

Geopolymer foams: An overview of recent advancements

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ABSTRACT

Geopolymer foams (highly porous materials) have emerged as one of the most exciting materials over the past few years due to their remarkable properties, low cost and green synthesis protocol, enabling their use in various high added-value applications. Review papers on porous geopolymers are uncommon, and the emphasis has been given to materials processing and properties, while the applications were only briefly addressed. This review aims to fill this gap by presenting a comprehensive literature survey and critical analysis of the most recent and exciting research carried out on geopolymer foams. Up to now, these bulk-type (not powders) materials have been mainly considered as thermal and acoustic insulators. However, besides addressing their use as building material, this review also shows that their use in less investigated, but environmentally and economically relevant applications (e.g. bulk-type adsorbents, pH buffering agents and catalysts), is feasible and might ensure performance and technical advantages over their powdered counterparts. The limitations, challenges and future prospects associated with the different applications are presented. This review shows the remarkable potential of geopolymer foams in high added-value applications, far beyond their historical use as Portland cement replacement, which may encourage the widespread technological use of these materials.

1. Introduction

Geopolymers are an exciting class of aluminosilicate binders [1,2] synthesised at low temperatures, typically below 100 °C [3], but often ambient temperature has been employed to decrease the binder's production cost [4–6]. The term “geopolymer” was coined by Davidovits in 1978 [7] to describe mineral polymers synthesised by geosynthesis, i.e., the chemical reaction of aluminosilicate precursors with alkali polysilicates, yielding Al-O-Si bonds [8]. The alkaline route is the most common approach towards the chemical activation of Si- and Al-rich precursors, but acidic conditions can also be used (e.g. phosphoric acid) [9–11]. Geopolymers have also been referred to in literature as inorganic polymers and alkali-activated materials [12–15]. The distinction between the different terminologies is beyond the scope of this review, but can be found in literature [3,16–21]. In fact, these materials can all be synthesised using the same chemistry [18], and their use in the applications considered in this review is suitable regardless of the calcium content in the precursors. Therefore, here the term “geopolymer” will be used generically.

Geopolymers were first envisioned for fire resistance applications [22]. However, since the early 1980's these materials have been mainly considered as an alternative to ordinary Portland cement, primarily due to their lower embodied CO₂ [23,24], but also to performance advantages (e.g. early compressive strength; greater chemical and heat resistance) [13,14,25]. The use of various industrial waste streams as raw materials, such as fly ash [26,27], metallurgical slags [28,29], glass wastes [30,31], is another advantage, particularly considering the new circular economy paradigm. Nonetheless, and despite tremendous efforts, the full

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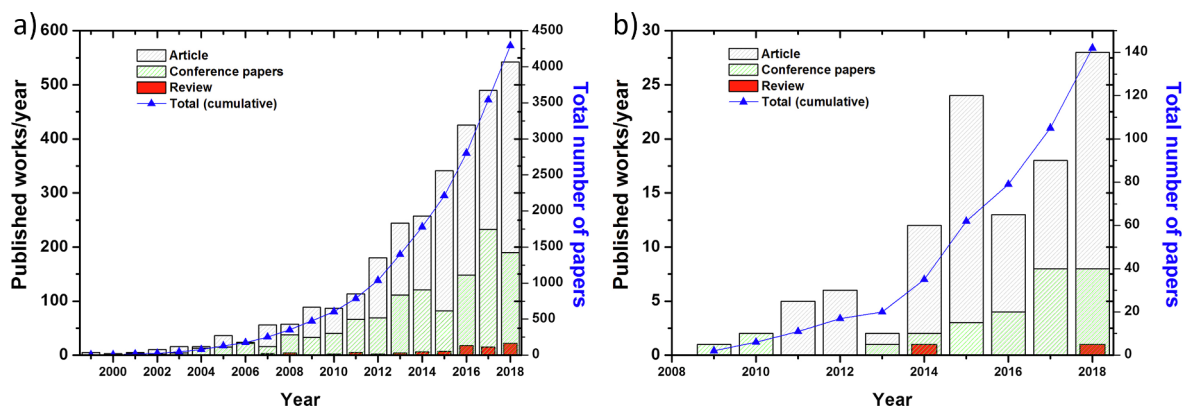


Fig. 1. Number of publications on (a) geopolymers and (b) porous geopolymers over the last 20 years.

potential of geopolymers has yet to be fully exploited [32,33], which is attributed to legislation, social and technical barriers [34]. A key driver to foster the use of geopolymers is by extending their application range to areas where Portland cement does not meet the requirements. In recent years, the use of porous geopolymers, intentionally designed to contain pores, for high-added value applications, such as thermal [35,36] and acoustic insulation [37,38], fire resistance [39,40], adsorbents [41,42] and pH regulators [43,44] has been considered. However, in other industrially relevant applications such as their use as catalysts or catalyst supports [45–49] this strategy (e.g. deliberately introducing porosity in the specimens) has yet to be explored. The interest in geopolymer foams (lightweight solid materials) has sharply increased in recent years, as demonstrated by the number of publications on this topic (see Fig. 1). Review papers focusing exclusively on porous geopolymers are uncommon, the exceptions being [32,50,51]. Nevertheless, these reviews were mainly focused on the processing and properties, while the applications were only briefly addressed. Here, the most promising and recent advances in the use of highly porous geopolymer foams are discussed, and the main challenges for future research identified, enabling their wider use.

2. Methods for identifying relevant literature

A systematic review of literature published over the past 20 years (between 1998 and 2018) focusing on geopolymers was carried out using Scopus in December 2018. Scopus database has around 70 million items and covers ~22,000 peer-reviewed journals. Papers were filtered using the keyword “geopolymer”. A total of 4295 papers, including articles, conference papers and reviews, and excluding book chapters and reprints, were identified. Then, the title and abstract of these papers was screened, by using a content analysis approach, to extract those dealing with porous geopolymers, reducing the number to 142. The initial survey was only used for the estimation shown in Fig. 1. For this initial survey, only porous geopolymers produced by using foaming agents or surfactants were counted, other lightweight materials such as composites and syntactic foams were not considered.

The literature survey used in Section 1 was further expanded by using additional search engines (e.g. Science Direct and Google Scholar) and keywords (e.g. thermal conductivity, sound absorption, adsorbent, pH buffering, catalysts). Results were crosschecked with those obtained using the Scopus database and relevant literature belonging to the scope included. In addition, references cited in the selected papers or citing these papers were also considered for the exhaustive literature review discussed in Section 3 (Potential Applications). The content analysis approach provides an adequate number of results for a systematic review, and it has been used in other review papers [52–54]. It should be highlighted that the literature survey used for the subsequent sections accounts for all porous geopolymer foams, regardless of the foaming method (e.g. foaming agent, air, surfactant). In addition, geopolymer lattices (porous components) produced by direct ink writing were also considered in this review.

This review focuses on the use of porous geopolymers that were intentionally synthesised to contain pores in their structure. Therefore, unless stated otherwise, all references correspond to materials that were deliberately made porous.

3. Geopolymer foams synthesis

In this section, the most relevant synthesis protocols to produce geopolymer foams will be briefly described. It is not our intention to provide a detailed description, as this has already been reported in literature [50].

The most common synthesis route to produce geopolymer foams is by the incorporation of a foaming agent (e.g. hydrogen peroxide, fine metallic powders) [55–58] into the geopolymeric slurry, usually known as the chemical foaming technique. This strategy takes advantage of in-situ reactions of the foaming agent in the alkaline medium, inherent in the alkali activation of aluminosilicate precursors. This process generates gas bubbles which are then trapped inside the slurry during setting, leading to the production of voids in the hardened body. Another strategy to create very porous materials without using foaming agents is by direct addition of gas bubbles [59–63], which can be achieved by using pre-made foams (e.g. prepared by passing air through a diluted surfactant), or foam concentrates which are then vigorously mixed with the slurry to produce a large volume of voids in the specimens.

An alternative approach to produce geopolymer foams is by using sacrificial fillers (e.g. polymers). In this technique, the porosity is generated by the extraction/removal of the fillers. When polymers are employed, thermal and/or chemical treatments are required to remove this filler and create the porous bodies [64,65]. However, the extraction of polymeric fillers is not only challenging, but raises environmental and economic concerns due to required amounts of chemical reagents, and gas emission arising from the polymer decomposition. Okada et al. observed that strong alkaline conditions collapsed polylactic acid (PLA) – geopolymer composites, or at least induced some damage in their structure, while the specimens' hydrothermal treatment also seems to affect the structure integrity [65]. According to these authors, a combination of methods (e.g. alkali and heat treatment) is the most suitable approach for removing the PLA without affecting the geopolymer product. The combination of chemical and thermal treatments was also employed in another work [66], in which the composites (PLA – geopolymer) were first immersed in 15 M KOH solution (72 °C; 24 h), and subsequently heat-treated at 330 °C for 24 h. Specimens with very high porosity, ranging from 66 to 71 vol%, were synthesised, but again the fillers' extraction was accomplished by using a rather complex procedure. An environmentally friendlier alternative to the use of fossil fuel derived materials is the freeze casting technique [67,68], also known as ice-templating, allowing the production of materials with aligned porosity. In this two-step route, the specimens are initially subjected to low temperatures to promote water freezing, and then in the second step (ice sublimation) water is removed from the samples, leaving behind uni-directional aligned pores.

Another recent, and much less investigated, avenue for producing porous geopolymers is through additive manufacturing. This technique can be used to produce complex structures with controlled size and pore distribution. Nevertheless, it has been mainly envisioned to produce geopolymer mortars and concrete components (dense specimens) for building applications where the specimen's strength, rather than their porosity, is the target [69–71]. Nonetheless, the production of highly porous components (e.g. scaffolds, filters) with well-defined and interconnected mm size pores has been reported [72,73]. Porous geopolymer components using the inverse replica of 3D printed sacrificial templates was reported by Franchin and Colombo [66]. The total porosity of these specimens varied between 66 and 71 vol%. However, the extraction of the PLA template required both chemical and thermal treatments which negatively affect the carbon footprint of the produced samples. Recently, the same group has reported a much more environmentally friendly approach to produce geopolymer lattices using direct ink writing [73]. The lattices' porosity ranged from 49.8 to 71.3 vol%, while their compressive strength was 11.5 and 2.0 MPa, respectively. The authors suggested the use of these lattices in applications such as air and water filtration, due to the mesoporosity intrinsic to geopolymeric materials. The use of powder-based additive manufacturing to produce 3D printed geopolymer structures was reported by Xia and Sanjayan [74]. The 3D printed cubic samples had 57 vol% porosity and a compressive strength of 0.7–0.9 MPa, depending on the selected orientation (x or z) in the mechanical tests. Despite their high porosity values, these specimens were not deliberately made porous since the authors' aim was the production of building materials.

The emulsion templating method is another methodology explored for the synthesis of geopolymer foams [75–78]. Usually the geopolymer slurry is mixed with an organic oil, leading to the production of an emulsion. The curing process promotes a saponification reaction, giving rise to a water-soluble soap and glycerol molecules. These products are then extracted (e.g. water washing step) to yield porous geopolymers [75].

4. Potential applications of geopolymer foams

4.1. Thermal and acoustic insulators

Geopolymer foams have important technical advantages (e.g. high thermal stability, green synthesis; non-flammability) over conventional low thermal conductivity materials and, therefore, a significant number of articles focusing on this topic is available. One of the first investigations was performed by Prud'homme et al. [36] in 2010. Silica fume was used as foaming agent to produce geopolymer foams with density of 534 kg/m³ and thermal conductivity between 220 and 240 mW/m K. In the same year, two other studies were performed [79,80]. Vaou and Pnias reported much lower thermal conductivities (as low as 30 mW/m K) by using H₂O₂ to foam perlite-based geopolymers [79]. Shu-heng et al. used aluminium powder to produce highly porous phosphoric acid-based geopolymers [80]. Their thermal conductivity was not provided, but samples having 83% porosity and 7 MPa compressive strength were produced. Since then, the number of investigations on porous geopolymers, and particularly those devoted to the synthesis of thermal insulating formulations, has sharply increased.

The influence of the foaming agent type [81,82] and concentration [83,84], water content [63,85], binder nature [86,87], curing temperature [35,88], among other influential parameters (e.g. mixture composition) [89,90], on the properties of geopolymer foams have been studied. Several studies have observed a decrease in the geopolymers' mechanical performance and density when the foaming agent concentration rises, while the porosity follows the opposite trend. When the foaming agent content exceeds a certain threshold, depending on several factors (e.g. mixture composition, nature of the foaming agent), pore coalescence [82,91] and eventually structure collapse [83] are observed. This phenomenon may be prevented, or at least attenuated, if a surfactant is used to stabilise the liquid–gas interface [62,92]. Surfactants are hugely important as they ensure a more homogeneous pore size distribution in comparison with the single use of foaming agents.

The influence of the foaming agent nature in the geopolymers properties has not yet been truly addressed. The comparison between different studies is hindered by the different synthesis protocols, binder compositions and curing conditions that have been employed. Studies addressing this topic are rare, one exception being the work of Ducman and Korat which studies the use of H₂O₂ and aluminium powder to produce geopolymer foams [81]. The use of H₂O₂ led to the production of smaller sized pores, while much coarser pores were obtained with Al powder. Nevertheless, the reason for this distinct behaviour was not explained. Additional

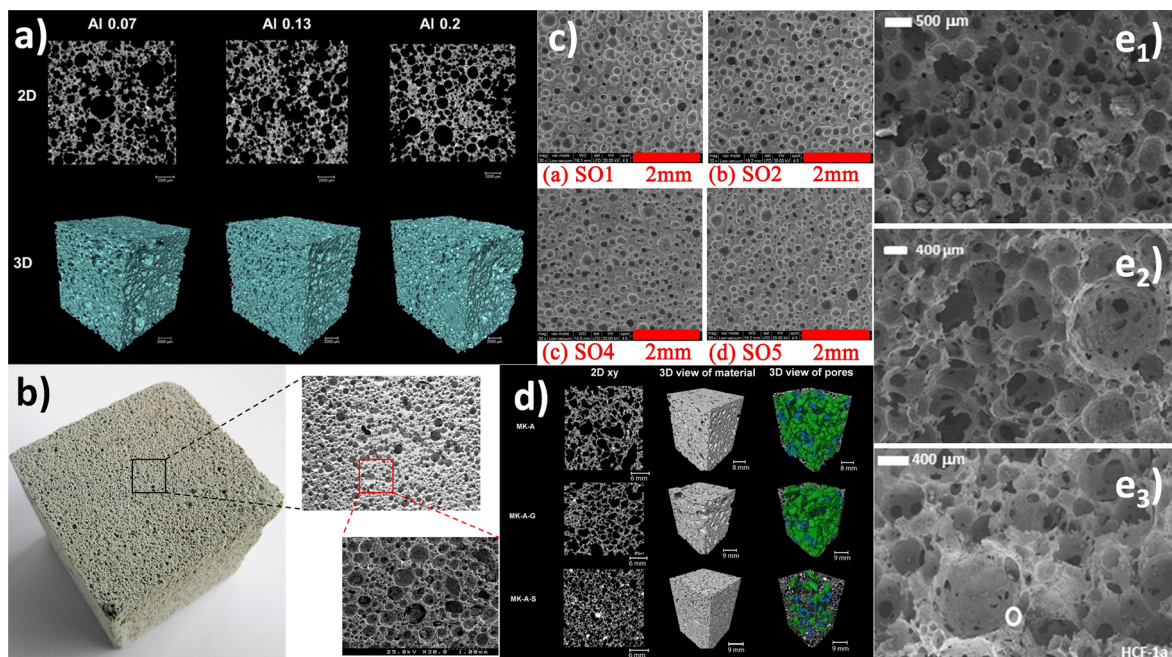


Fig. 2. Geopolymer foams prepared with different foaming agents showing homogeneously distributed pores: Al ((a) [81], (b) [85]), H_2O_2 + vegetable oil [94] (c), aluminium scrap recycling waste [86] (d), Si (e_1), protein (e_1) and Si + protein (e_3) [96].

studies allowing a direct comparison between different foaming agents are deeply needed to shed light on this influencing parameter. Nevertheless, adjusting the synthesis protocol enables the use of different foaming agents (e.g. H_2O_2 [83,93,94], Al [81,85,95], Si [36,96], limestone [97]) to produce highly porous geopolymer with homogeneous pore size distribution. Some examples are given in Fig. 2. The selection of the foaming agent should consider other parameters besides their direct effect on the performance, such as their carbon footprint, cost and availability.

Pore size and its distribution are known to strongly affect the thermal conductivity of foams, regardless of their nature (e.g. ceramics, polymers, metals). For similar porosity levels, lower thermal conductivity will be obtained as pore size decreases, due to the reduced heat transfer between solid phases [98,99].

Curing temperature [100,101] and activator concentration [102] can also be used to control foaming kinetics and setting time. Henon et al. observed higher and faster expansion when increasing temperature [101]. Denissen et al. also reported that increasing temperature causes faster foaming [100]; however, the influence of temperature was dependent on the $\text{SiO}_2/\text{Na}_2\text{O}$: higher ratios led to greater expansion at higher temperatures, but when using a low $\text{SiO}_2/\text{Na}_2\text{O}$ ratio, the highest volume expansion was achieved at 20–25 °C. This behaviour was attributed to the complex interaction between foaming kinetics, setting time and the physical properties of the paste. The viscosity of geopolymer slurries and their setting time can also play a significant role on the foams' ability to retain bubbles within their structure. Novais et al. observed a significant increase in the foams' expansion when decreasing the molarity of the activator, ultimately leading to higher total porosity, due to the lower viscosity of the slurries [102].

Table 1 summarises the thermal conductivity, porosity, density and mechanical performance of various literature studies. The ultimate comparison between these studies is hindered by the fact that different foaming agents, raw materials, water contents and curing regimes have been employed. Nevertheless, the thermal conductivity and apparent density were plotted, and results are shown in Fig. 3. The thermal conductivity of geopolymer foams typically falls below 200 mW/m K, and can be as low as 30 mW/m K [79]. The lowest values reported to date are inferior to those of some commercial low thermal conductivity materials, such as gypsum plasterboard, wood fibre board, aerated concrete, but are slightly superior to those of glass wool. These results demonstrate the interesting potential of geopolymer foams for low thermal conductivity applications. Despite this, the foam synthesis protocol (e.g. curing regime, activator concentration and content) must be carefully considered to ensure low energy consumption and carbon footprint. User-friendly procedures, such as the use of a low alkalinity source and curing at ambient temperature (avoiding energy inputs), should be adopted to fully explore the environmental advantages over conventional thermal insulating materials, such as polymer foams. A major driver would be the use of waste-based materials as activators, instead of commercial alkaline solutions. This possibility has received little attention [103–105], but is expected to be a very relevant topic in the near future, as it may strongly reduce the carbon footprint of these remarkable materials.

Besides very low thermal conductivity, thermal insulating materials must also present high vapour diffusion resistance, otherwise water can diffuse into the materials which may result in a severe loss in their insulation performance. High water uptake values have been reported by several authors: 26.2–41.1% [118], 31.9–56.3% [119], 30–50% [82] and 42.1–111.7% [85]. Nevertheless, this drawback can be overcome by the production of bi-layered foams, having a thin dense surface layer ensuring high vapour diffusion resistance, associated with a thicker highly porous layer. This smart solution has already been demonstrated in literature [83,120] as shown by the photographs presented in Fig. 4.

Table 1
Bulk density, total porosity, compressive strength and thermal conductivity of various geopolymer foams reported in literature.

Bulk density (g/cm ³)	Total porosity (%)	Compressive strength (MPa)	Thermal conductivity (mW/m K)	Reference
0.3–0.7	74–89	0.2–0.8	30–55	[79]
0.64	83	1.3	45	[106]
0.15–0.30	72–85	0.7–2.2	62–85	[88]
0.58–0.73	69–76	–	73–91	[97]
0.24–0.37	75–81	0.4–1.4	74–90	[35]
0.43–0.85	74–87	0.6–4.3	79–170	[85]
0.44–1.10	48–81	0.26–21.0	82–227	[102]
0.40–0.64	–	1.9–3.4	83–127	[107]
0.26–0.48	–	0.5–3.3	84–140	[93]
0.31–0.36	70–82	1.45–1.65	95–139	[108]
0.33–0.85	–	1.8–5.2	109–170	[83]
0.56–1.20	42–73	1.2–8.9	107–432	[84]
0.37–0.74	66–83	0.3–11.6	110–170	[94]
0.27–0.48	77–88	1.2–5.5	110–150	[109]
–	64–87	–	120–250	[110]
–	–	–	130–200	[111]
0.38–0.47	83–86	1.1–2.0	140–150	[86]
0.6–0.8	–	–	150–600	[112]
0.60–1.50	–	3–50	150–500	[37]
–	30–70	–	150–600	[95]
0.5	80	–	160	[89]
0.14–1.02	32–63	3.2–44.8	183–646	[113]
1.0–1.7	44–56	3.6–11.9	190–440	[114]
0.92	54.5	7.3	210	[109]
0.53	–	–	220–240	[36]
0.86–1.09	54.8–63.1	1.57–2.97	267–334	[115]
–	50	15	300	[90]
–	32–52	–	420–670	[116]
0.63–0.79	60–75	3.5	581–700	[117]
0.23–1.0	–	0.26–5.9	–	[91]
0.26–0.84	62–89	0.38–26.0	–	[60]
0.97–1.17	–	4–12	–	[38]

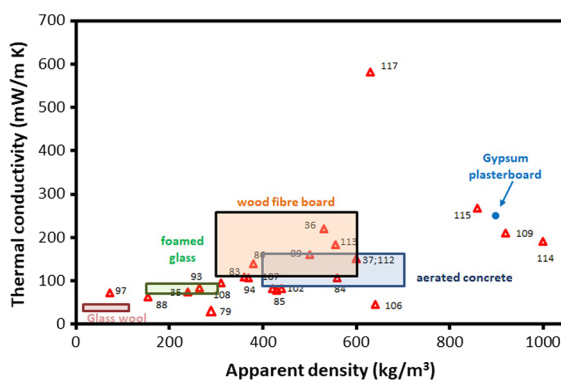


Fig. 3. Thermal conductivity of various geopolymer foams. Typical thermal conductivity ranges for commercial building materials were also included for comparison.

Sound absorbent materials are also of the utmost importance to address the increasing levels of noise pollution [121]. This is particularly relevant when considering building materials, since sound absorbents enhance the interior acoustic comfort for inhabitants and alleviate the health risks (e.g. sleep disturbance) [122] associated with sound pollution exposure. The acoustic performance of geopolymer foams has rarely been addressed, with few exceptions to date [38,61].

Nevertheless, these studies provided valuable information regarding the potential of geopolymer foams to act as acoustic barriers, besides studying influencing parameters on their performance such as porosity and bulk density [37,38], curing temperature [38], type of raw materials [37,89] and activating solution [38,89]. Luna-Galiano et al. observed an increase in the sound absorption coefficient (α) over the frequency range (100–5000 Hz) when the open porosity increases from 11.5 to 28.9% [38]. The spectrum showed two distinct peaks, one in the low frequency region (~500 Hz) and another at higher frequencies (~2500 Hz). The maximum α was roughly 0.25 (~2500 Hz). Similar findings were reported by Papa et al. where two absorption peaks were also observed, but at different ranges (between 500–3000 Hz and 3000–5000 Hz) [89]. Depending on the type of metakaolin and on the activating solution, the sound absorption ranged from 0.45 to 0.9 in the frequency ranges 1000–1500 Hz and 4200–6500 Hz. A different

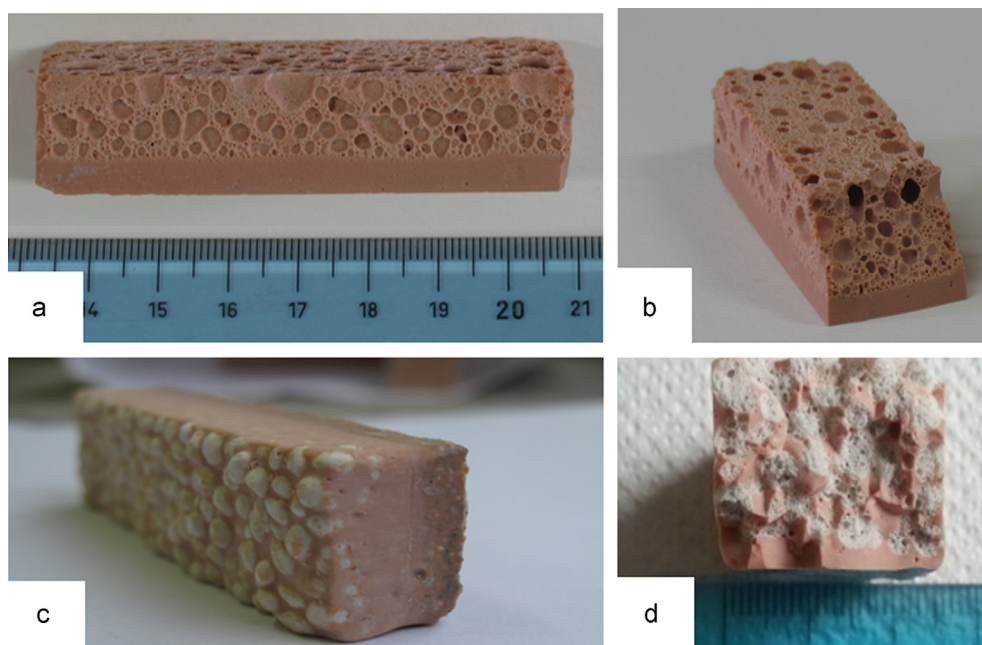


Fig. 4. Digital photographs of bi-layered geopolymers: (a and b) paste, (c) mortar and (d) composite containing glass spheres [83].

acoustic absorption trend was reported by Stolz et al., in which a very high α (up to ~ 0.85) was observed in the low frequency range (125–250 Hz), which then rapidly decreases to ~ 0.15 in the range of 500–2000 Hz, before increasing again at higher frequencies [61]. The influence of the raw materials ratio (fly ash:slag) and sample thickness on the geopolymer foams' acoustic performance was studied by Zhang et al. [37]. Fly ash partial substitution by granulated blast furnace slag (30%) induced only minor changes in the sound absorption behaviour, while the use of thicker samples increased the sound absorption in the lower frequency range but was ineffective in the higher range. These specimens showed very high α (0.7–1.0) in the low frequency range (from 40 to 150 Hz). Hung et al. studied the influence of the foams' bulk density on α , with lower densities inducing higher sound absorption over the frequency spectrum (100–4000 Hz) [123]. The lightest specimen (0.4 g/cm^3) showed very high α ranging from 0.5 (in the low frequency region) to 0.9 (in the higher frequency region), this being the most effective (geopolymer foam) sound absorbent reported to date. These investigations demonstrate the feasibility of using geopolymer foams as sound absorbents. Nevertheless, further studies are required to validate previous investigations, and clarify the role of relevant parameters such as the nature of the pores (open or closed), their size distribution and tortuosity. All the studies reported above showed interesting sound absorption only at specific frequencies, but fairly poor absorption behaviour in other ranges, the exception being [123] in which α was above 0.4 over the entire frequency range of 100–4000 Hz.

Another very desirable property of building materials is their ability to passively adjust the humidity levels inside buildings. This feature, associated with the materials' capacity to store and release moisture when exposed to daily/cyclic humidity variations, may decrease buildings' energy consumption and enhance the indoor environment quality [124–126]. The moisture buffer value (MBV) is often used to measure the amount of water adsorbed or desorbed by a hygroscopic material per open surface area during a certain period of time [127]. Hygroscopic materials such as wood [124], cellulose-based materials [128] and modified-mortars [129,130] have the ability to modulate indoor humidity fluctuations, without consuming additional energy [131]. The ability of mortars to control indoor humidity fluctuations can be enhanced by using foaming agents [127,132], superabsorbent polymers [130] or porous adsorbent aggregates [133]. The MBV ($\text{g/m}^2 \Delta\%RH$) of Portland cement-based mortars is typically classified as “good” ($1.0 < MBV < 2.0$) [130,132,134] according to the Nordtest protocol [135]. Surprisingly, the possibility of using geopolymers to buffer the daily humidity variations inside buildings has been almost neglected. The exception is the work of De Rossi et al. [114]. Waste-based geopolymer mortars having various porosities were prepared, and the MBV of the reference mortar ($0.80 \text{ g/m}^2 \Delta\%RH$) was substantially improved (up to $5.61 \text{ g/m}^2 \Delta\%RH$) by increasing the mortars' porosity. The MBV shown by these lightweight geopolymer mortars is the highest reported to date for inorganic binder materials. Besides their very high MBV, the mortars also showed low thermal conductivity (0.19 W/m K). These promising results demonstrate the feasibility of producing multifunctional geopolymers.

4.2. Adsorbents

The development of low cost and environmentally friendly adsorbents, such as waste-based geopolymers, might be a stimulating approach to depollute industrial wastewaters and contribute towards cleaner production. This is because their synthesis can be performed with a fairly low energy input, provided that wastes are used as solid precursors, the quantity of activating solution is kept at low values, and that their synthesis is performed at room temperature, mitigating the release of greenhouse gases. Furthermore, their reuse after

exhaustion in other applications (e.g. as filler or aggregate in the production of new building materials) is feasible and straightforward due to the strong binding of the pollutants to the geopolymer matrix, these being crucial advantages over the benchmark adsorbent activated carbon, which has very high production costs [136] and whose recovery after use is challenging. This possibility has long been recognised as a promising alternative to activated carbons [137,138], due to the geopolymers' ability to exchange cations with the solution [139]. Recent reviews on the topic are available [54,140,141]; however, none of these differentiated between the use of bulk-type and powdered geopolymer adsorbents, and this will be addressed here. Al-Zboon et al. reported a lead uptake of 81 mg/g when using coal fly ash-based geopolymer powders [142], while Cheng et al. reported even higher lead uptake (~ 100 mg/g) for metakaolin-based powders [143]. The same concept can also be applied for extracting dyes from wastewaters, for example, Liu et al. produced a floatable and permeable geopolymer block [144]. However, prior to adsorption the geopolymers were ground and passed through a 100 mesh sieve. Very high methylene blue removal (50.7 mg/g) was reported, but despite these remarkable results, the powdered geopolymers cannot be directly used in packed beds, or easily retrieved. Recently, the possibility of using monolithic bodies (e.g. membranes) instead of powders has attracted the interest of the scientific community, this being a safer and easier strategy, in comparison with the use of nano- or micro-sized powders, allowing their direct use in packed beds, without the need of support materials. Ge et al. used a metakaolin-based geopolymer cylindrical membrane to remove Ni^{2+} from a synthetic wastewater without the need of post-separation step [145]. Cylindrical discs were used by Novais et al. to extract lead from wastewaters [42]. Despite the poor lead uptake shown by the geopolymer monoliths, ranging from 0.95 to 6.34 mg/g, in comparison with powdered geopolymers [142,143], this was one of the first investigations concerning the use of monolith adsorbents (bulk-type, not powders). Another bulk-type geopolymer adsorbent was reported [146]. The maximum adsorption capacity for the geopolymer-supported zeolites was 37.9 mg/g. A cylindrical mesoporous adsorbent for dyes removal was reported by Salehi and Kani [147]. The adsorbent had a specific surface area (SSA) of $56.6 \text{ m}^2/\text{g}$ and an average pore diameter of 20 nm. The maximum adsorption capacity was 46.6 and 46.4 mg/g, respectively, for basic violet and malachite green oxalate. Monolithic foamed geopolymers have been used by Bai et al. for extracting copper and ammonium, with $\sim 87\%$ removal for copper and 95% for ammonium, corresponding to an uptake of 0.54 and 0.57 mg/g, respectively [72].

Another stimulating strategy has been reported by Tang et al. [148]: the use of metakaolin geopolymer spheres showing high SSA ($\sim 54 \text{ m}^2/\text{g}$) and 60% total porosity (see Fig. 5). The spheres affinity towards Cu^{2+} , Pb^{2+} and Ca^{2+} was demonstrated, with maximum uptake values being 35, 46 and 24 mg/g, respectively.

Recently, another group has synthesised waste-based geopolymer spheres (~ 3 mm), and then evaluated their performance to extract methylene blue (one of the most studied dyes due to its colour stability over a useful pH, and the possibility of using visible spectroscopy to evaluate its concentration change over time) [149]. The spheres could be used in multiple adsorption/regeneration cycles having a cumulative methylene blue uptake of ~ 80 mg/g, which ranks them amongst the highest ever reported for geopolymer adsorbents (powdered and bulk-type). Fig. 6 shows a typical SEM micrograph of the spheres after 8 adsorption/regeneration cycles, demonstrating that the integrity of the spheres was preserved even after being used for more than 200 h.

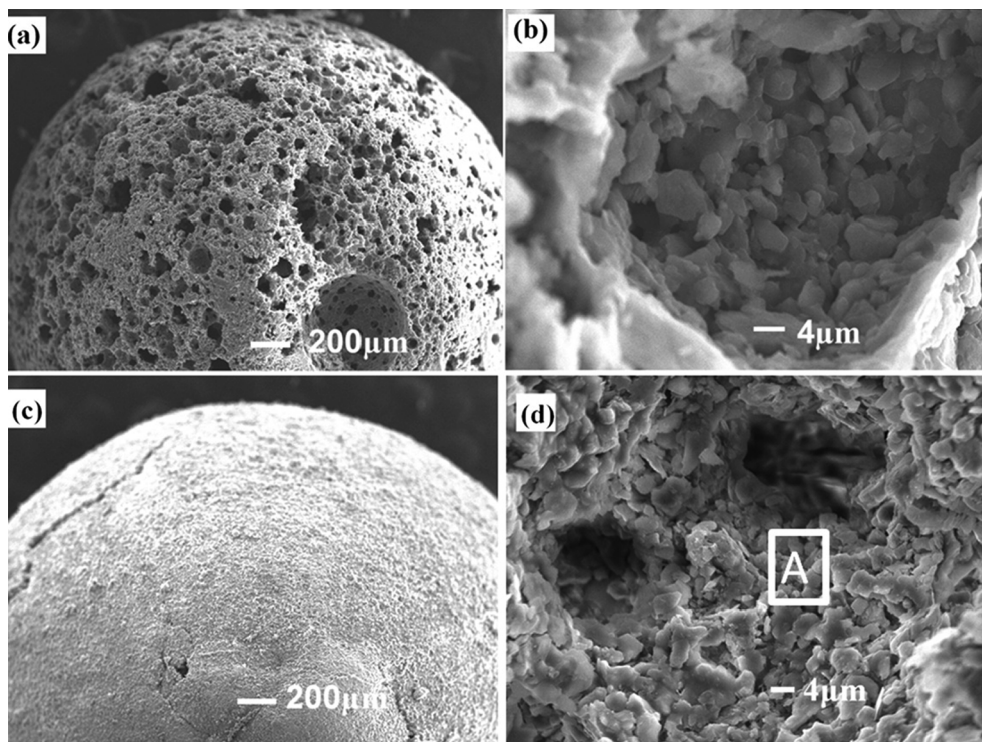


Fig. 5. SEM images of the surface of porous geopolymer spheres: (a) exterior surface of the spheres and (b) the pore microstructure, (c) exterior surface of the spheres without adding K12, (d) the pore microstructure after adsorption process on Cu(II) [148].

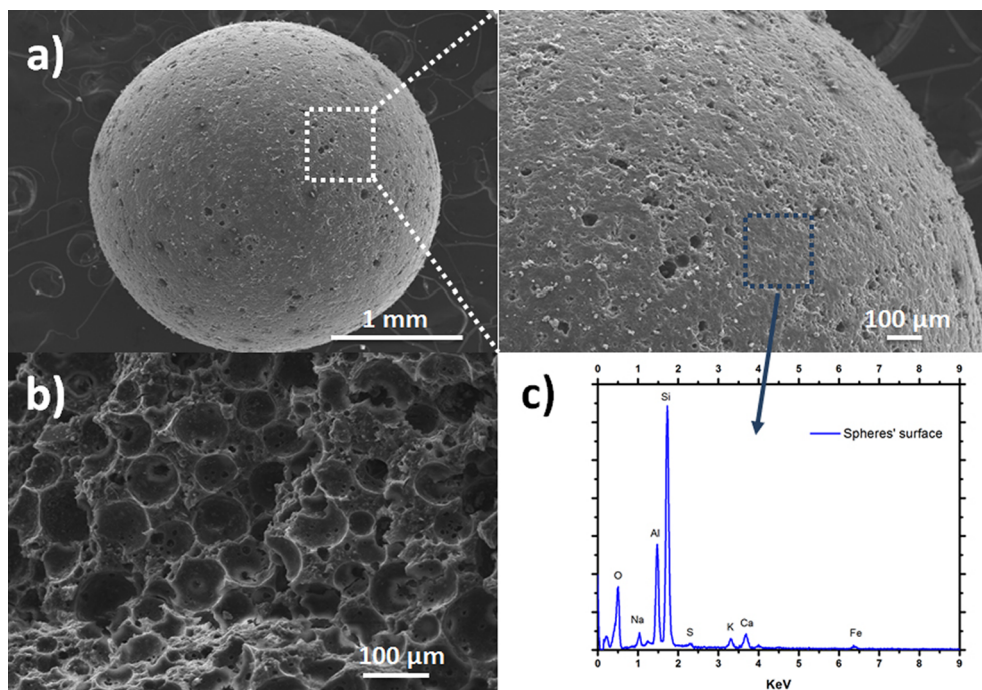


Fig. 6. SEM micrographs of the spheres' surface (a) and inner part (b) after eight regeneration cycles, illustrating the microstructural changes induced in the geopolymer spheres by the multiple adsorption and thermal regeneration cycles. Fig. 6c presents the EDS spectrum of the geopolymer sphere surface [149].

To better understand the performance of the bulk-type geopolymer adsorbents (encompassing monoliths, granules produced from porous monoliths, and spheres, but not powders) in comparison with their powdered counterparts, various literature studies are presented in Table 2 and Fig. 7 for heavy metals, and Table 3 and Fig. 8 for dyes extraction.

The comparison between literature values should be conducted with caution due to differences in the experimental conditions (see Table 2). Nevertheless, the comparison between the heavy metals' uptake clarifies the merits of the different strategies. Fig. 7 shows that bulk-type adsorbents behave surprisingly well in comparison with their powdered counterparts, considering that they are expected to show much lower SSA. The maximum Cu^{2+} uptake reported to date when using bulk-type adsorbents, in this case geopolymer/alginate hybrid spheres (~ 2 mm in diameter), was 60.8 mg/g [152], this being roughly only 33% lower than that reported by Wang et al. when using powders (size not provided) [138]. A much higher uptake was reported in [165] (152.3 mg/g) – however, this value was predicted by using a kinetic model (Langmuir), and is not an experimental value. In fact, the maximum experimental values were always below 60 mg/g.

Ge et al. also reported a Ni^{2+} uptake of 45.2 mg/g when using a cylindrical membrane (diameter = 40 mm; height = 10 mm) [41], which is slightly superior to that reported by Kara et al. by using 150 μm sized powders [167]. Even more impressive results for Pb^{2+} extraction were reported by Tang et al. [157]. A remarkable uptake of 626.2 mg/g was achieved by using geopolymer microspheres ($d = 100 \mu\text{m}$). This value is 2.4 times higher than the maximum lead uptake reported for powdered geopolymers [162] (size of the powders not given). However, the authors did not explain how the spheres could be recovered after their exhaustion. Considering their narrow size, a filtration step would most probably be required, similar to that happens with powders. This is opposed to the practical advantage of using larger size monoliths that are much easier to extract after use.

Up to now, only three studies considered the use of bulk-type geopolymer foams (membranes and spheres) to extract dyes from wastewaters [149,168,169]. The performance of monoliths, spheres and powdered adsorbents is compared in Fig. 8. The use of spheres promotes higher (30.1 mg/g) [149] dye uptake in the 1st adsorption cycle in comparison with the use of cylindrical discs ((15.4 mg/g) [87] and (17.3 mg/g) [169]). The methylene blue uptake shown by the geopolymer spheres (30.1 mg/g) is superior to several other geopolymer powders: 0.7 mg/g [170], 2.7 mg/g [171], 3.0 mg/g [172], 14.8 mg/g [173,174], 19.7 mg/g [175], 24.6 mg/g [176], 25.6 mg/g [177]; it was slightly inferior to others [137,178], and roughly 1.7 times lower than that reported by Liu et al. [144]. However, the bulk-type samples (spheres and membranes) can be easily retrieved and regenerated multiple times, leading to cumulative uptakes several times superior to those obtained with powdered geopolymers. The methylene blue cumulative uptake by the membranes after 9 adsorption cycles (84.9 mg/g) is the highest value ever reported for geopolymers, this being ~ 1.7 times higher than the highest value reported for powdered geopolymers [144]. These impressive results clearly demonstrate that the use of porous bulk-type specimens, instead of powders, could be an innovative and highly effective solution for wastewater treatment systems.

The results shown in this section demonstrate that the use of geopolymer foams for depolluting wastewaters might ensure similar, or even higher performance, in comparison to powdered geopolymers. The use of monoliths is a safer and easier strategy, allowing their direct use in packed beds, without the need of support materials. Nevertheless, additional investigations must be carried out to

Table 2

Maximum heavy metals adsorption capacity of various geopolymer foams (bulk-type adsorbents) and powdered-type adsorbents reported in literature.

Adsorbent shape	Heavy metal	C ₀ (ppm)	T (°C)	pH	Equilibrium time (h)	Removal efficiency (%)	q _{max} (mg/g)	Reference	
Bulk-type	As ⁵⁺	0.120	–	7.6	72	–	0.1 ^b	[150]	
	Cu ²⁺	3	RT	–	6	87 ^a	0.5 ^b	[72]	
	Cu ²⁺	250	–	3	24	–	7.8 ^b	[151]	
	Cu ²⁺	100	25	5	60	–	35.5 ^b	[148]	
	Cu ²⁺	120	25	5	48	–	52.6 ^c	[145]	
	Cu ²⁺	90	25	–	42	50 ^b	60.8 ^b (62.5°)	[152]	
	Cu ²⁺	100–200	40	6	3	–	113.4 ^c	[153]	
	Cs ⁺	250	30	7	6	–	50.8 ^b	[154]	
	NH ₄ ⁺	3	RT	–	24	95 ^a	0.6 ^b	[72]	
	NH ₄ ⁺	35.7	–	–	6	30–65 ^a	Not given	[155]	
	Ni ²⁺	700	10	5	–	73.3 ^a	45.2 ^b	[41]	
	Pb ²⁺	50	RT	5	24	–	6.3 ^b	[42]	
	Pb ²⁺	140	RT	–	4	99.4	16.5 ^b	[156]	
	Pb ²⁺	500	25	5	120	–	37.9 ^b	[146]	
	Pb ²⁺	100	25	5	60	–	45.6 ^b	[148]	
	Pb ²⁺	200	25	4	24	–	626.2 ^b	[157]	
	Zn ²⁺	–	–	–	2.5	–	82	1.3 ^b	[158]
	Zn ²⁺	140	RT	–	24	–	36.5	7.4 ^b	[156]
	Powder	Cd ²⁺	50–500	25	5	–	–	3 ^b	[159]
Cd ²⁺		10–50	35–70	–	10–90	–	7.82 ^c	[160]	
Cd ²⁺		–	–	5	7	–	26.2 ^c	[161]	
Cd ²⁺		100	45	4	24	–	75.7 ^b (76.1°)	[143]	
Cd ²⁺		20–3000	–	–	7	–	98.10 ^c	[162]	
Co ²⁺		–	45	–	24	–	~66 ^c	[163]	
Cr ³⁺		100	45	4	24	–	10.2 ^b (10.9°)	[143]	
Cr ³⁺		20–500	–	–	7	–	21.8 ^c	[162]	
Cu ²⁺		50–500	25	5	–	–	15 ^b	[159]	
Cu ²⁺		55–1700	–	–	4–6	–	40.0 ^b	[164]	
Cu ²⁺		100	25	6	2	87.98	44.0 ^b	[165]	
			45	–	–	93.91	47.0 ^b		
Cu ²⁺		20–500	–	–	7	–	44.7 ^c	[162]	
Cu ²⁺		100	45	4	24	–	54.5 ^b (53.9°)	[143]	
Cu ²⁺		–	45	–	24	–	~77 ^c	[163]	
Cu ²⁺		~748	45	–	0.5	–	77.3 ^b	[166]	
Cu ²⁺		50	30	6.2	72	–	92.0 ^b	[138]	
Cu ²⁺		–	25	6	–	–	96.8 ^c	[165]	
			45	–	–	–	152.3 ^c		
Cs ⁺		50–500	25	5	–	–	43 ^b	[159]	
Ni ²⁺		50–500	25	5	–	–	1 ^b	[159]	
Ni ²⁺		10–50	35–70	–	10–90	–	7.28 ^c	[160]	
Ni ²⁺		25–600	25	7.25	~1	–	42.6 ^c	[167]	
Pb ²⁺		10–50	35–70	–	10–90	–	7.54 ^c	[160]	
Pb ²⁺		50–500	25	5	–	–	35 ^b	[159]	
Pb ²⁺		140	–	5	120	81 ^a	81.0 ^b	[142]	
Pb ²⁺		100	45	4	24	–	100.0 ^b (100.8°)	[143]	
Pb ²⁺	20–3000	–	–	7	–	261.2 ^c	[162]		
Zn ²⁺	50–500	25	5	–	–	2 ^b	[159]		
Zn ²⁺	20–500	–	–	7	–	35.9 ^c	[162]		
Zn ²⁺	25–600	25	6.39	~1	–	74.5 ^c	[167]		

^a Maximum removal efficiency values extrapolated from the experimental data.

^b Maximum uptake extrapolated from the experimental data.

^c Value predicted from kinetic model.

fully demonstrate the monoliths' technical advantages over powdered materials. In addition, most of the studies were performed using synthetic wastewaters, while the adsorbents' potential to treat real industrial effluents, having several pollutants in their composition, remains unexplored.

Another exciting possibility, scarcely investigated to date, is the use of geopolymers for CO₂ adsorption. Pioneering work was performed by Minelli et al. [181], in which a geopolymer monolith (size not provided) was used to evaluate CO₂, CH₄ and N₂ adsorption. CO₂ adsorption was found to be higher than that of the other lighter gases, the maximum value reaching 0.62 mmol/g (1 atm). Recently, the same group reported much higher values (up to 2.5 mmol/g at 1 atm) by using geopolymer-zeolite composites [182]. These are promising results, considering that no foaming agent was used. In fact, the possibility of producing geopolymer foams with tailored porosity is expected to further enhance their adsorption potential, suggesting that geopolymer composites might play a relevant role in much needed CO₂ abatement [183].

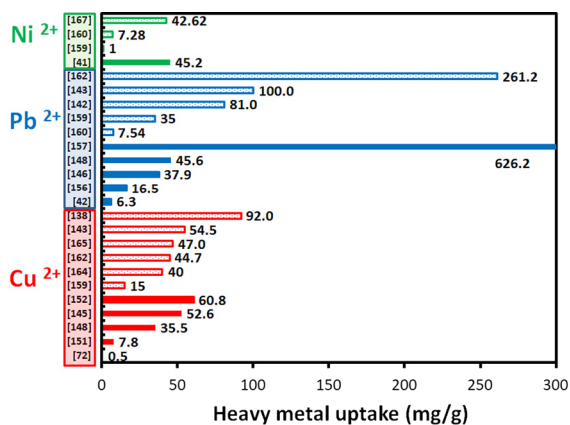


Fig. 7. Heavy metals uptake of various geopolymer adsorbents reported in literature. Bars filled with colour correspond to bulk-type adsorbents and bars with a dotted pattern to powdered adsorbents. The lead uptake achieved with the geopolymer microspheres reported in [157] should be read as 626.2 mg/g.

Table 3

Maximum dyes adsorption capacity of various geopolymer foams (bulk-type adsorbents) and powdered-type adsorbents reported in literature.

Adsorbent shape	Dye	C ₀ (ppm)	T (°C)	pH	Equilibrium time (h)	Removal efficiency (%)	q _{max} (mg/g)	Reference
Bulk-type	Methylene blue	1–50	RT	5.9–9.6	30	64.8	15.4 (1st adsorption) ^b	[168]
					48.4	109.6 (6th adsorption) ^b		
		1–75	RT	7–10	24	~75	17.3 (1st adsorption) ^b	[169]
					68	39.2 (5th adsorption) ^b		
10–250	RT	5.6–10	24	90.3	90.3	30.1 (1st adsorption) ^b	[149]	
				84.9	79.7 (9th adsorption) ^b			
Powder	Methylene blue	1.3	–	–	4	92.8	0.7 ^c	[170]
					30	86.8	2.7 ^b	[171]
		10–50	28	3–10	3	100 ^a	3.0 ^b	[172]
					3	–	14.8 ^b	[173]
		~30	–	–	3	–	14.8 ^b	[174]
					4–7	–	19.7 ^b	[175]
		30–650	–	–	12	–	24.6 ^b	[176]
					10	98	25.6 ^c	[177]
		50	25	–	10	–	37.0 ^c	[178]
					48	–	38.4 ^c	[137]
		~2–15	25	–	48	–	50.7 ^b	[144]
					~4	100 ^a	~78 ^b (276.9°)	[179]
		5–60	20–70	2–11	~4	–	24.8 ^a	[171]
					100	–	27.0	[180]
~0.3–3	30–40	6.3	100	–	–			
			48	25 ^a	–			
–	25	–	48	–	–			
			0–4	–	–			
25–300	55	4.5	0–4	–	–			
			–	–	–			
Direct sky blue 5B	20	–	1.7	–	–			
			0.5	–	–			
Basic violet 5BN	6	–	–	–	–			
			–	–	–			

^a maximum removal efficiency values extrapolated from the experimental data.

^b maximum uptake extrapolated from the experimental data.

^c value predicted from kinetic model.

4.3. pH regulators

The presence of free alkalis in the geopolymers framework remaining after geopolymerisation has been mostly considered as a drawback, both for durability [184] and aesthetic reasons. These alkalis are prone to diffuse into the geopolymers' surface and react with atmospheric CO₂ forming white deposits known as efflorescence [185]. This feature may be problematic for structural applications, especially those envisioned for moist environment, and different approaches are being proposed to inhibit or mitigate its impact on the materials' properties [184,186,187]. However, for other applications (e.g. pH buffering) the presence of free alkalis available for leaching is a desirable feature. Geopolymer foams with tailored and prolonged alkalis leaching might be a promising solution for applications where a narrow and strict pH fluctuation is required to preserve high efficiency yields (e.g. wastewater treatment and anaerobic digestion) [188]. However, only a few investigations were performed to date. Pioneering work was performed by Bajare and Bumanis on the use of monolithic specimens to adjust pH [189]. Cubic geopolymers (size not given; 3 g) were immersed in water and then the OH⁻ release with time was measured to assess their pH buffering ability. The samples' porosity was evaluated by comparing the SSA before and after the leaching tests. For some compositions, a major increase in the SSA from 4–6 to 118 m²/g was observed, while for those doped with glass powder a smaller increase was seen (from 0.7 to ~10 m²/g). The samples showed very distinct leaching behaviour, those experiencing higher SSA fluctuation leaching the greatest amounts of OH⁻ (up to 0.0270 mol/dm³.g), but with a significant drop in pH during the tests (Δ pH = 3; Δ pH – difference between the initial and final pH).

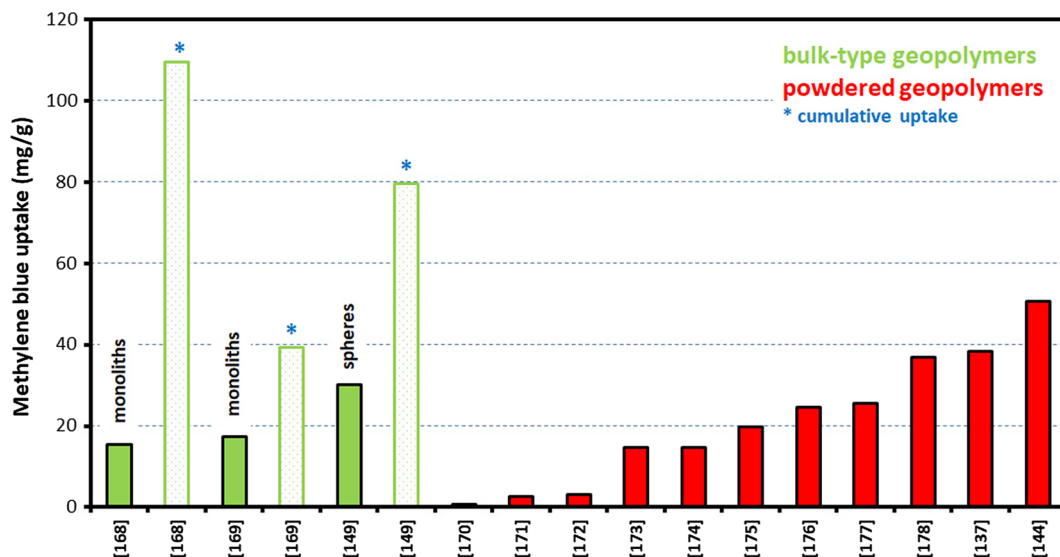


Fig. 8. Methylene blue uptake of various geopolymer adsorbents reported in literature.

The best performing sample, containing glass powder, showed a narrow pH fluctuation (from 11 to 10) within the 25 day measurement period. These were promising results, but the specimens were produced using an energy intensive protocol (heat treatment for 1 h at 200 or 400 °C). The same group has also studied the influence of particle size and mixture composition on the pH buffering capacity of geopolymers [190]. After synthesis, different sized granules were prepared by crushing prismatic samples (4 × 4 × 16 cm). The addition of sodium silicate glass fibre to the compositions was found to affect their pH fluctuation by reducing the open porosity, and for these compositions a smaller granule size led to a faster pH decrease. Nevertheless, the high pH fluctuation (ΔpH between 3 and 4) observed for these samples is unsuitable for an industrial application. Much lower pH fluctuations were reported by Novais et al. when using highly porous geopolymer monoliths (see Fig. 9a) [43]. The OH^- leaching was heavily dependent on porosity, samples having higher porosity exhibiting higher (up to 40%) OH^- leaching. The use of higher solid-to-liquid ratios promoted a gentler alkalis leaching from the foams. The total leaching of hydroxyl ions ranged from 0.0104 to 0.0180 mol/dm³ g, this being inferior to the maximum value (0.0270 mol/dm³ g) reported in [189]. Nevertheless, the pH gradient (ΔpH) was 1.14, narrower than those reported in [189] ($\Delta\text{pH} = 3$).

Ascensão et al. evaluated the pH regulation ability of red mud-containing geopolymer monoliths (see Fig. 9b) (cubic samples 8 cm³) [118]. Monoliths having various porosities and red mud contents were produced. The lowest pH fluctuation ($\Delta\text{pH} = 1.64$) was observed for the composition containing the highest amount of red mud which was associated with both the higher number of open pores, and the higher sodium content introduced by the red mud.

The possibility of using mm size geopolymer spheres (see Fig. 9c) to promote pH control, instead of granules [190] or membranes [43,118], was first reported by Novais et al. [191]. The alkalis leaching from the porous spheres could be tailored by the fly ash content in the compositions. Metakaolin-based spheres showed poor pH buffering capacity with a major decay in pH from 11.9 (1st day) to 8.2 (30th day). By contrast, the fly ash-based spheres showed much higher alkalis leaching which enabled a gentler fluctuation in pH of ΔpH between 1.6 and 1.9 over the 30 days. The maximum hydroxyl ions release observed for the fly ash-based spheres was 0.0337 mol/dm³ g, this being the highest value reported to date for geopolymers.

Recently, and for the first time, red mud-based geopolymer spheres were synthesised by Novais et al. [87]. Typical optical and SEM micrographs of the highly porous spheres are shown in Fig. 10, while a photograph of the spheres was included in Fig. 9d. The influence of the spheres' porosity and red mud content on their alkalis leachability was evaluated. Results showed that the spheres' porosity exerted a strong influence on the OH^- leaching, while the red mud content played a minor role. The best performing samples showed continuous and prolonged pH buffering capacity over the 28 days ($\Delta\text{pH} = 2.4$), the maximum OH^- ions release being 0.0237 mol/dm³ g.

A direct comparison between the available studies is challenging, since different synthesis conditions (e.g. curing temperature, solid precursors, activator type and concentration, foaming agents) were used. Nevertheless, the comparison between the cumulative leaching of hydroxyl ions, shown in Fig. 11, can provide valuable information regarding the ability of the geopolymer foams to buffer pH. The alkalis leaching from the geopolymer foams is affected by several factors, such as chemical composition, degree of porosity and the amount of alkalis added during the specimens synthesis. As shown in Fig. 11, the highest leaching reported to date was observed when using fly ash-based geopolymer spheres [191]. The very high leaching can be partially ascribed to the high content of activators used in the spheres' synthesis (56 wt%). However, the alkalis content cannot fully explain the major differences in comparison with the other published data. In fact, the fly ash-based spheres [191] showed ~1.9 times higher OH^- leaching in comparison with the use of cylindrical discs [43] prepared using ~44 wt% activators. This suggests that the geometry of the samples also has a major impact on the foams' leaching behaviour. The use of spherical (mm size) samples, instead of cm scale discs or cubes, seems to favour the alkalis leaching due to the expected increase in the exposed area. Indeed, red mud-based spheres [87] leached

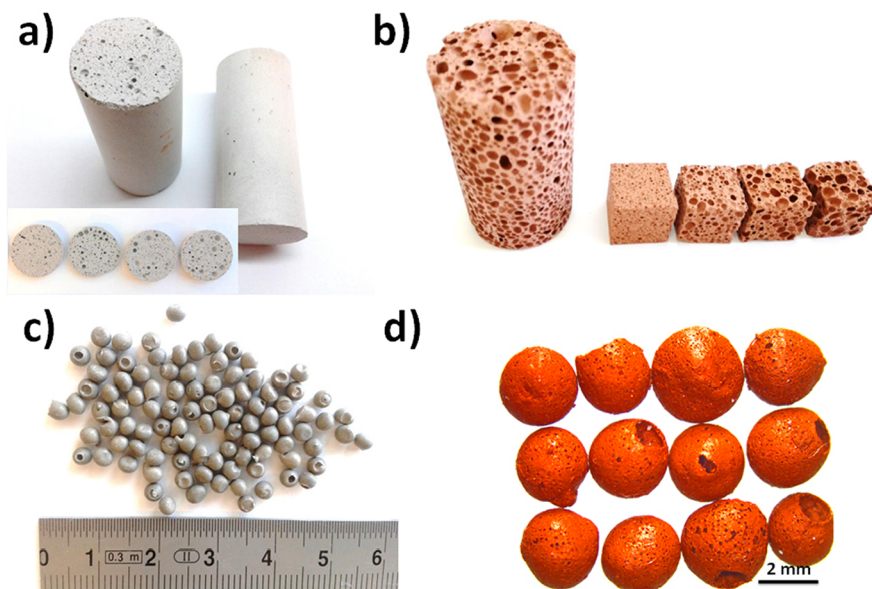


Fig. 9. Distinct geopolymer monoliths (a and b) and spheres (c and d) used as pH buffering materials: (a) fly ash-containing cylindrical discs used in [43], (b) red mud-containing cubes used in [118], (c) fly ash-based spheres used in [191] and (d) red mud-based spheres used in [87]. Photograph of the red mud cubes was kindly provided by G. Ascensão.

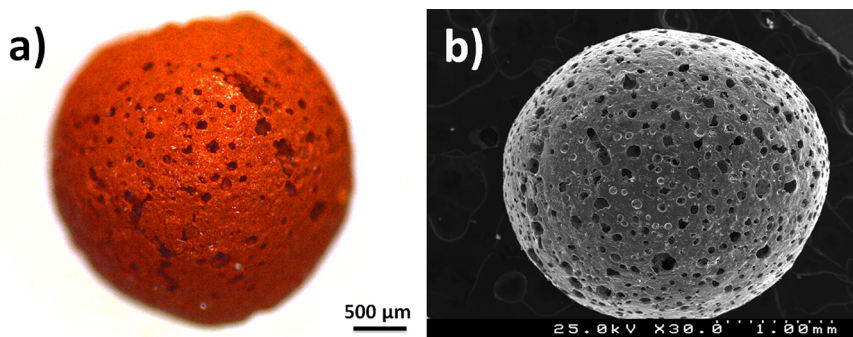


Fig. 10. (a) Optical and (b) SEM micrographs of red mud-based geopolymer spheres used in [87].

~1.9 times more hydroxyl ions than cubic red mud samples [118], despite the fact that much lower amounts of activator were employed in their synthesis (spheres ~38 wt%; cubes ~51 wt%). These results demonstrate the advantage of using mm size spheres in comparison with monolithic materials such as membranes or cubes. The selection of the most suitable pH adjustment agent should also consider other relevant parameters, such as the raw materials availability and the specimens' durability. The use of waste materials both as solid precursor and as activator [192] is not only feasible, but desirable, and will contribute to cleaner production and towards the sustainability of wastewater treatment and anaerobic digestion systems.

While these studies suggest the viability of using geopolymer foams as pH adjustment agents, all of them were tested in distilled water media, while their use in more demanding and realistic conditions, closest to real scenarios, has almost never been studied. Up to now there are only two exceptions [44,193] where the possibility of using geopolymer foams to regulate the pH level inside anaerobic digestion bioreactors was evaluated. Rugele et al. carried out anaerobic digestion batch tests for ~25 days [193]. After this period, the reactor containing geopolymer granules (the actual size of the granules is unclear, but they seem to be between 2 and 8 mm) exhibited 22% higher methane production in comparison with the control reactor (without granules). Novais et al. studied the performance of fly ash-based geopolymer spheres as pH regulators in the anaerobic digestion of a substrate with high acidogenic potential (cheese whey) [44]. Anaerobic batch operated assays were run for 70 days. The pH of the reference reactor (without spheres) remained mostly between 3.8 and 4.4, preventing methane production, whereas in the reactors with spheres pH ranged between 6.5 and 7.9 (see Fig. 12a). Additionally, the amount of spheres added to the reactors was found to significantly affect the methane production rate, shown in Fig. 12b and c. Higher dosages delay methane production rate, but lead to a higher overall methane yield. The fast pH stabilisation (with lower dosages) stimulated early methane production, demonstrating the interesting potential of these novel materials as pH adjustment agents in anaerobic digestion processes. The proposed methodology was also found to be cost-effective, considering the cost of the raw materials, in comparison with commercial buffer solutions (NaHCO_3 and KHCO_3), further supporting the potential of this innovative material.

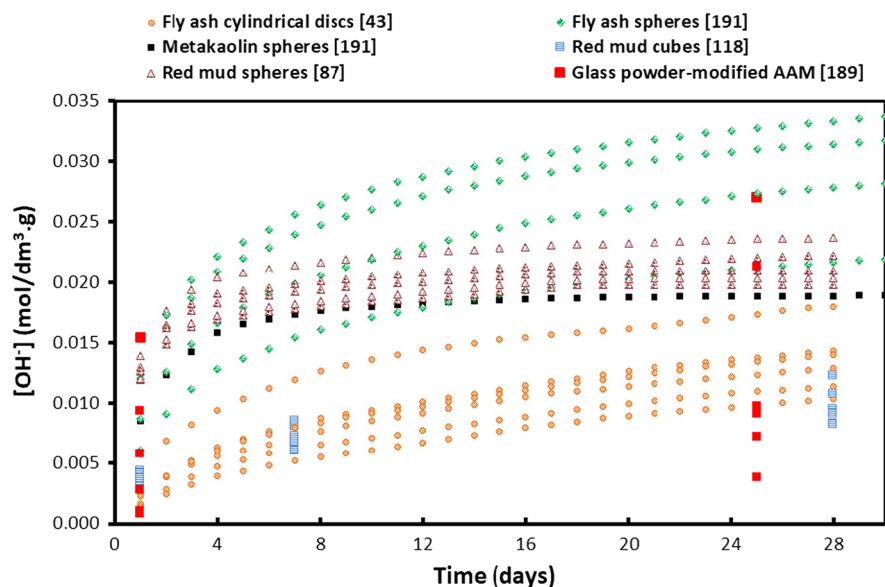


Fig. 11. Comparison between the cumulative hydroxyl ions release from porous geopolymers extracted from different literature studies.

Despite these very promising results, the performance of geopolymer foams in more demanding environments (e.g. extremely acidic mediums), their use in multiple cycles, and their long-term performance in continuous anaerobic digestion systems remains unexplored, and should be validated.

4.4. Catalysts

The possibility of using geopolymers in catalytic applications has long been predicted [194]. Properties such as their high SSA, permeability, chemical durability and mechanical strength suggest the use of geopolymers for catalysts [195]. However, up to now very few investigations have considered the possibility of using them as catalyst supports [47,175,194], and even fewer as catalysts themselves [45,46,170]. Nevertheless, studies addressing the use of geopolymer powders in wastewater treatment [171,196,197], syngas [198] and biodiesel production [47], amongst other catalytic applications [46,199] have been studied. This review is focused on the use of geopolymer foams in their bulk-type form, not as a powder (relevant literature can be found in [195,200]). To the best of our knowledge, there is only one study addressing the use bulk-type geopolymer for biodiesel synthesis [201]. In this work, a geopolymer mixture was shaped into a lattice by additive manufacturing (see Fig. 13), and then this innovative material was tested for the heterogeneous transesterification of soybean oil with methanol. The use of 3 wt% of the structured catalyst yielded 43.5 wt% of biodiesel in a 4 h transesterification of soybean oil. These are very promising results that demonstrate the feasibility of using bulk-type geopolymers as catalysts in relevant industrial applications.

5. Future prospects and challenges

Over recent decades, geopolymers have been considered as a potentially more eco-friendly substitute for Portland cement, yet recently the possibility of tailoring their porosity, adsorption and leaching has boosted the interest in using them in environmental remediation applications (e.g. wastewater treatment), renewable energy production (e.g. biogas) and as energy-saving building materials (e.g. thermal insulation).

Geopolymers have demonstrated interesting potential as low thermal conductivity materials. Nevertheless, other relevant properties for building materials, such as their acoustic absorption and moisture storage/release capacity, have been considerably less investigated, and should be considered for future work. Additional studies should also determine the most suitable processing techniques (e.g. direct foaming, replica method) and synthesis conditions to fulfil the requirements of such applications. Innovative processing techniques (e.g. 3D printing) should be explored to produce monoliths with highly complex shapes, allowing a better control of the pore size distribution, which will enhance their performance. Despite the interesting possibilities offered by 3D printing, engineering challenges associated with the modification of the slurries' viscosity with time, induced by geopolymerisation reactions, must be overcome [73]. Studies focusing on different ways to extend slurry setting times should be performed to ensure a suitable printing timespan. Regardless of the processing technique, it is paramount to use local and widely abundant precursors, ideally unexplored waste streams that cannot be used in Portland cement blends, and compositions should be carefully designed to ensure competitive production costs under a net zero emission scenario. Life cycle analysis should be a key tool in future studies to validate the environmental advantages of using geopolymer foams in building applications.

Another exciting avenue for geopolymer foams is their use as adsorbents. Most of the studies performed to date focused the

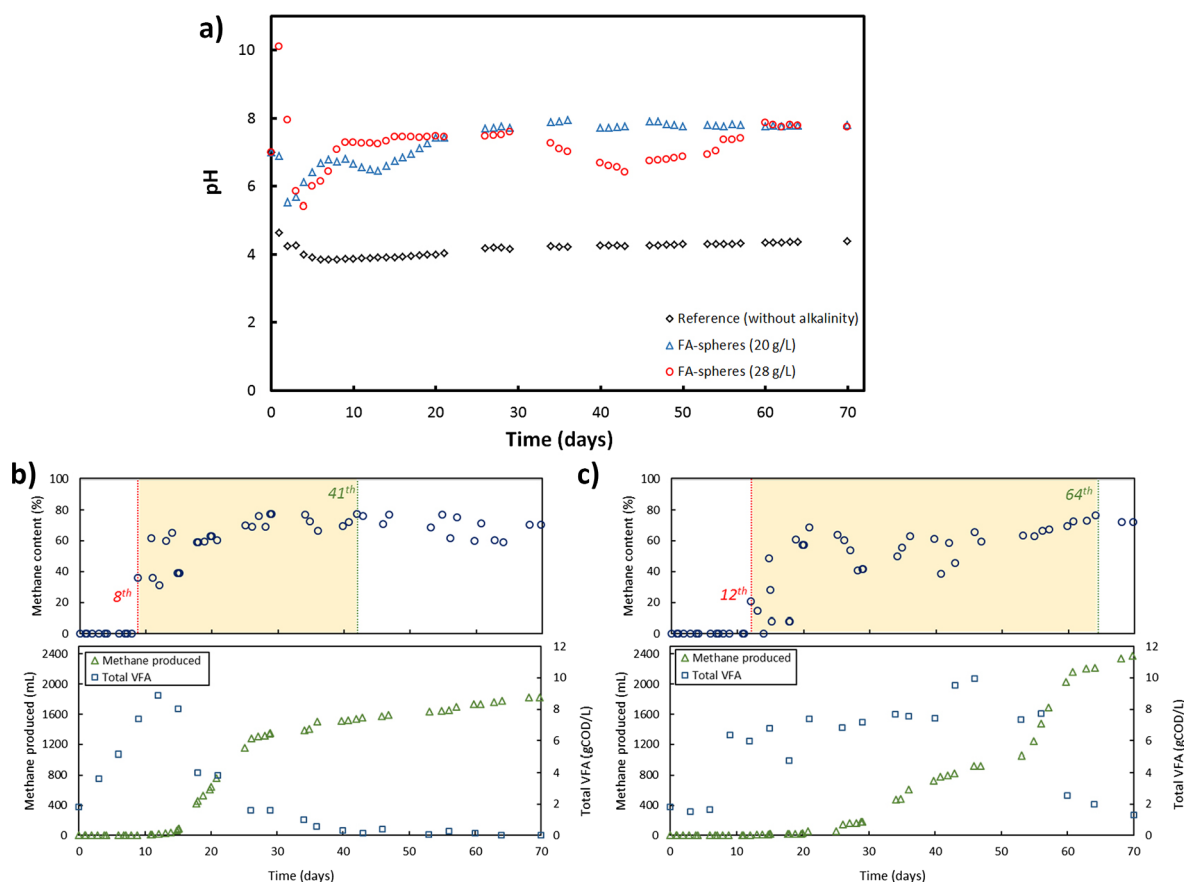


Fig. 12. (a) pH fluctuation in anaerobic digesters for the optimisation of methane production as a function of time with addition of distinct amounts of FA-based geopolymer spheres, and methane content (vol%) in the biogas, total VFA and cumulative methane produced in anaerobic digester with addition of (b) 20 g and (c) 28 g of FA-based geopolymer spheres [44].

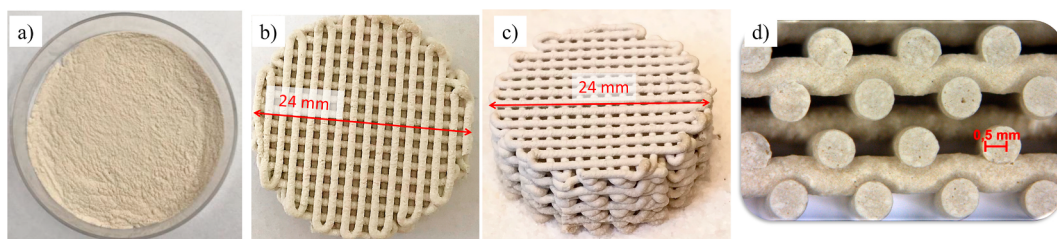


Fig. 13. Images of the powder Na-based geopolymer (a) and the graded lattice structure fabricated using Direct Ink Writing (b–d) [201].

extraction of various cationic dyes and heavy metals from synthetic wastewaters. Anionic species are also found in industrial effluents, however, their extraction using geopolymer foams (not powders) has never been reported, and even the use of powdered geopolymers is uncommon [202]. Future work should be carried out on this topic. Moreover, other emerging sources of pollution, such as pharmaceuticals and crude oil, should be investigated. Studies addressing the functionalisation of the geopolymer surface and the production of geopolymer composites (e.g. containing zeolites or activated carbons) might further enhance the performance of these innovative adsorbents. The main bottleneck hindering the wider use of geopolymer adsorbents is the gap between research studies, often using unrealistic scenarios (e.g. synthetic wastewaters), and real effluents which are much more complex than synthetic wastewaters [139,203]. Studies focusing on industrial effluents are anticipated to be a hot topic in the near future.

The use of geopolymer foams as pH buffering materials has barely been investigated. Nonetheless, the few studies performed to date suggest their feasibility for this high added value application. Additional studies should be carried out in more demanding conditions and for longer periods, in order to be more similar to their actual industrial use (e.g. continuous anaerobic digestion systems), to further demonstrate their potential. Likewise, the evaluation of the catalytic properties of geopolymer foams should also be explored. Coupling the geopolymer foams with distinct reactive species could greatly improve their catalytic properties.

6. Conclusions

The use of geopolymer foams in environmental remediation applications, renewable energy production, and as multifunctional and energy-saving building materials might be a driver to allow the widespread of this technology. Geopolymer foams have shown promising thermal insulation performance. However, to set them apart from other conventional building materials, multifunctional foams combining thermal and acoustic insulation, coupled with thermal stability and moisture buffering capacity must be developed. This strategy might tackle the energy losses inside buildings, promote wastes valorisation, and contribute towards a sustainable construction model. Other exciting avenues such as their use as bulk-type adsorbents, pH regulators and catalysts are still in an embryonic stage, despite the promising results achieved so far. This review shows that the use of bulk-type adsorbents (monoliths and spheres) is a greener, sustainable, highly efficient and safer alternative in comparison with the use of powders for wastewater treatment systems, while their use as pH regulators in anaerobic digestion might boost the biogas production efficiency, reducing the consumption of fossil fuels and promoting climate change mitigation. Nevertheless, additional and deeper investigations are required before this technology can be industrialised.

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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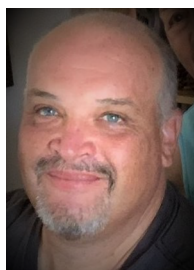
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