He} value of the DW-only pellets (CCDW 0/10) is slightly lower than the rest, which are in turn almost identical to that of pure CC ($\rho_{He} = 1.51 \text{ cm}^3 \text{ g}^{-1}$). The ρ_{He} value of CCDW 0/10 also differs from that of carbons prepared from whey powders in absence of added water [35]. In this case, the addition of water during the green pellet extrusion might alter slightly the skeleton of the resulting carbon, especially considering that the carbonisation of DW is incomplete at $450 \text{ }^\circ\text{C}$ (Fig. 2). ρ_{bulk} values of all CCDW samples are again very similar except for CCDW 0/10, which indicates that adding CC to the dough slightly increases the porosity of the carbonised pellets.

A CC/DW ratio of 7/3 was then selected to carry out the following experiments in the study of the carbonisation of the CCDW pellets. This is an acceptable binder ratio for practical use since, in average, conventional organic binders represent around 25 wt% of a pellet (before carbonisation) of commercial extruded ACs [19,38,39]. Different particle sizes were next used to prepare green pellets, keeping the carbonisation temperature constant at $450 \text{ }^\circ\text{C}$. The particle size fractions were obtained by sieving the original CC powders with particle sizes $< 212 \mu\text{m}$. Three additional fractions were prepared, namely the fine fraction with particles passing through the $75 \mu\text{m}$ sieve, and two intermediate fractions corresponding to particles with sizes between 75 and $150 \mu\text{m}$ and between 150 and $212 \mu\text{m}$. The quality parameters obtained for the carbonised pellets of these four different fractions are plotted in Fig. 3b. As expected [9], the use of the smallest particle size fraction ($< 75 \mu\text{m}$) improved both the bulk density and ball mill hardness of the carbonised pellets. Intermediate fractions of CC brought about less dense pellets with lower mechanical consistency. A very relevant result, from the application point of view, is that the original powdered CC, with a particle size below $212 \mu\text{m}$, also rendered a very good result in terms of the I_a of the carbonised pellets. This suggests that the presence of the char fines ($< 75 \mu\text{m}$) in the sample seems enough to guarantee a good mechanical performance of the CCDW pellets. So, in spite of the lower bulk density of the CCDW 7/3 $< 212 \mu\text{m}$ sample, pellets prepared from this fraction are preferred due to the eventual savings of eluding the milling of CC at particle sizes below $75 \mu\text{m}$.

Fig. 3c shows the quality parameters of a series of carbonised pellets at different temperatures, all of them using a CC/DW mass ratio of 7/3 and CC powders with a particle size $< 212 \mu\text{m}$. The ball mill hardness of all carbonised materials is $< 1\%$, which corroborates the high binding capacity of whey even at a relatively low temperature as $300 \text{ }^\circ\text{C}$. Bulk densities are also quite independent of the carbonisation temperature, and they seem to be controlled mainly by the extrusion process. Real

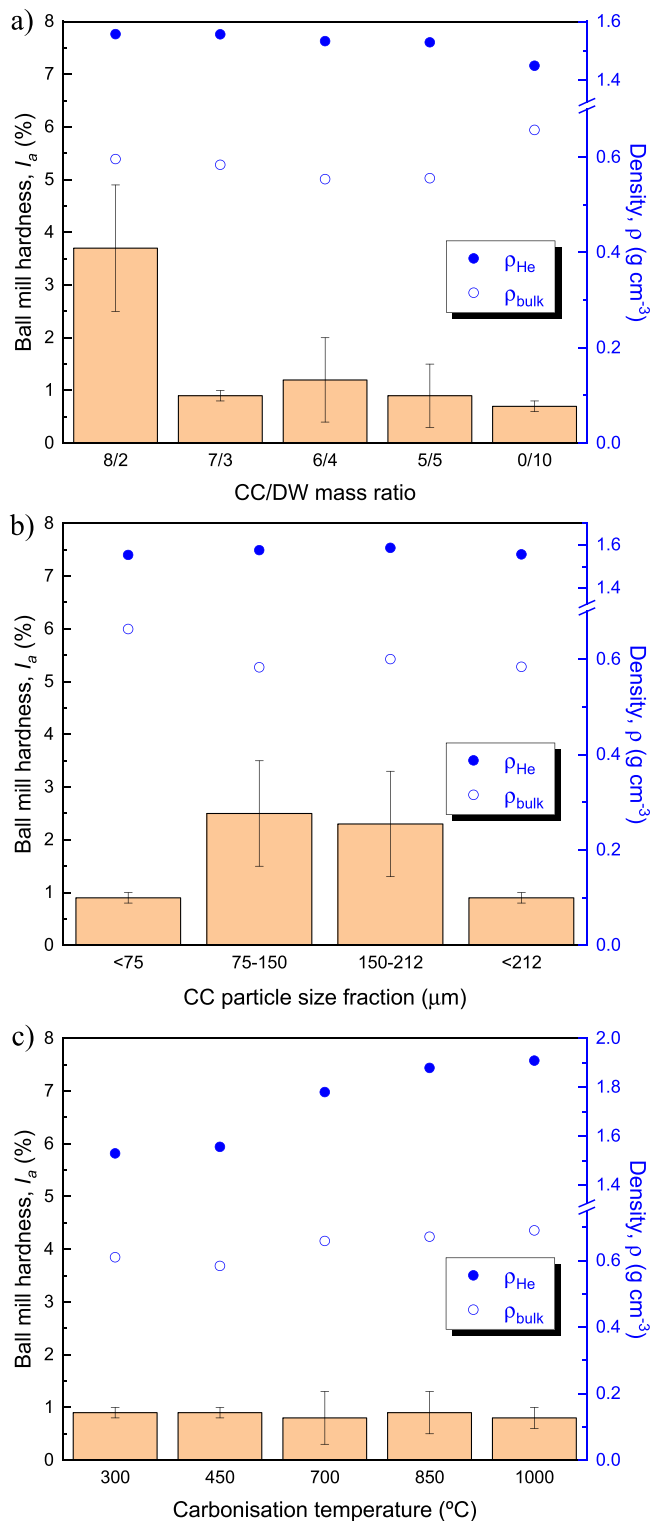


Fig. 3. Ball mill hardness and densities of carbonised pellets prepared using rehydrated whey powders (DW) as a binder: a) effect of the binder ratio (carbonisation temperature: $450 \text{ }^\circ\text{C}$; CC particle size: $< 212 \mu\text{m}$); b) effect of the CC particle size (carbonisation temperature: $450 \text{ }^\circ\text{C}$; CC/DW mass ratio size: 7/3); c) effect of the carbonisation temperature (CC particle size: $< 212 \mu\text{m}$; CC/DW mass ratio size: 7/3).

densities, however, depend strongly on the carbonisation temperature, increasing as this temperature increases. A maximum ρ_{He} value of 1.91 g cm^{-3} was obtained for the pellets carbonised at $1000 \text{ }^\circ\text{C}$. As a consequence of the increase in their real density and the fairly constant bulk density, the porosity of the pellets increases from 60% at $300 \text{ }^\circ\text{C}$ to 64% at $1000 \text{ }^\circ\text{C}$.

To conclude this section, some SEM microphotographs of the carbonised pellets are included to illustrate the binder capacity of whey. Fig. 4a shows an image of a CCDW 0/10 (all-binder) carbonised pellet. The structure of the material is sponge-like with macropores of different size. This structure is different to that of materials prepared by moulding plus carbonisation of DW particles, in absence of additional water [35], where the original whey powder particles preserved their shape after carbonisation. This was something expected since adding water to DW transform the powder into a sticky paste by partially dissolving the DW cenospheres. Still, it is postulated that the protein/lactose combination in the DW aqueous paste would promote Maillard reactions that originate thermostable resin-like compounds (melanoidins). Those compounds would endure carbonisation without melting thus preserving the shape of the original pellets. The macropores of Fig. 4a could be then ascribed either to bubbles originated during the emission of volatiles, or to deformed DW original cenospheres that would stick together after carbonisation [35]. In any case, the sticky, glue-like DW aqueous suspensions binder the CC particles in the kneading process and the thermal treatment hardens the glue by transforming it into a carbon rich matrix (Fig. 4b). The identification of CC particles of different size in the carbonised CCDW 7/3 < 212 pellet (Fig. 4c) was done after an exhaustive SEM analysis of CCDW materials. The CC particles of Fig. 4c have a rather smooth surface which was never observed in the case of whey-only materials. It should be noted that EDX was of little help in this

case for a direct identification of CC particles, due to the essentially identical composition of CC and the carbonised whey matrix.

3.1.3. Activation of the CCDW pellets

The activation of carbon precursors to obtain ACs is a process intended for the development of the microporosity on those precursors. We start this subsection by analysing the textural properties of the carbonised CCDW pellets in order to find the eventual pore development brought about by the thermal treatment under inert atmosphere. Fig. 5 shows the N_2 and CO_2 adsorption-desorption isotherms at $-196 \text{ }^\circ\text{C}$ and $0 \text{ }^\circ\text{C}$, respectively, of the CCDW 7/3 pellets carbonised at different temperatures. The most relevant result is the null N_2 adsorption of all carbonised pellets (Fig. 5a). Since the original CC has some N_2 capacity (Fig. 5a), which remains unaltered even when CC is re-heated at $700 \text{ }^\circ\text{C}$ (Fig. S2 in the Supplementary Information), it seems clear that the co-carbonisation of the binder and the CC leads to the blocking of the pores of the coconut char that were accessible to N_2 at $-196 \text{ }^\circ\text{C}$. The volatile emission of DW during the carbonisation would be responsible of such pore blockage.

However, this micropore blocking of the carbonised CCDW pellets, as revealed by the N_2 adsorption isotherms (Fig. 5a), resembles a molecular sieve-like behaviour in the light of the CO_2 adsorption isotherms (Fig. 5b). Indeed, significant CO_2 adsorption is observed for all carbonised pellets except for those treated at $1000 \text{ }^\circ\text{C}$. This means that micropores are not blocked but they have pore mouths restricting the adsorption of N_2 at cryogenic temperatures. The volatile emission and further carbonisation would then act as a chemical vapour deposition treatment similar to that required in the fabrication of carbon molecular sieves (CMSs). The carbonisation of the pellets at $850 \text{ }^\circ\text{C}$ reduces their CO_2 adsorption in the whole relative pressure range. A similar effect is

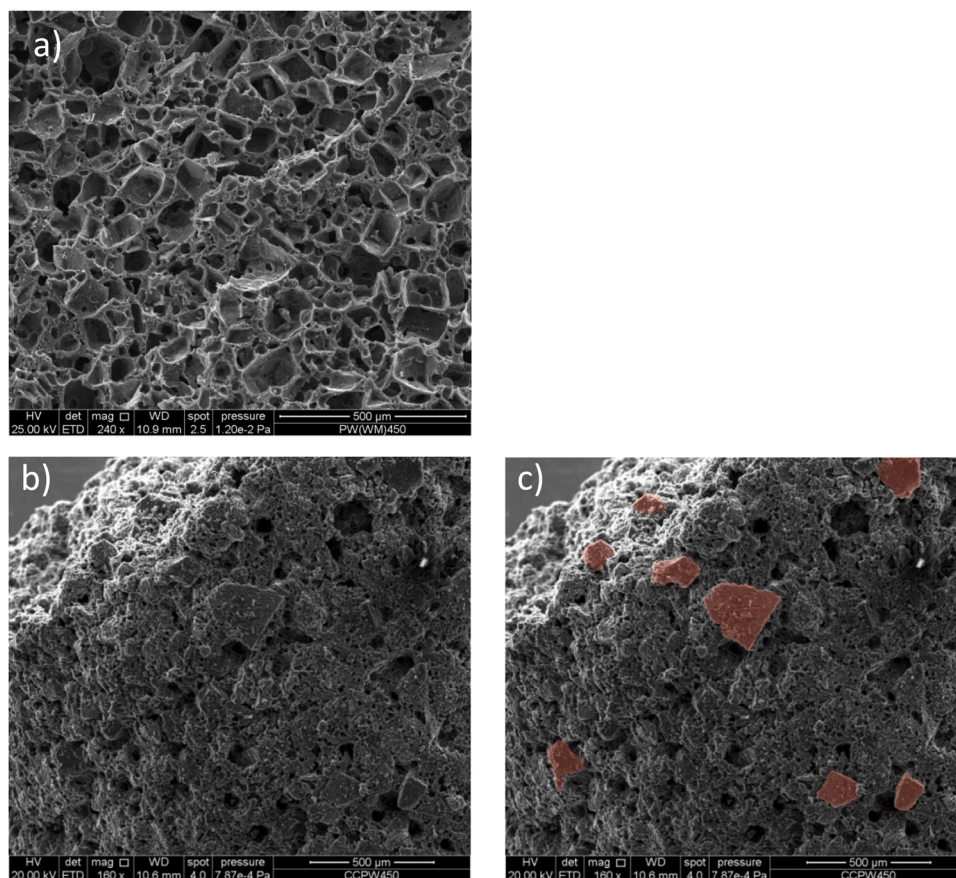


Fig. 4. SEM micrographs of a) CCDW 0/10 (DW-only) pellet carbonised at $450 \text{ }^\circ\text{C}$; b) CCDW 7/3 < 212 pellet carbonised at $450 \text{ }^\circ\text{C}$, c) same as b) but with CC particles that were clearly visible highlighted.

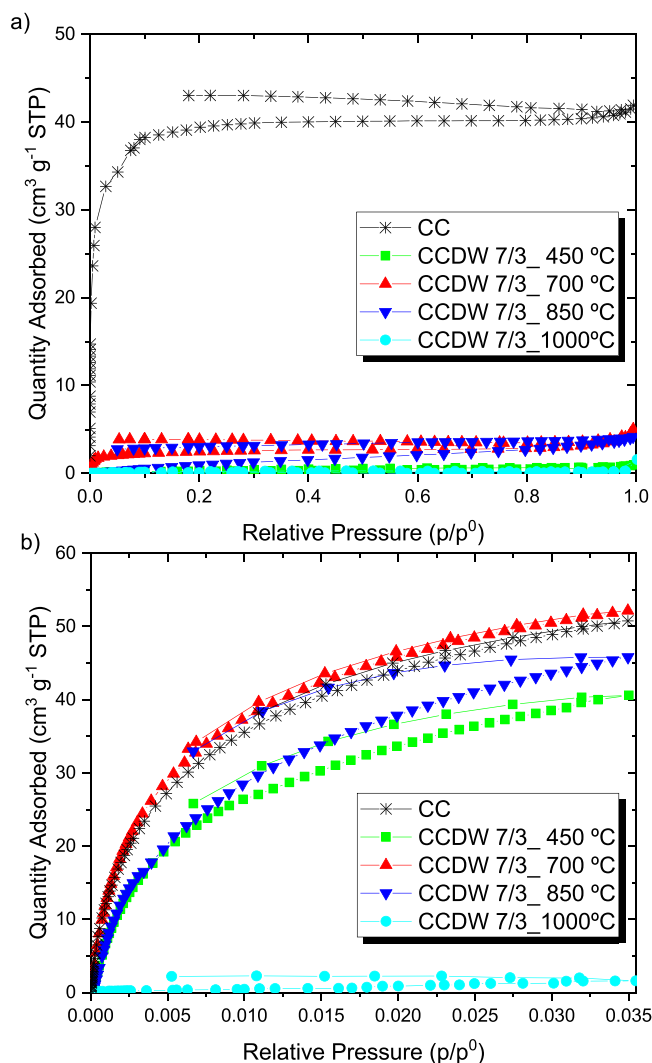


Fig. 5. (a) N₂ adsorption-desorption isotherms at -196 °C; and (b) CO₂ adsorption-desorption isotherms at 0 °C of the carbonised CCDW pellets and the CC precursor.

observed for the CC carbonised at the same temperature (Fig. S2 in the Supplementary Information), thus indicating a progressive collapse of the microporosity. The collapse seems to be complete at 1000 °C, as evidenced by the negligible adsorption of CO₂ on the materials treated at such high temperature (Figs. 5b and S2 in the Supplementary Information).

The CO₂ capacity at 0 °C of the pellets carbonised at 700 and 850 °C points out the feasibility of a physical activation process to increase their microporosity. Fig. 6 shows the CO₂ thermogravimetric profiles of the CCDW 7/3 pellets. Also included are the CO₂ reactivity profiles of CC powders and DW-only pellets (CCDW 0/10). Profiles shown are restricted to the gasification regime (i.e. from 500 °C onwards) for clarity. The CO₂ reactivity of the coconut char has a maximum at ca. 940 °C. When pellets are more reactive than CC, with the maximum weight loss found at 890 °C. The CCDW 7/3 extrudates show a profile with the maximum at ca. 900 °C which is somehow an intermediate temperature found for two components, DW and CC, respectively, although the whole profile resembles more that of DW.

A temperature of 850 °C was then selected to carry out the activation of the CCDW pellets. At this temperature, a slow gasification regime of the pellets is guaranteed thus allowing the control of the physical activation reactions. As mentioned in the Experimental Section, different CO₂ flows and residence times were explored (Table 1). Activation in all

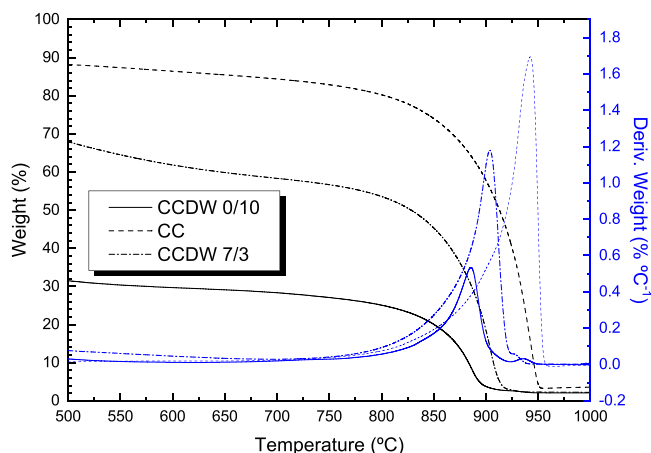


Fig. 6. TG and DTG CO₂ profiles of different green CCDW pellets and the CC precursor.

cases was successfully attained as confirmed by the porosity analysis of the resulting materials (Fig. 7). Regarding the N₂ adsorption isotherms (Fig. 7a), all activated CCDW pellets are essentially microporous materials with the characteristic Type I isotherms. N₂ isotherms of these

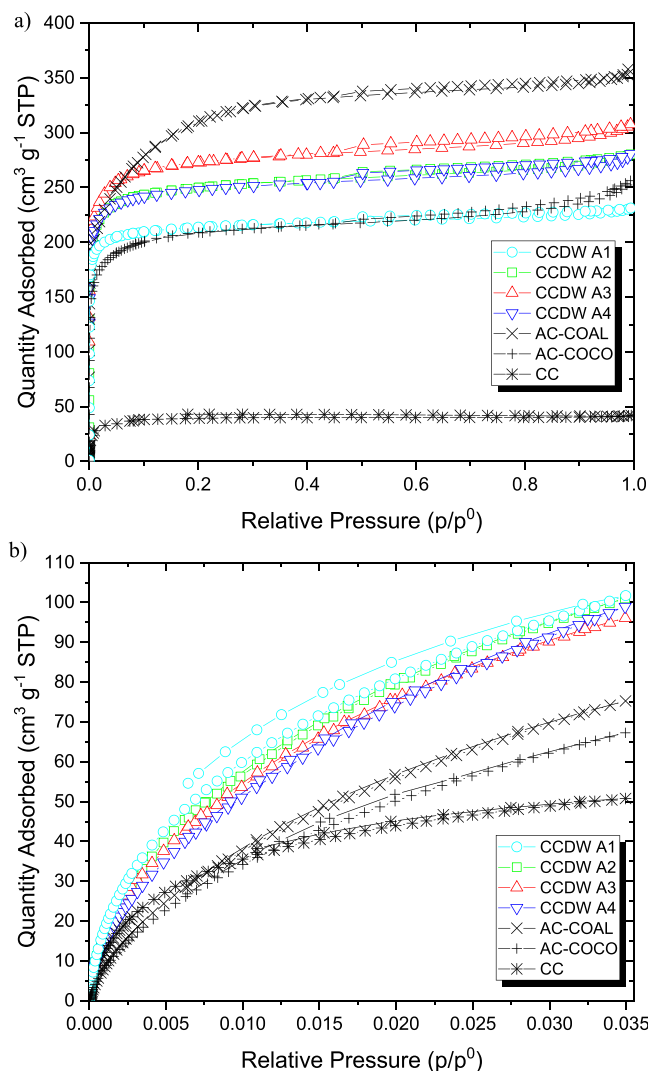


Fig. 7. (a) N₂ adsorption-desorption isotherms at -196 °C; and (b) CO₂ adsorption-desorption isotherms at 0 °C of the activated CCDW pellets.

extrudates also resemble Type IV, with a minimal but perceptible hysteresis adsorption-desorption loop. This indicates the presence of some mesopores on the pellets. As for the CO₂ isotherms (Fig. 7b), the physical activation of the CCDW extrudates enhances the adsorption of CO₂ in the whole relative pressure range.

Selected textural parameters obtained from these isotherms are collected in Table 4. CO₂ activation of the pellets replicates a well-known burn-off pattern [1], attending to the different activation conditions (Table 1). Thus, the increase of the CO₂ flow increases the porosity of the resulting AC through the development of micropores (compare samples CCDW A1 to CCDW A2). This microporosity is further enhanced when increasing the residence time, for a given CO₂ flow (compare samples CCDW A2 to CCDW A3). Finally, a longer treatment (CCDW A4) overcooks the extrudates, i.e. reduces their pore volumes. The ash contents of CCDW A1 to CCDW A3 are very similar, around 10%, which also matches those of AC-COCO and AC-COAL. The over-activation of CCDW A4 also portrays a significant increase of the ash content of this material.

The level of activation of the CCDW pellets is similar to that of the two commercial extruded ACs used as reference materials. The AC-COAL is the activated carbon showing the highest N₂ adsorption (Fig. 7a). The knee of the N₂ isotherm is less closed than those of the coconut derived carbons, including the CCDW materials, thus suggesting a wider micropore size distribution of the coal derived AC. AC-COCO, on the other hand, is the AC showing the lowest S_{BET} and micropore volume (V_{DRN2}). The N₂ adsorption-desorption isotherm of this reference material is, nonetheless, very similar to that of CCDW A1, the less activated CCDW extrudate. Possibly the most remarkable difference between the textural parameters of the two reference ACs and the activated CCDW pellets is the relative percentage of narrow microporosity (V_{DRCO2}/V_{DRN2}%) which is related to their CO₂ adsorption capacity at 0 °C (Fig. 7b). A plausible reason is that steam rather than CO₂ had been used for the activation of the commercial extruded ACs. For a given burn-off, steam activation is known to develop wider micropores on different carbon precursors when compared to CO₂ activation [1].

The analysis of the porosity of the activated CCDW pellets has demonstrated that ACs with similar textural properties to commercial AC extrudates can be obtained using whey as a binder in the extrusion process. Next, the mechanical integrity of those activated pellets needs evaluation. Fig. 8 shows the results obtained. In general, the activated CCDW extrudates have a very low attrition as measured in the ball hardness test. Their I_a values are comparable to those of the commercial ACs. The two materials with the highest burn-offs (CCDW A3 and A4, Table 4) significantly underperform in the attrition test when compared to the rest of pellets, including the commercial ones.

The relatively high I_a values of CCDW A3 and A4 are most likely

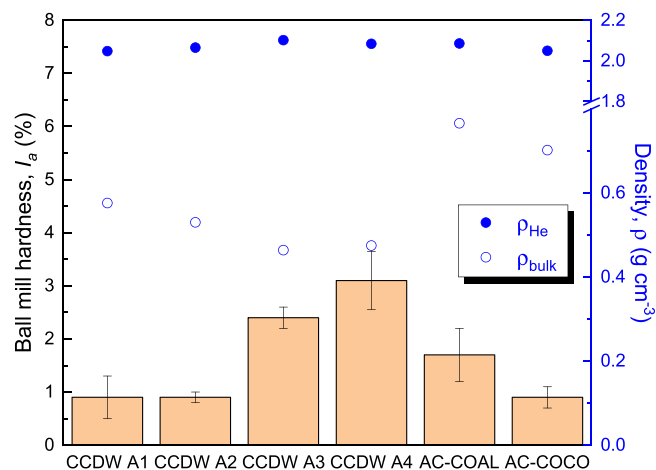


Fig. 8. Ball mill hardness and densities of the activated carbon pellets prepared using rehydrated whey powders (DW) as a binder.

related to the very high overall porosity of these materials, 78% and 77%, respectively (Table 4). Since the real density of all activated materials including the commercial ACs is almost identical (ρ_{He} ca. 2.1 g cm⁻³, Fig. 8), this high porosity is the consequence of a lower bulk density of all activated CCDW pellets when compared to that of the commercial ACs ($\rho_{bulk} > 0.7$ g cm⁻³, Fig. 8). The low ρ_{bulk} constitutes a drawback of the CCDW activated pellets considering that most industrial AC filters work on a volumetric rather than a gravimetric basis [40]. As mentioned above (Fig. 3b), the use of CC with a particle size < 75 μm increases significantly the bulk density of the pellets. Nonetheless, we will demonstrate in the next section that the extrusion processing parameters, specifically the temperature of the extruded dough, can be determinant in attaining ACs with optimal ρ_{bulk} .

3.2. Liquid whey (LW) as a binder for AC extrudates. Performance example (H₂S removal)

So far, it has been shown that activated carbon pellets with properties similar to those of commercial AC extrudates can be prepared using mixtures of whey powders (DW) and water as binders. Since whey is a liquid waste containing approx. 95% of water (Table 2), it makes full sense to explore the possibility of using the original waste as a binder after partial dehydration (Fig. 1). Thus, the water content of the LW was reduced by evaporation until the solids content of the LW increased tenfold from the initial 4–42%. This later value corresponds to the solids

Table 4

Selected parameters of the CO₂ activation process and textural properties of the activated carbon pellets, using whey as a binder. Textural properties of two commercial ACs are included for comparison.

	CCDW A1	CCDW A2	CCDW A3	CCDW A4	CCLW A1	CCLW A3	AC-COAL	AC-COCO
Yield (%)	54.8	49.7	43.7	37.5	55.1	45.6	–	–
Burn-off (%) ^a	18	26	35	44	18	32	–	–
Ash (%) ^b	9.8	9.7	10.1	11.4	8	8	9.9	9.6
Porosity (%) ^c	72	74	78	77	65	68	63	66
S _{BET} (m ² g ⁻¹)	859	991	1078	987	796	1170	1095	809
V _t (cm ³ g ⁻¹) ^d	0.36	0.43	0.48	0.43	0.34	0.51	0.55	0.40
V _{DRN2} (cm ³ g ⁻¹) ^e	0.34	0.40	0.43	0.38	0.30	0.46	0.53	0.33
V _{DRCO2} (cm ³ g ⁻¹) ^f	0.27	0.25	0.23	0.22	0.22	0.23	0.18	0.15
V _{meso} (cm ³ g ⁻¹) ^g	0.02	0.03	0.05	0.05	0.04	0.05	0.02	0.07

^a Burn-off percentage calculated assuming a CCDW 850 yield of 67% (see Fig. 2).

^b Gravimetric analysis.

^c Eq. (1) and Figs. 8 and 9 for densities data.

^d Total pore volume, as measured from the N₂ adsorption isotherm at p/p⁰ = 0.99.

^e Total micropore volume, as calculated from the Dubinin-Radushkevich model applied to the N₂ adsorption isotherm at -196 °C.

^f Narrow (< 0.7 nm) micropore volume, as calculated from the Dubinin-Radushkevich model applied to the CO₂ adsorption isotherm at 0 °C.

^g Mesopore volume, V_{meso} = V_t - V_{DRN2}.

content of a simulated liquid whey prepared from DW + added water in the CCDW 7/3 formulation (Table 3). CC powders ($< 212 \mu\text{m}$) were then added to the hot ($70 \text{ }^\circ\text{C}$), partially dehydrated LW and the mixture was immediately extruded to obtain the green pellets (Fig. 1). After cooling down and room temperature drying, two different batches of the extrudates were activated under the A1 and A3 conditions (Table 1). The N_2 and CO_2 isotherms at $-196 \text{ }^\circ\text{C}$ and $0 \text{ }^\circ\text{C}$, respectively, of the resulting materials (CCLW A1 and CCLW A3) are shown in Fig. 9. Additional isotherms are included for comparative purposes. Textural parameters are also collected in Table 4.

Replication of the activation process using LW instead of DW was very good in terms of the porosity development. Differences between the textural parameters of the activated CCLWs and their CCDW counterparts (Table 4) are within the tolerance normally found in commercial activated carbons. In other words and in spite of a number of other possible factors that could contribute to those differences (LW and DW composition, use of heat in the extrusion of CCLWs as mentioned in the Experimental Section, etc.), they should be considered batch-to-batch variations in the activation process since there is not a systematic trend in the textural parameters obtained (e.g. always higher pore volumes for CCLWs than for CCDWs, which is not the case). This is an indication of the high reproducibility of using whey as a binder, which is related to its relatively homogeneous composition due to a highly

automated process in the dairy industry [26].

There are, however, significant differences in the ash content of the CCLWs vs. CCDWs (Table 4), with pellets of CCLW ACs showing lower ash contents. Furthermore, the use of LW to bind the CC precursor improved significantly the attrition resistance and, more crucially, the bulk density of the activated CCLW pellets (Fig. 10). This improvement of the ρ_{bulk} and ball mill hardness is postulated to be a consequence of heating of the mixture that preserved the dough hot during the extrusion process. It is well known that temperature and pressure are usually applied in the extrusion of commercial pellets to improve their quality [41,42].

CCLW A3 was selected to test the performance of the ACs obtained with this novel binder. It should be clear that the ACs prepared using whey as a binder should be dealt with as “conventional” or “multi-purpose” activated carbons that can be used in multiple applications unless, obviously, a specific treatment makes them “specialty” carbons. Nonetheless, the removal of H_2S from gases at room temperature was spotted as a potential niche for these particular ACs due to, i) the alkalinity of their surface [43,44] (the pH_{pzc} of the CCLW A3 is 11.5); and ii) our previous experience in this specific application [45]. Thus, dynamic adsorption experiments were carried out using fixed beds of ACs pellets until bed exhaustion. An example of the results obtained is shown in Fig. 11, where the breakthrough curve of a reference carbon (AC-H2S) under identical operational conditions is also included. The adsorption capacities of the two carbons, the breakthrough times and other performance parameters (height of the mass transfer zone or H_{mtz} , and fractional capacity or ϕ) calculated from these adsorption experiments [45,46] are collected in Table 5. The adsorption capacities and breakthrough times of both ACs are very similar. However, the commercial AC-H2S performs slightly better than the CCLW A3 beds in terms of the column efficiency parameters H_{mtz} and ϕ . Higher H_{mtz} values means a faster adsorption process and higher ϕ values correspond to sharper breakthrough curves [46]. Since we do not have further information regarding origin or trademark of the AC-H2S, the reader is referred to previous publications on the field for comparison [47]. Bearing in mind the different experimental conditions used in the different works, the adsorption capacities of CCLW A3 and AC-H2S are similar to those of the RB-4 AC (Norit) or the S208c AC (Waterlinsk Barnebey Sutcliffe) [47].

3.3. Economics of using whey as a binder for AC extrudates

It has been thus demonstrated that partially dehydrated (liquid) whey is adequate as a binder to obtain activated carbon pellets with textural and mechanical properties similar to commercial alternatives.

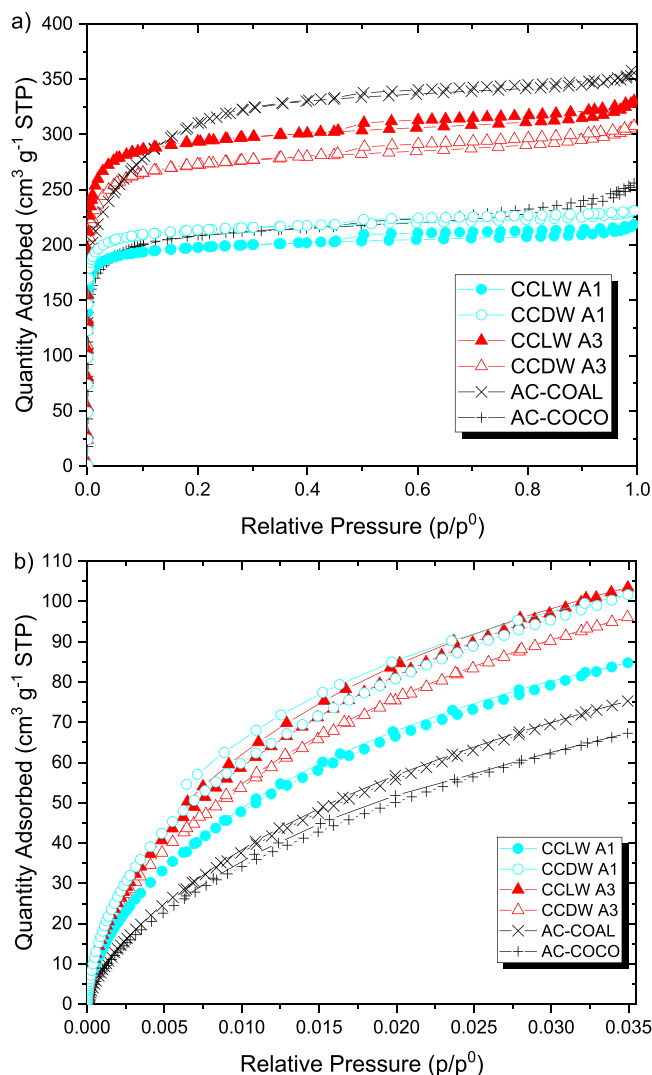


Fig. 9. (a) N_2 adsorption-desorption isotherms at $-196 \text{ }^\circ\text{C}$; and (b) CO_2 adsorption-desorption isotherms at $0 \text{ }^\circ\text{C}$ of the activated CCLW pellets.

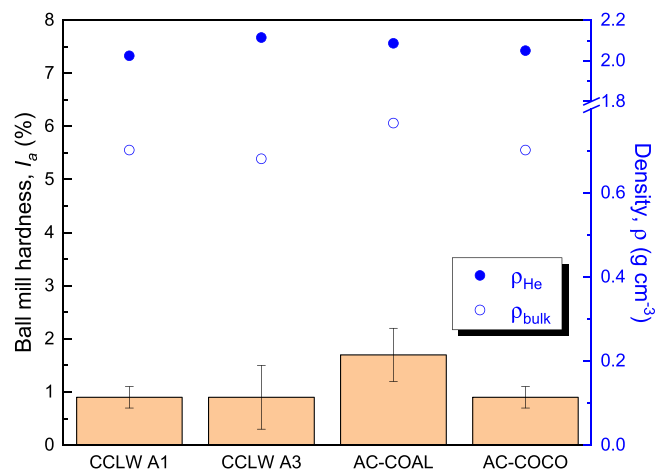


Fig. 10. Ball mill hardness and densities of the activated carbon pellets prepared using partially dehydrated liquid whey (LW) as a binder.

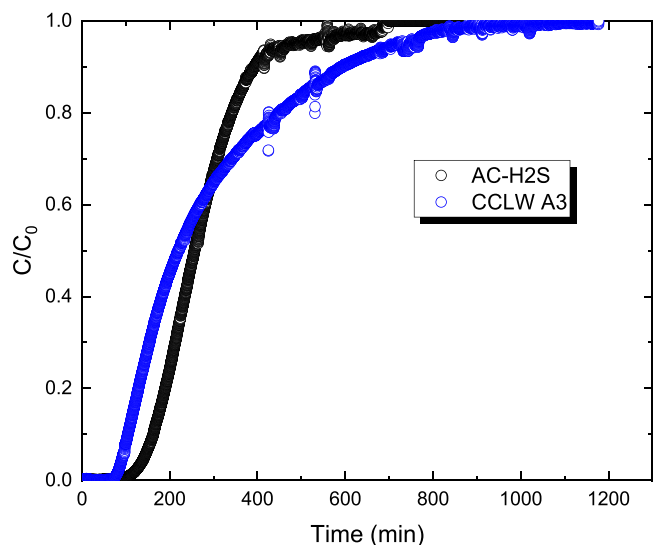


Fig. 11. Examples of H_2S breakthrough curves on AC beds. Test conditions: $22\text{ }^\circ\text{C}$, 100 ml min^{-1} of a 1% H_2S /moist air mixture; 1 h of bed pre-humidification; bed dimensions 10 (id) x 100 (height) mm; AC mass, ca. 4 g of pellets.

Table 5

Adsorption capacities (x/M), breakthrough times (t_B), height of the mass transfer zone (H_{mtz}) and fractional capacity (ϕ) calculated from the H_2S removal experiments on AC beds. Average values with standard deviations in parentheses. L_0 is the height of the bed (100 mm).

	(x/M) mg g^{-1}	t_B min	L_0/H_{mtz}	ϕ
CCLW A3	124 (17)	116 (8)	0.41 (0.1)	0.209 (0.07)
AC-H2S	138 (28)	129 (12)	0.55 (0.1)	0.373 (0.02)

Also, their performance on a given application (H_2S removal from gases at room temperature) is also competitive. The environmental impact of replacing part of the traditional binders with whey for the production of extruded ACs can be quantified based on the following data: (i) the global AC production in 2020 was estimated in $2.8 \cdot 10^6$ tons [48]; (ii) approximately 20 wt% of such production was extruded AC [49]. Thus, results of the potential utilisation of whey for the fabrication of extruded ACs are plotted in Fig. 12a, assuming a CCLW A3 formulation (approx. 75 g of LW are required to obtain 6 g of CCLW A3 pellets) (Table 4). Even in a very conservative scenario of only a 15 wt% replacement of conventional binders, this novel use would valorise $1 \cdot 10^6$ ton year $^{-1}$ of LW. This is far from the whey surplus that is currently being produced (ca. $40 \cdot 10^6$ ton year $^{-1}$), but using LW as a binder in the AC pellets industry would be still a significant contribution to the recovery of whey that should otherwise be disposed of as a residue.

Regarding binder economics, Fig. 12b shows the prices of different whey products and by-products [50]. As expected, DW is much more expensive (almost two orders of magnitude) than LW, a consequence of the heavy dehydration process required to obtain DW. DW prices are quite similar to those of other organic binders such as pitches and organic resins, with low-grade DWs (i.e., animal feed) being significantly cheaper. Raw clays (bentonite) are however much cheaper ($80\text{ }^\circ\text{C}$ ton $^{-1}$) [51], even after clay processing that normally raises the bentonite price up to $120\text{--}150\text{ }^\circ\text{C}$ ton $^{-1}$.

Selection of DW as a potential binder in the fabrication of ACs would only be justified in terms of handling and storage. Using LW instead would effect a strong reduction in the energy consumption of the whole process, since less water needs to be evaporated. Moreover, the technology (evaporation) to obtain partially dehydrated whey (either

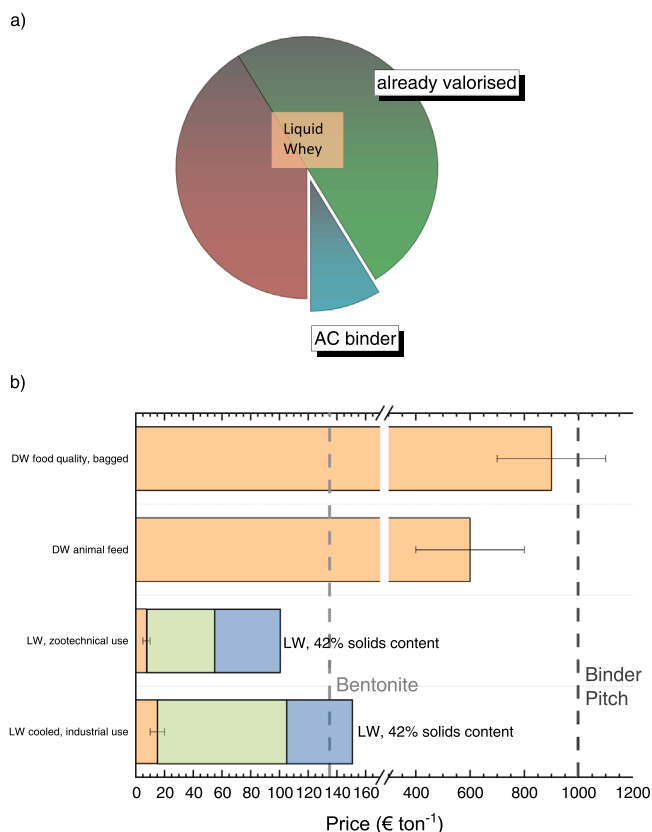


Fig. 12. A) Percentage of liquid whey (LW) that could eventually be valorised as a binder for extruded AC manufacture; b) average pricing of LW and dry whey (DW) of different qualities in the last two years; error bars represent oscillations in price (source: [50]); green bars represent the cost of 7 tons of raw LW that is needed to obtain 1 ton of LW with 42% solids content; blue bars represent the estimated evaporation cost of those 7 tons or raw LW from 6% to 42% solids content (see text).

concentrated or pre-concentrated whey) is already available in big dairy industries. This is so because LW with a solids content of 58–62 wt% (i.e. concentrated whey) is required before the spray-drying process to obtain DW [52,53], percentages that are well above the 42 wt% of solid content used in the CCLW A3 formulation (Table 3). This latter value is very close to the solids content (32 wt%) attained in the pre-concentration of whey [53].

Tagging a price for concentrated or pre-concentrated LW is not simple as most dairy companies do not market these products and different technologies are currently available for LW evaporation. Generally speaking, multi-stage evaporators with either thermal vapour recompression (TVR) or mechanical vapour recompression (MVR) are used for whey concentration or pre-concentration, respectively [52,53]. Jensen and Oxlund published in 1988 the costs of concentrating LW from 6% to 53.3% solids content using different evaporators, including a seven-stage evaporator with TVR and a 2-stage evaporator with MVR [52,54]. The running costs (OPEX) of those two evaporators were estimated in 3.89 and 4.26 US\$ per ton of water removed, respectively. Prices after upgrading due to the US inflation (126% from 1988 to 2021) would be 8.8 and 9.6 US\$ per ton of water removed. These costs agree reasonably well with the energy consumption of 418 kJ kg^{-1} of evaporated water estimated for a six-stage evaporator with TVR reported more recently [55]. Hence, the evaporation cost per ton of LW with 42% solids content (CCLW A3 formulation, Table 3) would be around 43–47 euros, starting from a conventional LW with a 6% of solids content. Since approx. 7 ton of LW 6% solids content renders 1 ton of LW 42% solids content, the ton of 42% concentrated LW would finally amount to 100–150 euros as plotted in Fig. 12b. The concentrated LW (42%) would

then rival bentonite in the binder market for AC extrudates. In addition, and as mentioned before in this paper, the advantage of using LW instead of clays for AC extrusion is the expected lower ash content of the LW-based pellets when compared to bentonite ones, assuming all bentonite in the binder will contribute to the ash content of the materials. Although we do not know the binder used for the preparation of AC-COCO and AC-COAL extrudates, they show a 25% higher ash content than the CCLW ACs (Table 4).

4. Conclusions

Whey is a remarkable organic binder for the manufacture of activated carbon pellets, offering a new possibility to valorise this waste. Carbonisation of extrudates obtained from mixtures of coconut shell char, whey and water brings about pellets with an outstanding attrition resistance, as measured by the ball-mill hardness test. In particular, we have found that CC/whey weight ratio (dry basis) of 7/3 are the best proportion in terms of hardness. Also, whey is able to bind CC particles with particle sizes of $< 212 \mu\text{m}$, thus avoiding intensive milling of the activated carbon precursor. Finally, the attrition resistance of the carbonised pellets seems unaffected at temperatures above the complete carbonisation of whey ($450 \text{ }^\circ\text{C}$) up to $1000 \text{ }^\circ\text{C}$. In that sense, whey behaviour resembles that of a thermosetting resin. Physical activation of the pellets with CO_2 at $850 \text{ }^\circ\text{C}$ renders activated carbons with porosities similar to those of commercial extrudates. The performance of the AC pellets manufactured with whey on the removal of H_2S from gas streams at room temperature is also comparable to that of ACs designed for odour control applications, with retention capacities around $120 \text{ mg H}_2\text{S g}^{-1}$ of AC.

Since pellets of similar quality are obtained with powdered or partially dehydrated liquid whey, this opens the possibility of using whey in two different formats. While the use of whey powders as a binder would simplify the handling and storage of the material, using partially dehydrated liquid whey would save energy in the overall process by avoiding the high costs associated to evaporation. In any case, the cost of any of the whey formats is competitive with that of conventional binders, i.e. clays (bentonite) or fossil-based materials (pitch, resins). All these features make whey a definite replacement of the conventional binders towards a more sustainable fabrication of ACs.

CRedit authorship contribution statement

Raúl Llamas-Unzueta: Investigation, Visualization. **J. Angel Menéndez:** Conceptualization, Writing – original draft. **Luis A. Ramírez-Montoya:** Investigation, Visualization. **Alejandro Concheso:** Investigation, Visualization. **Miguel A. Montes-Morán:** Conceptualization, Writing – original draft.

Declaration of Competing Interest

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.

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Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2022.107590.

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