

Review

An Overview on the Manufacture and Properties of Clay-Based Porous Ceramics for Water Filtration

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Abstract: This study explores the different techniques used to manufacture porous clay-based ceramics, examining their properties such as porosity, strength, permeability and filtration efficiency. Different techniques are discussed in this review, with additive manufacturing being one of the most innovative techniques for manufacturing porous ceramics. Porous ceramics have their applications in numerous domains. Such ceramic filters have the advantages of retaining heavy materials, suspended particles, bacteria, viruses and water turbidity. Thus, the choice of the technique and propriety is a crucial step in obtaining a porous ceramic with the best performance. Barry et al. prepared porous phyllosilicate-based ceramics by freeze-tape casting on four samples and obtained porosity values in the range of 67–79% and diametrical compressive strength in the range of 3–7 MPa. Manni et al. prepared porous red ceramics from Moroccan clay and coffee waste (10, 20 and 30 wt.%) via uniaxial pressing and sintering at 1150 °C. They obtained porosities ranging from 30.2 to 63.8% and flexural strength values from 1.8 to 19.5 MPa. Medri et al. prepared ZrB₂-based porous bodies with the use of sponges and polyurethane foams as templates via the replica method and obtained high porosity over 80% and compressive strength up to 4.8 MPa. The use of clay and peanut shell mixtures was used in preparing porous silicate ceramics after unidirectional pressing and sintering at 1100 °C. These samples included 25 mass% of peanut shells, and exhibited porosity in the range of 40 to 60% and diametrical compressive strength in the range of 1–6 MPa. Such properties are suitable for domestic use of these types of clay-based ceramic filters. Moreover, the permeability values and removal of some pollutants, like arsenic, have been satisfactory for the first set of samples.

Keywords: clay materials; porous ceramics; processing; properties; water filtration



Academic Editors: Gilbert Fantozzi and Francesco Baino

Received: 30 September 2024

Revised: 10 December 2024

Accepted: 18 December 2024

Published: 30 December 2024

Citation: Maury Njoya, I.Q.; Lecomte-Nana, G.L.; Barry, K.; Njoya, D.; El Hafiane, Y.; Peyratout, C. An Overview on the Manufacture and Properties of Clay-Based Porous Ceramics for Water Filtration. *Ceramics* **2025**, *8*, 3. <https://doi.org/10.3390/ceramics8010003>

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1. Introduction

The World Water Council estimates that by 2030, about 3.9 billion people will live in regions characterized as “water scarce”. According to the World Health Organization, diarrheal diseases cause 1.5 million deaths every year, and it is estimated that more than half of these deaths can be attributed to a lack of sanitation and hygiene, as well as to the consumption of contaminated water [1]. In order to satisfy the lack of good-quality drinking water, the majority of the population in under-developed countries makes use of well, river or even drilling water (Figure 1). Water from these sources is not suitable for human

consumption because it is generally polluted by anthropic activities. The consumption of this type of water by populations tends to expose them to many diseases such as typhoid, cholera, dysentery, etc. In order to produce drinking water, some people utilize decantation accompanied by chlorination and filtration using a filter, whose principal component is an organic or inorganic membrane.

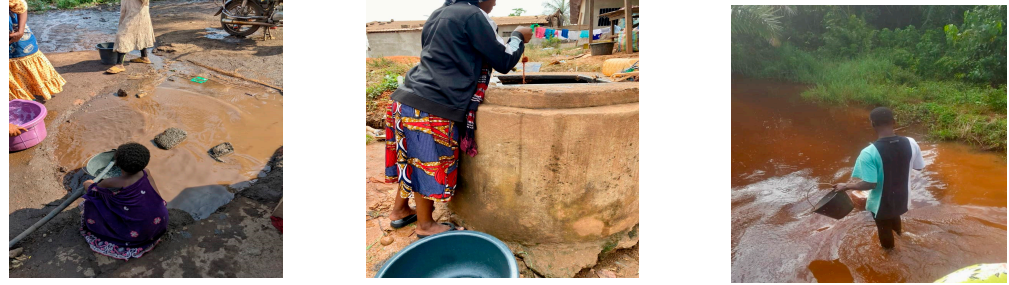


Figure 1. Illustrating the use of water from a well, river and drill for drinking purposes.

Porous ceramics are mostly recommended because of their good chemical and thermal stability, good mechanical resistance, ease of cleaning and long lifespan [2–4]. In general, these membranes are made from metal oxides, such as alumina, silica, zirconia and titanium oxide. They present some disadvantages, which are related to their relatively high cost because of the expensive raw materials and the complexity of the fabrication process [5–7]. Today, porous ceramics are used for a wide variety of applications (Figure 2).

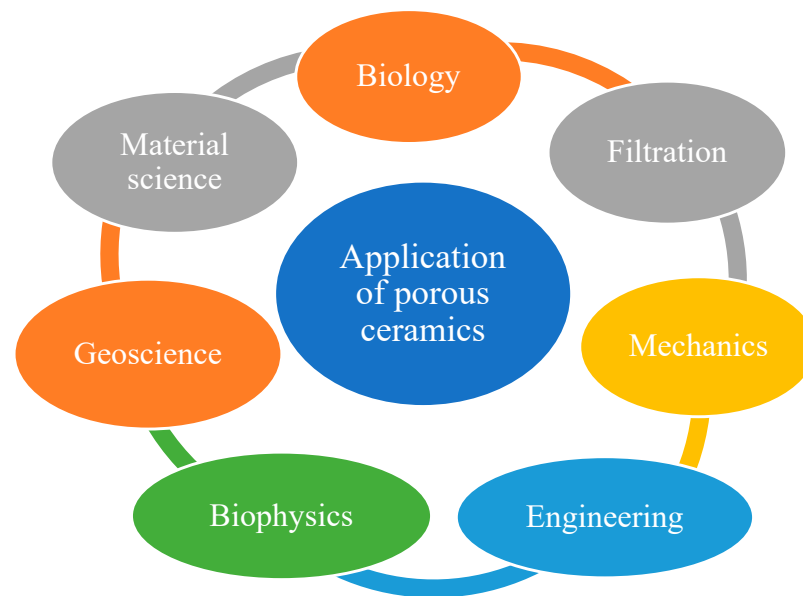


Figure 2. Applications of porous ceramics.

Porous ceramics are generally characterized by their pore size, surface, thickness and porosity [7]. Porous ceramics are divided into three main categories based on pore size according to the International Union of Pure and Applied Chemistry (IUPAC) nomenclature: microporous (pore diameter less than $0.002\ \mu\text{m}$), mesoporous (diameter ranging between 0.002 and $0.050\ \mu\text{m}$) and macroporous (diameter greater than $0.050\ \mu\text{m}$). Depending on the particular applications, different pore sizes may be desired. Liquid transport occurs only in mesoporous and macroporous ceramics, while the transport of gaseous molecules can take place in all three categories [8].

Almost 15,000 research articles have been published on porous ceramics since 2010, according to the Scopus database. Figure 3 shows the evolution of the number of research

articles published each year obtained by searching the string “porous ceramics” since 2010. The processing techniques of porous ceramics have also experienced enormous evolution. Another area that is presently at the forefront of every technological sector globally is waste utilization through recycling. In this context, there is a circular use of porous ceramics, and it is essential to use the methods with filtration in mind. Thus, the aim of future studies will be to develop and produce conventional additive manufacturing processing-based porous silicate ceramics, with emphasis on the initial composition, pore-forming process and the final characteristics (connectivity) of the prepared porous ceramics.

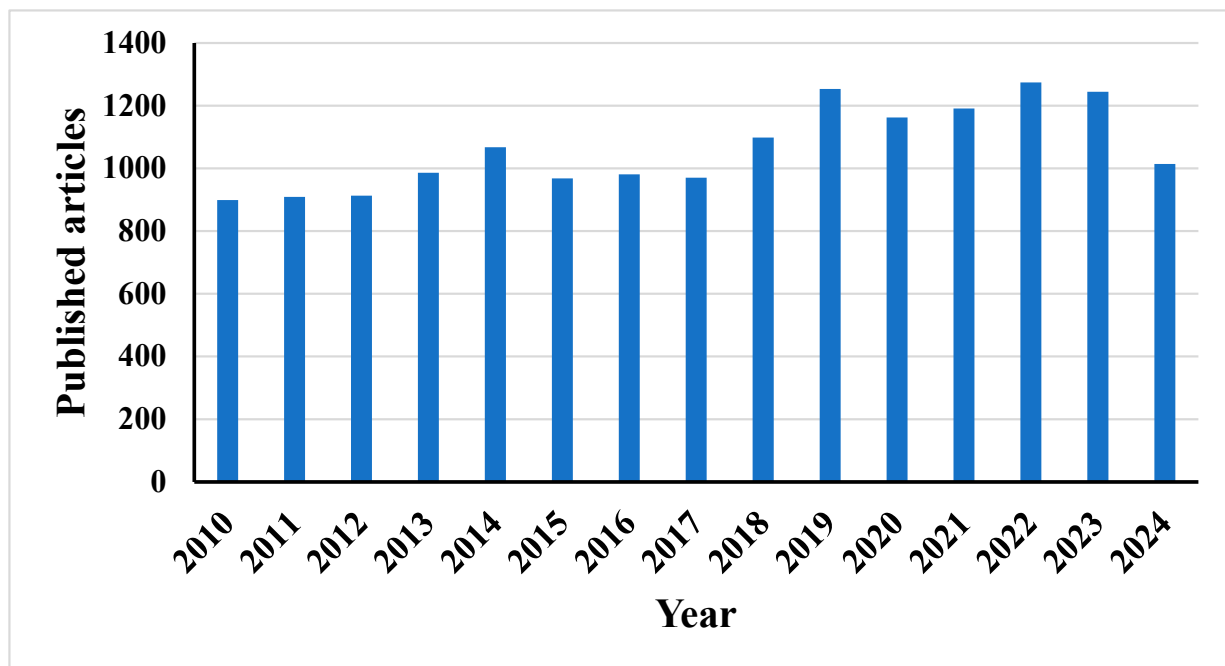


Figure 3. Evolution of the number of research articles published on “porous ceramics” according to the Scopus database since 2010 [3].

Previous work shows a variety of different methods for manufacturing porous ceramics. However, most of these methods seem to be adhere to the following path: choice of materials (clay and other additives), formulation, sintering and characterization of obtained products. Their properties are highly dependent on the powder or slurry (suspension) characteristics (plasticity, size and shape of particles, etc.), shaping method (uniaxial pressing, etc.) and sintering process (firing rate, temperature, etc.). Traditionally, porous ceramics are manufactured using techniques such as partial sintering, freeze-casting, tin plating, replica sacrificial template, direct foaming and gel casting [9–16]. Zhang et al. [17] prepared porous ceramics from lead zirconate titanate PZT (raw material), polyvinyl alcohol (organic binder) and acrylic acid (dispersant) by freeze-casting with water as a medium. As the solid content of PZT in the sample varies from 20 to 40%, porosity varies from 36 to 67%, and the compressive strength varies from ~1 to 73 MPa. They conclude that the freeze-casting method is favorable to improving the porous PZT ceramics properties. Zhu et al. [18] prepared porous ceramics with Tungsten ore tailings (raw material), CaO (binder), Kaolin (sintering additive) and polymethyl methacrylate (pore foaming agent) via pressing using the sintering method (1150–1210 °C, 5 °C/min and a dwell time of 1 h). A pore size of 0.18 μm, open porosity of 44.85% and compressive strength of 14.10 MPa were obtained at a sintering temperature of 1200 °C.

This paper gives a brief overview of the manufacture and properties of porous ceramics. In the last two decades, porous ceramics have been extensively studied because of

their excellent performance characteristics and wide range of applications. In recent years, a novel approach for manufacturing porous ceramics has emerged, which is known as additive manufacturing. It is quite a challenging technique because it enables the manufacturing of ceramics with complex shapes and structures, needs less material and enables the recycling of material. This technique, which has been studied by several authors [19–21], consists of joining materials to make objects from three-dimensional model data, usually layer upon layer, as opposed to subtractive manufacturing [19].

Shaping is the key stage in ceramic production. To this end, supports can be shaped using a variety of techniques. These include pressing (uniaxial and isostatic), extrusion, casting (in porous molds, under pressure or in strips) and injection (Figure 4). Several consolidation processes are available for manufacturing ceramics, with the aim of controlling the pore volume. These processes belong to two main categories:

- Hydraulic setting, characterized by its ease of use. This generally involves mixing a powder with excess water during the mixing stage, resulting in residual porosity after the setting reaction, followed by a drying stage.
- Incomplete densification through partial sintering, used in the majority of industrial ceramics. By controlling the sintering cycle (temperature, time and/or pressure), materials with appropriate residual porosity are obtained.

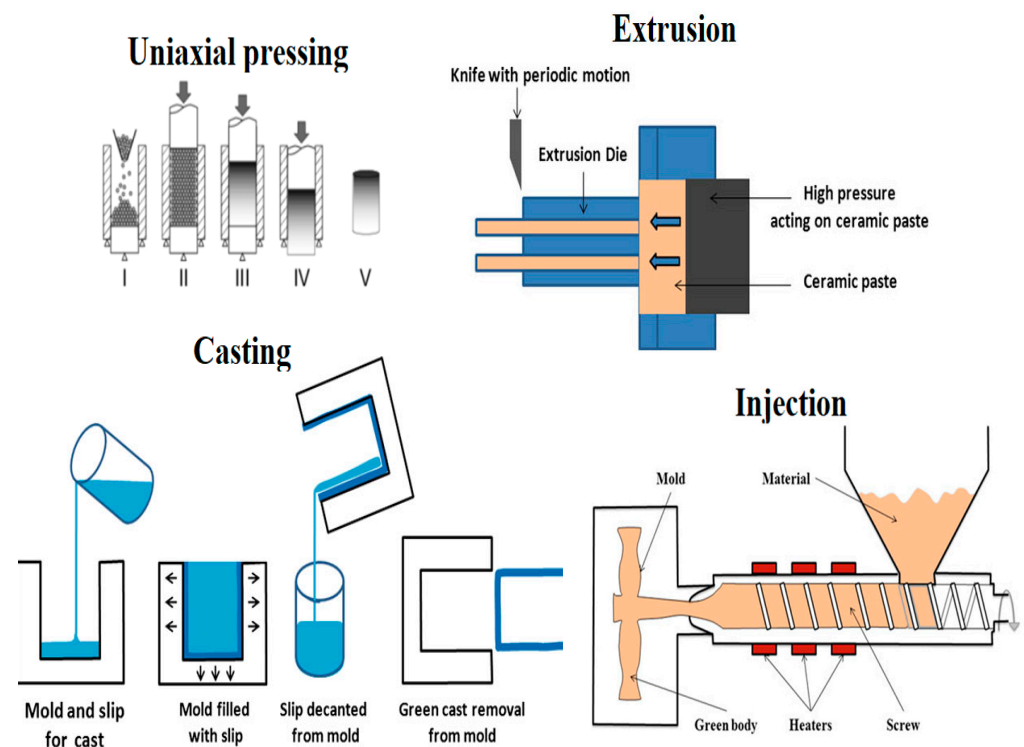


Figure 4. Some shaping techniques for ceramic production [22,23].

Furthermore, it is also possible to combine partial sintering with another process to obtain a material exhibiting hierarchical porosity.

Porous ceramic materials are produced by a variety of methods, the choice of which is mainly determined by the desired porous structure. The main production methods (Figure 5) are as follows: direct foaming, replication technique, partial sintering process or methods using pore-forming agents mixed with ceramic powders [6,7,24]. These processes enable a very wide range of porosities to be obtained, with controlled pore shape and size distribution.

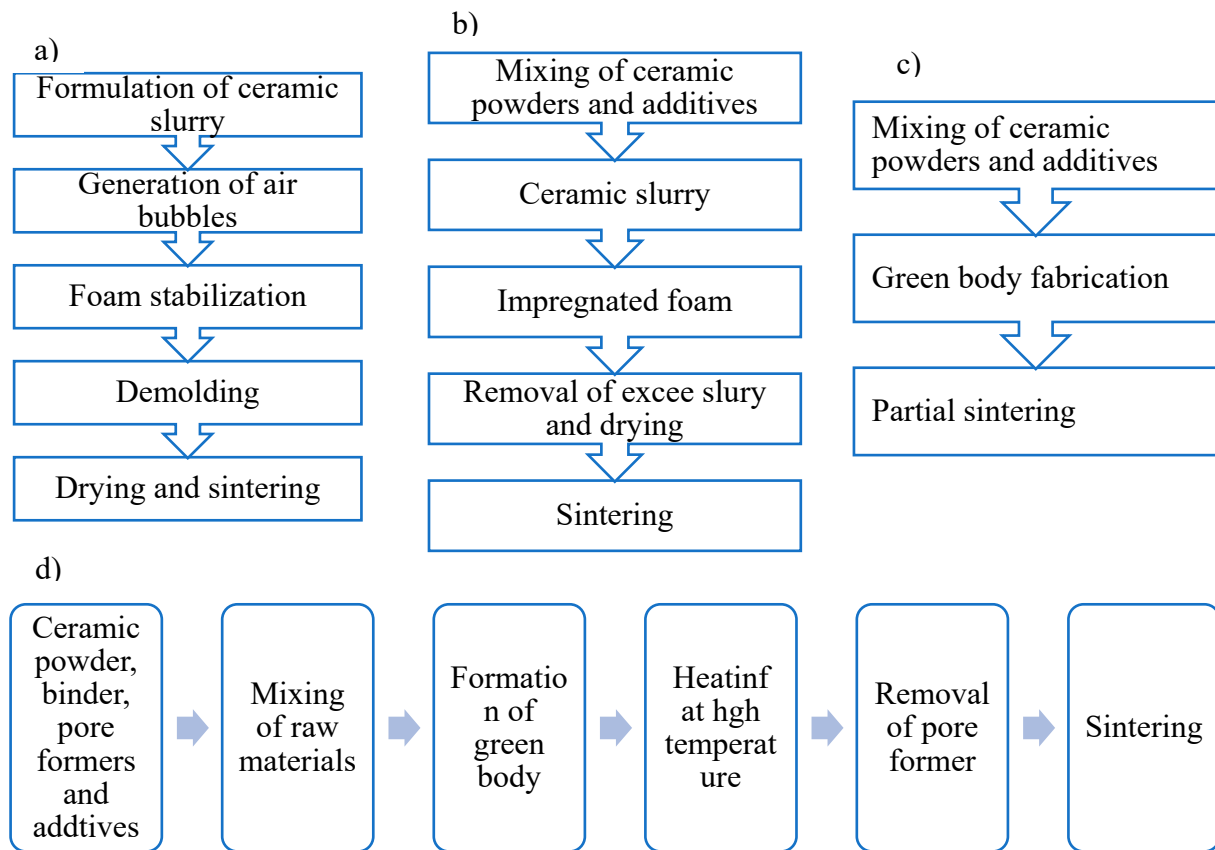


Figure 5. Main steps in the manufacturing of ceramics: direct foaming (a), replication technique (b), partial sintering process (c) and methods using pore-forming agents mixed with ceramic powders (d).

2. Experimental Procedure

2.1. Materials and Methods

To prepare porous ceramics, authors have used raw materials [9,25–27], synthesized materials [28–30] or raw materials and waste [24,31–33]. The formation of pores can be attributed to the embedment of air bubbles and the use of organic or inorganic waste, such as rice husks, banana peels, coffee husks, bovine bone ash, corn cob ash, cassava starch, eggshells, peanut shells, coal ash and cocoa cortex. The way in which ceramics are prepared and shaped is critical to the performance of the finished product.

Material preparation is an essential step, as the physical, chemical and technological properties of the materials have a major influence on the quality of the substrate. This step includes grinding, sieving and mixing.

In our work, two types clays were selected, namely kaolin and halloysite, noted K and H, respectively. Also, we choose to use a pore-forming agent mixed with clay powders for manufacturing our porous silicate ceramics. This porogenic agent is an agro-waste product, namely peanut shells (noted C). The clays were collected from the west region of Cameroun, while the waste (peanut shell) came from the southwest of Burkina Faso. Indeed, the properties of these groundnut shells are similar in most tropical regions. These materials were chosen because of their abundance in such developing countries, relative low cost, beneficial properties and for waste valorization under the scope of the circular economy. These materials were collected, then ball-milled for 1 h, sieved at 500 μm , air dried and oven dried at 105 $^{\circ}\text{C}$ for 48 h.

The powder mixtures (clay powder + peanut shell) were mixed using a rotating pelletizer at 32 rpm for 15 min. Then, the mixtures were humidified with progressive addition of water close to 15 mass% to obtain mixtures with good homogeneity. Subsequently, the

pastes were stored for 12 h under high humidity to improve their rheological property, avoid premature drying and ensure complete diffusion of water within the pellets. The peanut shell content was 25% by mass. The samples were shaped using uniaxial pressing (this is advantageous because it produces dense samples with precise dimensions, very smooth surface quality and results in good homogeneity within the sample) and then sintered at 1100 °C, 5 °C/min with a soaking time of 1 h.

Evidently, there is a strong need to evaluate the circular economy of porous ceramics in the future in order to define a suitable tradeoff between their manufacturing and reducing the environmental impact [34,35]. As such, it is important to explore the circular economy by using biosourced additives for the preparation of porous ceramics.

2.2. Characterization

Here, we mention just a few of the characterization methods. A number of authors have studied these parameters in their works, with the aim of highlighting some correlations and improving the useful properties.

X-ray diffraction is a technique used in materials science to determine the atomic and molecular structure of a crystalline material [36]. This technique is usually complementary to the elemental analysis. It provides qualitative control over the elemental composition and crystalline structure of materials. Furthermore, more information can be obtained from a careful analysis of the diffraction patterns or by using specific XRD settings.

Fourier transform infrared spectroscopy (FTIR) is a technique used for identifying the functional groups of molecules on the basis of their vibrational modes and frequencies. The absorbed energy characterizes the functional group and close chemical environment. The absorbed energy is described by Beer-Lambert's Law.

Scanning electron microscopy (SEM) is an electron microscopy technique capable of producing high-resolution images of the surface of a sample using the principle of electron-matter interactions [37].

X-ray fluorescence spectrometry is a global non-destructive elemental analysis technique for identifying and determining the chemical elements that constitute a sample in a given order of concentration. It enables the elemental composition of a sample to be determined both qualitatively and quantitatively [38].

Specific surface area is the total surface area per unit mass of the membrane support accessible to atoms and molecules. The aim of this measurement is to assess the ability of the support to facilitate fluid flow through their structures. It is determined according to the theory of Brunauer, Emmett and Teller (BET) [39]. To achieve this, measurements are carried out on samples, and each measurement is preceded by degassing to remove the water molecules adsorbed in the porous structure of the sample.

Porosity is an important parameter for the characterization of the materials' microstructures. In general, it corresponds to the volume of the interstices that can contain fluid, related to the total volume of the material. Porosity is also influenced by the type of material used, the proportion of pore-forming agent and the sintering temperature. Some methods for porosity analyses are X-ray computed microtomography (MCT), mercury intrusion porosimetry (MIP), geometric calculation and tripled weighed method based on the principle of Archimedes.

- MCT is used to form three-dimensional images, thus observing the geometry of the pore space in samples, such as the shape, connectivity, size and distribution of pores. MCT imaging is performed using a micro-focused X-ray tube that obtains shadow images of the object transmitted by multiple X-rays from different angles [39].
- Mercury intrusion porosimetry method measures open porosity and is appropriate for pores with diameters ranging from 0.01 microns to 800 microns. Measuring the volume

of mercury included in the sample at each pressure value gives the size distribution of its open pores. Considered a standard method of macropore analysis [40], it also enables the calculation of apparent density and total open porosity.

- Porosity is calculated from the absolute (or real) ρ_r and apparent bulk densities ρ_a . The real bulk density can be determined by pycnometry on powdered materials (obtained by a fine grinding of samples), and the apparent bulk density is calculated using both dimensions and mass of the dry material. Thus, total porosity P is hence determined by Equation (1) [41].

$$P = \left(1 - \frac{\rho_a}{\rho_r}\right) \times 100 \quad (1)$$

- The principle of Archimedes states that the force exerted on a body immersed in a fluid, whether fully or partially, is equal to the weight of the fluid that the body displaces. Thus, the tripled weighed method consists of weighing three different masses (M_1 , M_2 and M_3) based on the Archimedes system, where M_1 is the dry mass of samples, M_2 is the mass of the sample completely immersed in liquid and M_3 is the wet mass of the samples. Hence, with clearly defined formulae, the open porosity P_o of the sample can be calculated using Equation (2) below [42]:

$$P_o = \frac{M_3 - M_1}{M_3 - M_2} \times 100 \quad (2)$$

Permeability is a parameter used to determine the membrane's ability to allow liquid to flow through its pores. It is mainly controlled by pore size, hydrophilic character and membrane thickness. However, this parameter is not an intrinsic characteristic of ceramics, as it also depends on the fluid's viscosity. It characterizes the surface area required for flow, the geometry of the internal pore network, the hydraulic conductivity of the pore network and the physicochemical interactions between the material and the fluid. Permeability L_p ($L/h/m^2$), according to Darcy's law, enables us to relate fluid flow to the pressure gradient applied by a parameter characteristic of the medium through which it passes, which is expressed by the relation (3) [43].

$$L_p = \frac{J}{\Delta P} \quad (3)$$

where J ($L/h/m^2/\text{bar}$) is the hydraulic flow and ΔP the transmembrane pressure (bar).

3. Results and Discussion

Some key properties reported in the previous studies are summarized in this section. These studies were devoted to the development of porous ceramics using either raw aluminosilicate materials, synthesized materials or waste combined with raw materials.

3.1. Porous Ceramics Obtained from Raw Materials

Table 1 summarizes the properties of some porous ceramic materials that were obtained by using raw materials. The data reveal that porous ceramic materials with satisfactory porosity (44–88%) and compressive strength can be obtained from a variety of raw materials when sintered in the range of 1200 to 1650 °C. Bai 2010, [26] prepared porous mullite ceramics from carbonaceous kaolinite clay, alumina powder and graphite as a pore former using the sintering method. Porous ceramics sintered at 1500 °C led to 36.4% open porosity and 0.3–5 μm pore size (in a narrow range). This higher sintering temperature led to less porosity, and the mullitization was nearly completed. Li et al. [16] prepared porous mullite matrix ceramics from quartz powder, alumina powder, glass powder, ammonium polycrylate aqueous solution (dispersant) and propyl gallate (foaming agent), which

were sintered from 1200 to 1650 °C for 1 h. When sintered at 1550 °C, the open porosity was 29.38% (porosity 81.37%), while the compressive strength and average pore size were 6.25 ± 0.91 MPa and 850 μm , respectively. Lui et al. [21] prepared porous ceramics from photocurable resin and zirconia slurry to perform multi-material printing experiments sintered at 1500 °C. They developed a ceramic multi-material 3D printing apparatus (CMM) with the aim of manufacturing porous ceramics with <100 μm pore size and designable distribution of pores directly. They obtained a pore size of 60 $\mu\text{m} \times 20 \mu\text{m}$. This pore size is the smallest ceramic pore size known that can be directly printed, especially the pore size of 20 μm in the longitudinal direction, which cannot be achieved by other ceramic additive manufacturing technologies.

Table 1. Properties of porous ceramic materials obtained by using raw materials.

Composition	Final Product	Sintering Conditions	Apparent Porosity (%)	Pore Size (μm)	Compressive Strength (MPa)	Ref.
ZrO ₂ powder + SiO ₂ + boron carbide + carbon black	Porous ZrB ₂ -SiC ceramic	1500 °C/2 h	67–78		0.2–9.8	[15]
Quartz powder + alumina powder + glass powder + ammonium polycrylates solution + propyl gallate	Porous mullite matrix ceramic	1200 °C/1 h 1300 °C/1 h 1400 °C/1 h 1500 °C/1 h 1550 °C/1 h 1600 °C/1 h 1650 °C/1 h	~45 ~80 ~82 ~83 81.37 ~81.4 ~88	~750	88.3 ± 13.61 - - - 6.25 ± 0.91 - -	[16]
Tungsten ore tailing (75 wt%) + CaO + Kaolin + polymethyl methacrylate (18 wt%)	Porous ceramics	1200 °C/60 min	44.85	180	14.10	[18]
Alumina powder + milled carbon coal + stearin	Porous ceramic	1530 °C/2 h	-	60 × 20	-	[25]
Carbonaceous kaolinite clay + alumina powder	Porous ceramic	1400 °C/4 h 1450 °C/4 h 1500 °C/4 h 1550 °C/4 h	~43–46 ~44–48 ~36–38 ~17–32	- - - -	- - 42.1 75.9	[26]
Al ₂ O ₃ + SiO ₂ PHMs (0–40 wt%) + epoxy resin	Porous Al ₂ O ₃ Ploy-hollow microspheres (PHM) ceramic	1550 °C/4 h	~77 ~76 ~71 65.0 ~66	51.95 45.51 38.25 38.25 30.14	~0.2 ~0.1 ~1 4 ~1.8	[27]

As a result, highly porous ceramics with good properties (high porosity, compressive strength, etc) can be obtained at sintering temperatures < 1200 °C, although it depends on the materials used. Also, additive manufacturing is a challenging technique because it has advantages such as high design freedom, a short manufacturing cycle and a low manufacturing cost.

Figure 6a,b shows the SEM images of halloysite- and kaolinite-based porous ceramics, respectively, obtained via uniaxial pressing and sintering at 1100 °C with a dwell time of 1 h. There is no defect on the support sections, as observed in these images. Ceramics (a) and (b) show a very compact texture and dense microstructure corresponding to the total porosity of 45 and 33%, respectively, and mechanical resistance to diametrical compression

strength of 3.9 and 3.8 ± 0.5 MPa, respectively. The formation of intergranular contacts led to increased densification of the ceramic. This densification makes them more robust and does not prevent pore formation. Ceramic morphology shows granules with pores of various sizes.

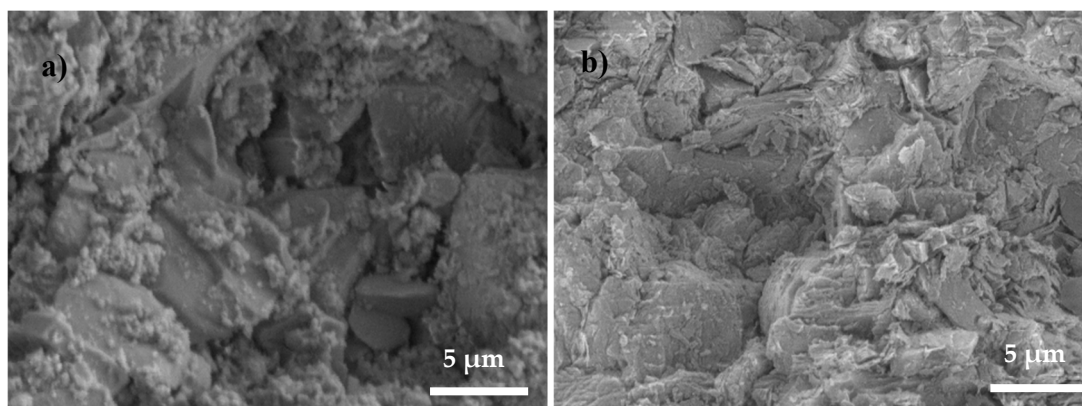


Figure 6. SEM images of Halloysite (a) and Kaolin (b) based porous ceramics (shaped by uniaxial pressing and sintered at 1100 °C).

Barry et al. [9] prepared porous phyllosilicate-based ceramics by freeze-tape casting and sintering at 1200 °C. For that, they prepared four slurries labeled HCR (77% halloysite), KORS (29% kaolinite), KCR (98% kaolin) and KHCR (mixture of KCR and HCR). The SEM images (Figure 7) reveal a difference in the microstructure and texture of all four ceramic disks. According to this study, the pores in the KCR ceramic disks were more textured compared to others, and they noted the formation of the primary mullite in rigid skeleton shape. The SEM images of the KORS ceramic disks show the formation of secondary mullite needles with a relatively small quantity and a disordered structure in a vitreous phase. HCR led to the bulk formation of small mullite particles due to the relatively important vitreous phase in the porous material. X-ray diffraction patterns showed the presence of mullite in all four ceramics.

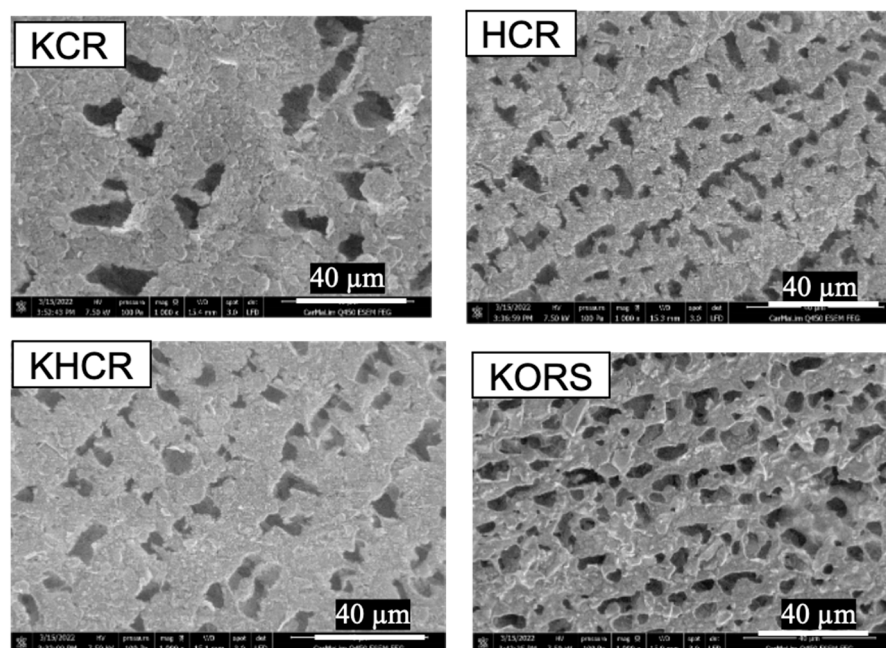


Figure 7. SEM images of porous kaolin- and halloysite-based ceramics (shaped by freeze-tape casting and sintered at 1200 °C).

3.2. Porous Ceramics Obtained from Synthesized Materials

Porous ceramics can be produced by using synthesized materials. Table 2 summarizes the properties of some porous ceramic materials that were obtained by using synthesized materials. Nowadays, the trend is to reduce the environmental impact by limiting the use of synthesized materials in the manufacture of porous ceramics and to optimize the utilization of naturally occurring raw materials (reuse and recycling), such as most clays. Xu et al. [28] prepared porous ceramics from a variety of materials and concluded that there is a possibility to control the pore volume, pore size and other properties of green bodies by adjusting the ratio of the starting materials used or changing the sintering cycle. Despite the high mechanical resistance, the consolidation of such mixtures requires very high temperatures (>1300 °C), thus leading to an increased carbon footprint.

Table 2. Properties of porous ceramic materials obtained by using synthesized materials.

Composition	Final Product	Sintering Conditions	Apparent Porosity (%)	Pore Size (µm)	Compressive Strength (MPa)	Ref.
Al(NO ₃) ₃ ·9H ₂ O + Mg(NO ₃) ₃ ·9H ₂ O + Urea + Soluble starch	Porous ceramics	1400 °C/2 h	35.2–51.6	~0.2–20	~36.1–454.7	[29]
Si ₃ N ₄ + Y ₂ O ₃ + SrCO ₃ + Al ₂ O ₃ + premix solution + polyacrylamide + methylethylenediamine + ammonium persulfate	Porous ceramics	1750 °C/1 h	~47–57	-	52.67–106.33	[28]

3.3. Porous Ceramics Obtained from Raw Materials and Waste

Waste management is a very important issue from both the public health perspective and the industrial point of view because an ever-increasing amount of hazardous materials needs to be disposed of in a safe and economical way. The development of new ceramic, glass and glass-ceramic materials made by recycling waste is acquiring particular importance [44]. A large number of articles have been published by researchers regarding the manufacture of porous ceramics using different types of waste. Table 3 summarizes the properties of some porous ceramic materials that were obtained by using waste combined with raw materials. The incorporation of rice husk ash promotes the formation of high porosity. According to Görhan et al. [45], an increase in rice husk leads to an increase in the apparent porosity and tends to decrease the unit weight. Dong et al. [46] manufactured porous ceramic membranes using waste fly ash, and Zhu et al. [47] manufactured porous ceramic membranes using coal fly. According to their studies, porous ceramic membranes with high porosities were obtained at sintering temperatures lower than 1200 °C. Thus, including some wastes in the formulation of green bodies can help in manufacturing porous ceramics at temperatures < 1200 °C with good properties (porosity, compressive strength, etc.).

Table 3. Properties of porous ceramic materials obtained by using clay materials and waste.

Composition	Final Product	Sintering Conditions	Apparent Porosity (%)	Compressive Strength (MPa)	Ref.
Ground rice husk (5–15 vol%) + brick raw material	Porous clay brick	800 °C/1 h	~39–44.5	~9.5	[45]
		900 °C/1 h	~38–44	~5.75–9.25	
		1000 °C/1 h	~37–43.5	~6–9	
Coffee waste (10–30 wt%) + red clay	Porous red ceramics	1150 °C	~30.2–63.8	~1.8–19.5	[48]

Table 3. Cont.

Composition	Final Product	Sintering Conditions	Apparent Porosity (%)	Compressive Strength (MPa)	Ref.
Wheat straw (4–8 wt%) + clay	Porous clay brick	950 °C	~40–50	-	[49]
Ceramic waste (80%) + flux + cement + clay	Ceramic foam	1000 °C/3 h	~40–83	~0–9.3	[50]
Polished stoneware residue (90%) + soda-lime glass	Highly porous glass ceramic	900 °C/1 h	75.1	2.5	[51]

According to Simonis et al. [52], porous ceramics consist of a high level of porosity, and that results in properties such as high specific area, high permeability and high tortuosity. These factors make ceramic filters effective by physically (non-chemical process) removing suspended solids, filamentous bacteria and protozoa having sizes of several micrometers to nanometers from water (thus used for water treatment). Moreover, the filtration of waste water rejected by many industries reduces emissions that are harmful to the environment [53]. Sobsey et al. [54], compared several household water treatment techniques based on several factors affecting the sustainability of the membrane. It was concluded that ceramic and bio-sand filters were potential options for a sustainable water treatment technique. Shirasaki et al. [55], suggested that due to the fact that the pore sizes of a ceramic filter are not sufficiently small to remove viruses efficiently, a coagulation process as a pre-treatment can be combined with a ceramic water filter for viral removal. They reported that such systems are used in Japan for the treatment of drinking water.

Figure 8 shows the SEM images of halloysite clay and peanut shells (25% mass percent)-based porous ceramic obtained via uniaxial pressing and sintering at 1100 °C, with a soaking time of 1 h. The image shows a very compact texture and dense microstructure related to the total porosity and diametrical compressive strength of 59.74% and 0.92 MPa, respectively. The creation of pores within materials is due to the incorporation of the pore-forming agent (peanut shells). The pores observed vary in size and geometry. The SEM image presents no defect on the analyzed support sections.

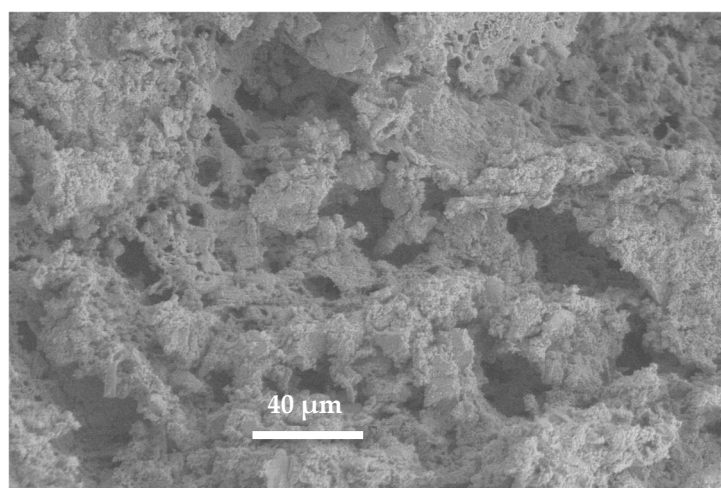


Figure 8. SEM image of halloysite clay and peanut shell-based porous ceramic (shaped by uniaxial pressing and sintered at 1100 °C).

Barry et al. [56] prepared porous ceramics from kaolinitic clay and peanut shells (25% mass percent) via unidirectional pressing and sintering at 900 and 1100 °C with a dwell time of 1 h. There is no defect on the support sections, as observed in these images (Figure 9). According to them, the porous ceramic sintered at 1100 °C (Figure 9b)

had a porous microstructure that is fairly developed with interconnected pores. On the other hand, the sample fired at 900 °C (Figure 9a) had a poorly developed interconnected porosity and a relatively dense structure. The presence of cristobalite within the porous ceramic fired at 1100 °C (Figure 9b) had an effect on the microstructure by modifying the porous architecture.

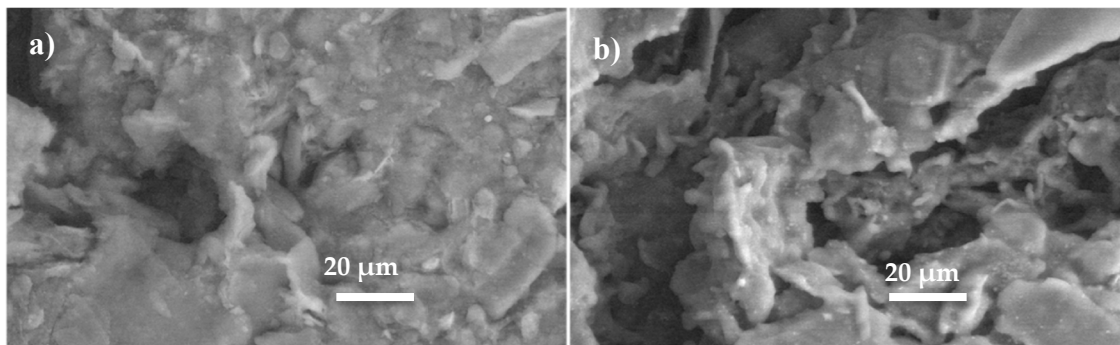


Figure 9. SEM images of kaolinitic clay and peanut shell-based porous ceramics sintered at 900 (a) and 1100 °C (b) [56].

Together with the mechanical properties, the efficiency of these filters for water treatment is of great importance. Water treatment is a process that enables wastewater to be returned to a quality defined by various articles of law and prefectural decrees. There are several water treatment methods, including physicochemical, biological and chemical methods [57–60].

Physicochemical methods, which include coagulation-flocculation, ion exchange, adsorption and ceramic filtration, are one of the most preponderant. Activated carbon was the first adsorbent used for water treatment. Today, other types of natural or synthetic adsorbents are available, such as laterites, clays, resins, etc. The adsorption technique is effective for low concentrations of adsorbate, but it can be relatively expensive depending on the adsorbent used. In general, the disadvantages of adsorption lie both in the competition between the molecules (adsorbate) of different sizes or similar properties and the relatively high price of the commercial adsorbent materials. In a water treatment process, filtration coupled with adsorption makes it possible to improve the retention properties of the filter material. This coupled treatment process is used in Bangladesh to remove arsenic from groundwater with significant efficiency [61]. Nd'e-Tchoup'e et al. [62] showed a removal rate of 90% in a column of multiple layers. Similarly, Shafiquzzaman et al. [63] reported an arsenic removal rate of 86% on ceramic filters after double filtration at two different levels. The study by Barry et al. [56], reported an arsenic removal rate of 95% on the ceramic filters prepared from kaolinitic clay and peanut shells (sintered at 1100 °C). This was due to the fact that, the ceramic material of this filter had a more developed microstructure, and they formed crystalline mullite, which had a strong affinity with arsenic. The presence of mullite and the pores' architecture increases the retention capacity of this filter with respect to arsenic, thus highlighting the impact of mullite on the retention properties of the filters. Barry et al. [56] presented an example of a brief mechanism of arsenic absorption, as illustrated in Figure 10.

There are many types of filters, as presented in Table 4. Ceramic filters use the specific physical and chemical properties associated with porous ceramics, namely: filtration, ion exchange and adsorption on internal and external surfaces. Filtration is based on the gradient retention of particles according to their size and the size of the pores. At the same time, adsorption can be used since it enables the molecules to be attached to the surface of the solid by covalent bonds or specific interactions.

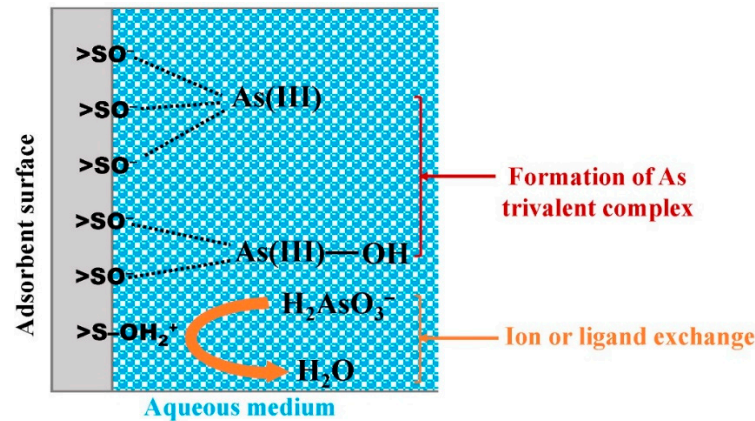


Figure 10. Example of arsenic (III) adsorption mechanism onto a kaolinitic-based porous ceramic [56].

Table 4. Types of filters: costs, efficiency and pollutants that they eliminate.

Filters	Price (Euro)	Pollutant Eliminated	Yield Rate (%)
Reverse osmosis filter	60–400	Microorganisms, particles	85–95
UV filter	150–1000	Parasite, viruses	>86
Ion exchange filter		Heavy metals, limestone	82
Glass fiber filter		Suspended particles	95
Ceramic filter	150–600	Viruses, suspended particles, protozoaires, bacteria	98
Alkali water ionizer filter	400–2000	Suspended particles, bacteria, viruses	92

The permeability of a ceramic filter depends mainly on its physical and geometric characteristics, and it is essentially influenced by the morphological characteristics of the pore space: interconnectivity, pore size and many others. Table 5 shows some permeability values for porous ceramic materials. The difference in permeability values could be due to the presence or absence of particles that can easily foul the membrane pores and subsequently decrease the flow rate. Those with lower permeability values may be the result of lower connectivity between their pores and therefore the presence of a high or low proportion of dead-end pores.

Table 5. Permeability of some clay-based porous ceramics.

Composition	Permeability (L/h.m ² .Bar)	References
Clay + coconut husk + eggshell	14,013	[43]
Kaolinitic clay + peanut shell (sintered at 1100 °C)	53,802	[56]
Kaolinitic clay + peanut shell (sintered at 900 °C)	18,596	[56]
Metakaolin + corn cob ash waste	1359.93	[64]
Clays + cassava starch + bovine bone ash	2902	[65]

Fouling may occur on the surface during filtration, requiring specific cleaning, such as washing the top layer with hot water when the flow rate drops [66]. Fouling is a phenomenon that leads to a loss of performance through the deposition of suspended substances on its external surfaces, at the inlet or inside the pores [67]. As such, the efficiency of the ceramic filters depends on the porosity (the distribution, size and volume of the pores), the tortuosity of the porous network, and the density of the surface-active sites. Hence, the mastery of filter manufacturing technology is essential for controlling the filtration properties [68,69].

4. Conclusions

This paper presents a review on the manufacture and properties of porous ceramics for water filtration. The principle, applications and manufacturing strategies are discussed extensively. For the manufacture of porous ceramics, certain parameters such as compressive strength, porosity and pore size can be effectively increased by controlling the particle size of the material used, additives, sintering temperature and technique used. Concerning filters, it is necessary to improve their performance with antibiofilm substances. For instance, the impregnation of ceramic filters with bioactive compounds, such as silver, is often used to improve their performance, particularly in the removal of micro-organisms. Filters modified with an internal silver deposit are effective in removing at least 99% of protozoa and 90 to 99% of bacteria. The properties of filters can also be improved by moderate incorporation of organic adsorbent or by grafting organic molecules such as alkoxy silane.

Author Contributions: Conceptualization, G.L.L.-N., K.B., D.N., Y.E.H., C.P. and I.Q.M.N.; methodology, G.L.L.-N. and I.Q.M.N.; software, G.L.L.-N. and I.Q.M.N.; validation, G.L.L.-N. and I.Q.M.N.; formal analysis, G.L.L.-N., K.B. and I.Q.M.N.; investigation G.L.L.-N., K.B. and I.Q.M.N.; resources, G.L.L.-N., K.B., D.N., Y.E.H. and C.P.; data curation, G.L.L.-N., K.B. and I.Q.M.N.; writing-original draft preparation, G.L.L.-N. and I.Q.M.N.; writing-review and editing G.L.L.-N. and I.Q.M.N.; visualization, G.L.L.-N. and I.Q.M.N.; supervision, G.L.L.-N., K.B., D.N., Y.E.H. and C.P.; project administration, G.L.L.-N., K.B., D.N., Y.E.H. and C.P.; funding acquisition, G.L.L.-N., K.B., D.N., Y.E.H. and C.P. All authors have agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The authors of this work express their sincere gratitude to the staff of the Institute of Research on Ceramics (IRCER, UMR CNRS 7315) for their availability during this work. The CNRS-JRP GRAAL-EMC2 project is gratefully acknowledged.

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

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