



Application of alkali-activated materials for water and wastewater treatment: a review

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Abstract Alkali-activation (or geopolymer) technology has gained a great deal of interest for its potential applications in water and wastewater treatment during the last decade. Alkali-activated materials can be prepared via a relatively simple and low-energy process, most commonly by treating aluminosilicate precursors with concentrated alkali hydroxide and/or silicate solutions at (near) ambient conditions. The resulting materials are, in general, amorphous, have good physical and chemical stability, ion-exchange properties, and a porous structure. Several of the precursors are industrial by-products or other readily available low-cost materials, which further enhances the environmental and economic feasibility. The application areas of alkali-activated materials in water and wastewater treatment are adsorbents/ion-exchangers,

photocatalysts, high-pressure membranes, filter media, anti-microbial materials, pH buffers, carrier media in bioreactors, and solidification/stabilization of water treatment residues. The purpose of this review is to present a comprehensive evaluation of the rapidly growing prospects of alkali-activation technology in water and wastewater treatment.

Keywords Adsorption · Alkali-activation · Catalysis · Geopolymer · Solidification/stabilization · Wastewater treatment

Introduction

Alkali-activated materials (AAMs), and geopolymers as their subgroup, are generally known as alternative low-CO₂ binders, which can be used instead of Portland cement in construction (Provis 2014a, 2018). Additionally, alkali-activation technology is an important tool in promoting the circular economy, as it is a method to convert many inorganic wastes into useful products (Mehta and Siddique 2016). However, one of the emerging application areas for AAMs is in the water and wastewater treatment field (Mackenzie 2011). Drivers for this interest include simpler and less-energy intensive preparation process compared to similar materials, such as ceramics or synthetic zeolites, and useful

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properties: for instance, high mechanical strength (Luukkonen et al. 2018), good durability (Pacheco-Torgal et al. 2012), mesoporous structure (Glad and Kriven 2013), and ion-exchange capacity (Bortnovsky et al. 2008; Skorina 2014; O'Connor et al. 2010).

Definition and chemical composition

AAMs are amorphous aluminosilicate materials in which the calcium content affects significantly the chemical structure (Bernal et al. 2014a; Wan et al. 2017). The low-calcium AAMs (also known as geopolymers) consist of a three-dimensional and highly interconnected aluminosilicate framework (Provis and van Deventer 2009) described as sodium aluminosilicate hydrate gel (N–A–S–H in cement chemist notation) (Barbosa et al. 2000; Rowles et al. 2007; García-Lodeiro et al. 2010). The structure of high calcium-content AAMs (or the C–(N)–A–S–H gel), on the other hand, consists of cross-linked and non-cross linked structures resembling tobermorite (Bernal et al. 2014a; Myers et al. 2013, 2014; Walkley et al. 2016). Finally, also materials prepared by a reaction between phosphoric acid and an aluminosilicate precursor are sometimes referred to as phosphoric acid-activated or phosphate-based geopolymers (Le-ping et al. 2010; Louati et al. 2016a, b; Wagh 2005). The structure of phosphate-based geopolymers has been reported to consist of amorphous $\text{SiO}_2\text{-Al}_2\text{-O}_3\text{-P}_2\text{O}_5\text{-nH}_2\text{O}$ and $\text{AlH}_3(\text{PO}_4)_2\text{-3H}_2\text{O}$ (Wang et al. 2017).

Applications in water and wastewater treatment

AAMs have many potential applications in water and wastewater treatment, including adsorbents/ion-exchangers, membranes and filtration media, photocatalysts, and solidification/stabilization of water and wastewater treatment residues. In addition, they can be used as antibacterial materials after the incorporation of copper (Hashimoto et al. 2015) or silver (O'Connor et al. 2010) through ion exchange or addition of nanoparticles (such as silver silica nanocomposites) into the aluminosilicate matrix of AAMs (Adak et al. 2015). Although the aforementioned examples were intended as antimicrobial binders, there are numerous examples with similarly modified zeolites to indicate potential applicability for disinfection of wastewaters or groundwater (Akhigbe et al. 2014; De la Rosa-

Gómez et al. 2008a, b; Dolic et al. 2015; Mpenyana-Monyatsi et al. 2012; Johari et al. 2016).

Another example of the AAM applications is as the pH adjustment agent. For instance, during wastewater sludge biogasification, a significant pH drop can occur due to the formation of acids by bacteria metabolism, making maintaining a constant pH challenging. AAMs are potential pH buffering materials as they contain free leachable alkalis in pore solution (Lloyd et al. 2010; Bumanis and Bajare 2014; Bumanis 2015; Ascensão et al. 2017; Novais et al. 2016a, 2017).

Fixed-film wastewater treatment processes (biofilm reactors) use various types of floating carrier media to allow adhesion and biofilm development. Examples of currently used carrier materials include polystyrene and lightweight expanded clay aggregate (LECA). Silva et al. (2012) prepared AAM-based biofilm carrier media (2–3 cm in size) from thermally treated (800 °C, 2 h) tungsten mine waste mud, sodium silicate, and sodium hydroxide. One of their mixes showed good potential in terms of pH (should be lower than 8) and stability when submerged in water (Silva et al. 2012). Therefore, AAM-based biofilm carrier media could be a low-cost alternative for wastewater treatment.

Scope of the review

There are numerous review articles about the AAM technology discussing general properties, chemistry, possible raw materials, and various applications (Zhuang et al. 2016; Khale and Chaudhary 2007; Singh et al. 2015; Mohd Salahuddin et al. 2015; Part et al. 2015; Rao and Liu 2015; Shaikh 2013; Obonyo et al. 2011; Provis et al. 2010; Majidi 2009; Komnitsas and Zaharaki 2007). AAM adsorbents were recently reviewed by Ariffin et al. (2017) and by Siyal et al. (2018). However, the purpose of this review is to represent a more comprehensive overview about all current AAM uses in the water and wastewater treatment fields (summarized in Fig. 1). The discussed applications are adsorbents/ion-exchangers, membranes and filtration media, photocatalysts, solidification/stabilization of water and wastewater treatment residues, and other niche uses (antimicrobial materials, pH buffers, and carrier media for bioreactors).

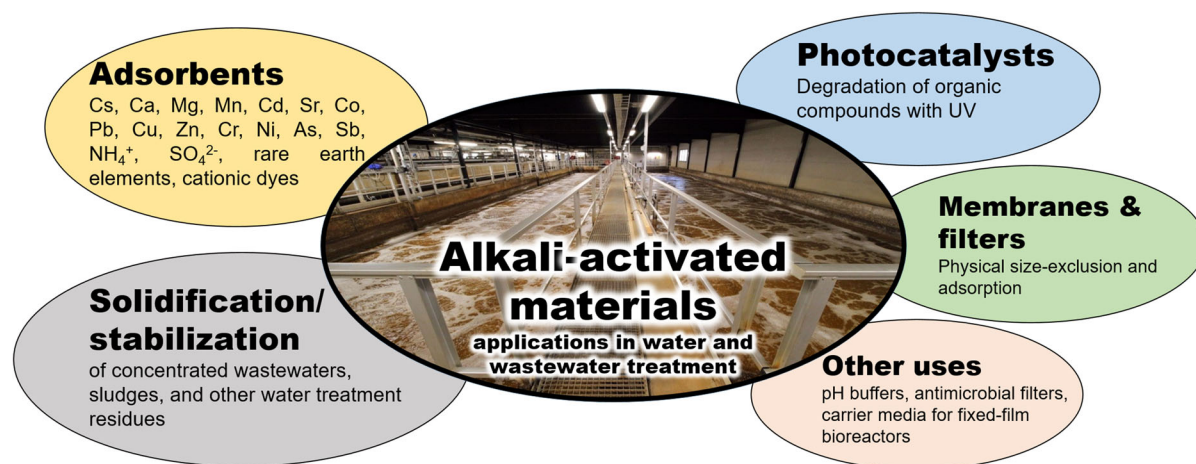


Fig. 1 Summary of current applications of alkali-activated materials in water and wastewater treatment

Application as adsorbents/ion-exchangers

Preparation

The reaction mechanisms of AAM synthesis have been discussed in numerous papers (Li et al. 2010; Rees 2007; Rees et al. 2008; Bernal et al. 2014a; Provis et al. 2014). An initial description of alkali activation was as a process consisting of dissolution, rearrangement, condensation, and resolidification (Glukhovskiy 1959). Provis and Van Deventer (2007) described the AAM formation mechanism in detail based on the weathering of aluminosilicate minerals. Their model included the formation of multiple, differently cross-linked aluminosilicate species and oligomerization of silicate species in concentrated aqueous solution (Provis 2014b). According to current knowledge, alkali-activation process includes the following main steps: (1) dissolution of aluminosilicate source, (2) speciation and equilibrium of aluminate and silicate, (3) gelation, (4) reorganization, and (5) polymerization and hardening (Duxson et al. 2007). In addition, the temperature, amount of water, mixing method, and physical properties of the raw materials (particle size, shape and surface area) can all significantly affect the synthesis. Also magnesium and iron can also affect the structure if they are present (Bernal et al. 2014b; García-Lodeiro et al. 2013; Bell and Kriven 2010), which makes the overall reaction and resulting structures very complicated when chemically heterogeneous raw materials are used.

The two basic approaches to preparing powdered AAM adsorbents are hydrothermal processing and the fusion method. In the hydrothermal method, solid aluminosilicate precursor is mixed with an alkaline solution, and the mixture is left to cure at (near) ambient temperature. The fusion method, on the other hand, involves mixing the solid aluminosilicate precursor with solid hydroxide and heating the mixture, followed by addition of water, filtration, washing and drying. Typically for adsorption studies, materials are pulverized as a last step. Granular or spherical AAM adsorbents (with a diameter in a millimeter range) have been fabricated by the geopolymerization-granulation process (Luukkonen et al. 2017b), by the addition of alginate and Ca^{2+} to promote cross-linking (Ge et al. 2017), and by the suspension and solidification method (Ge et al. 2015b).

The most commonly used aluminosilicate raw materials for AAM adsorbents are metakaolin and class F fly ash activated by sodium hydroxide and/or silicate (Table 1). Only few other aluminosilicate precursors (such as blast furnace slag, slag from Linz-Donawitz (LD) converters, aluminum waste, and pyrophyllite) and activators (phosphoric acid) have been studied. It should be noted that metakaolin is purer and more consistent in chemical quality than industrial by-products and is thus more suitable for high-value products (MacKenzie 2014). For instance, adsorbents for ground water softening require a certain level of purity. Luukkonen et al. (2017a) showed that sodium-based activators resulted in better capacity

Table 1 Studies concerning the use of alkali-activated materials as adsorbents

Adsorbate	Precursor	Activator	Other reagents	C ₀ (mg/L)	Optimum adsorption conditions			q (mg/g)	Regeneration	References
					pH	t (h)	Dose (g/L)			
MB	FA	NaOH, (Na ₂ SiO ₂) _n O	Oleic acid, H ₂ O ₂	n.r.	n.d.	n.d. (48)	4	n.d. (25)	n.d.	Liu et al. (2016c)
MB	FA	NaOH	–	32	n.d. (6.3)	≈ 75	n.d. (0.2)	18.3 ^b	n.d.	Li et al. (2006)
MB	Kaolin, ZT	NaOH	–	0.47–2.36	n.r.	30	0.2	4.75 ^b	n.d.	Yousef et al. (2009)
MB	MK, α-Al ₂ O ₃	H ₃ PO ₄	–	10–50	3	0.5	8	4.26 ^b	400 °C for 2 h	Khan et al. (2015)
CV	FA	NaOH	–	41	n.d. (6.3)	≈ 100	n.d. (0.2)	17.2 ^b	n.d.	Li et al. (2006)
CV	MK, RHA	KOH	Soybean oil	25–300	4.5	≈ 0.5	1.5	276.9 ^b	n.d.	Barbosa et al. (2018)
SO ₄ ^{2–}	BFS	NaOH, (Na ₂ SiO ₂) _n O	BaCl	50–1200	4–6	3.33	10	119 ^a	n.d.	Runtti et al. (2016)
NH ₄ ⁺	MK	NaOH, (Na ₂ SiO ₂) _n O	–	32–40	n.d.	0.5	0.5	32 ^a	0.2 M NaCl + 0.1 M NaOH	Luukkonen et al. (2017b)
NH ₄ ⁺	MK	NaOH, (Na ₂ SiO ₂) _n O	–	10–1000	4–8	0.17	2	21.07 ^b	0.2 M NaCl + 0.1 M NaOH	Luukkonen et al. (2016b)
As(III)	BFS	NaOH, (Na ₂ SiO ₂) _n O	–	2.40 ^d	6	5	7	0.52 ^b	n.d.	Luukkonen et al. (2016a)
Ca ²⁺	MK	NaOH	K12, PEG-600	100	n.d. (5)	50–60	n.d. (1.5)	24 ^a	n.d.	Tang et al. (2015)
Cd ²⁺	MK	NaOH, (Na ₂ SiO ₂) _n O	–	20–3000	6	8	n.d. (≈ 10)	98.10	n.d.	Andrejkovicová et al. (2016)
Cd ²⁺	MK	NaOH, (Na ₂ SiO ₂) _n O	–	50–300	4	n.r.	n.r.	67.57 ^b	2 M HCl	Cheng et al. (2012)
Cd ²⁺	FA	NaOH	–	10–100	5	7	3.2	26.25 ^b	1 M NaOH	Javadian et al. (2013)
Cd ²⁺	FA	NaOH, (Na ₂ SiO ₂) _n O	–	10–120	5	2	3.5	9.02 ^b	n.d.	Onutai et al. (2018)
Cd ²⁺	Pyrophyllite	NaOH	–	10–50	7.8	1.5	2.5	7.82 ^b	n.d.	Panda et al. (2018)
Co ²⁺	Pyrophyllite	NaOH	–	10–50	7.8	1.5	2.5	7.18 ^b	n.d.	Panda et al. (2018)
Co ²⁺	MK	NaOH, (Na ₂ SiO ₂) _n O	–	25–800	> 3	0.3	3.2	69.23 ^b	Unspecified acid, six cycles	Kara et al. (2018)
Co ²⁺	MK, FA	NaOH	–	118	> 5	≈ 1	n.d. (2)	152.91 ^b	0.1 M HCl	Chen et al. (2013)
Co ²⁺	FA	NaOH, (Na ₂ SiO ₂) _n O	–	229–2321	n.d.	n.d.	n.d. (5)	≈ 66 ^b	n.d.	Mužek et al. (2016b)
Co ²⁺	FA	NaOH, (Na ₂ SiO ₂) _n O	–	0.25–0.70	n.r.	≈ 0.25	n.d. (5)	≈ 59	n.d.	Mužek et al. (2016a)
Co ²⁺	FA	NaOH, (Na ₂ SiO ₂) _n O	–	≈ 250–700	n.d.	≈ 0.2	n.d. (5)	≈ 52	n.d.	Mužek et al. (2016a)

Table 1 continued

Adsorbate	Precursor	Activator	Other reagents	C ₀ (mg/L)	Optimum adsorption conditions			q (mg/g)	Regeneration	References
					pH	t (h)	Dose (g/L)			
Cu ²⁺	MK, CL	NaOH, (Na ₂ SiO ₂) _n O	–	20–500	6	8	n.d. (≈ 10)	21.84	n.d.	Andrejkovicová et al. (2016)
Cu ²⁺	MK	NaOH, (Na ₂ SiO ₂) _n O	–	50–300	≥ 3	n.r.	n.r.	19.94 ^b	2 M HCl	Cheng et al. (2012)
Cs ⁺	MK, FA	NaOH	–	266	7	≈ 1	n.d. (2)	113.26 ^a 564.97 ^b	0.1 M HCl	Chen et al. (2013)
Cs ⁺	MK, RHA	NaOH	–	50–500	n.d. (7)	n.d. (6)	n.d. (5)	50.8 ^b	n.d.	López et al. (2014a)
Cs ⁺	MK, silica fume	NaOH	–	50–500	n.d. (5)	n.r.	n.d. (1.25)	43 ^{a, c}	n.d.	López et al. (2014b)
Cs ⁺	FA, BFS	NaOH ₄	–	10–150	4	24	n.d. (10)	15.24 ^a	n.d.	Lee et al. (2017)
Cu ²⁺	MK	KOH, silica fume	CTAB	55–1700	n.d.	≈ 1	n.d. (4)	40	n.d.	Singhal et al. (2017)
Cu ²⁺	FA	NaOH	–	10–160	6	1	2	152.3 ^b	n.d.	Al-Harashsheh et al. (2015)
Cu ²⁺	FA, iron ore tailings	NaOH, (Na ₂ SiO ₂) _n O	H ₂ O ₂	100–200	5	1.17	5	113.41 ^b	n.d.	Duan et al. (2016)
Cu ²⁺	FA	NaOH	–	50–250	n.d.	30	n.d. (0.15)	101 ^b	n.d.	Wang et al. (2007)
Cu ²⁺	FA	NaOH, (Na ₂ SiO ₂) _n O	–	247–2503	n.d.	n.d.	n.d. (5)	≈ 77 ^b	n.d.	Mužek et al. (2016b)
Cu ²⁺	FA	NaOH, (Na ₂ SiO ₂) _n O	–	≈ 376–747	n.d.	≈ 0.5	n.d. (5)	77.3 ^a	n.d.	Mužek et al. (2014)
Cu ²⁺	MK	NaOH, (Na ₂ SiO ₂) _n O	Alginate	10–120	5	41.67	1.5	62.5	n.d.	Ge et al. (2017)
Cu ²⁺	Kaolin, ZT	NaOH	–	10–100	6	n.d. (24)	n.d. (1)	55	n.d.	Alshaar et al. (2010)
Cu ²⁺	Kaolin, ZT	NaOH	–	10–100	6	n.d. (24)	n.d. (1)	52.7 ^b	n.d.	Yousef et al. (2009)
Cu ²⁺	MK	NaOH, (Na ₂ SiO ₂) _n O	H ₂ O ₂ , K12, PEG-600	10–120	5	36	1.5	52.63 ^b	n.d.	Ge et al. (2015b)
Cu ²⁺	MK	NaOH, (Na ₂ SiO ₂) _n O	–	50–300	4	n.r.	n.r.	48.78 ^b	2 M HCl	Cheng et al. (2012)
Cu ²⁺	MK	NaOH, (Na ₂ SiO ₂) _n O	–	20–500	6	8	n.d. (≈ 10)	44.73	n.d.	Andrejkovicová et al. (2016)
Cu ²⁺	MK	NaOH	K12, PEG-600	100	n.d. (5)	50–60	n.d. (1.5)	34.5 ^a	n.d.	Tang et al. (2015)
Cu ²⁺	MK	NaOH	–	50–500	n.d.	n.r.	n.d. (1.25)	15 ^{b, c}	n.d.	López et al. (2014b)
Cu ²⁺	MK, ZT	NaOH, (Na ₂ SiO ₂) _n O	–	250	n.d. (3)	n.d. (24)	n.r.	7.80 ^a	n.d.	Alshaar et al. (2014)
Mn ²⁺	MK	NaOH, (Na ₂ SiO ₂) _n O	–	25–800	> 3	≈ 0.3	3.2	72.34 ^b	Unspecified acid	Kara et al. (2018)

Table 1 continued

Adsorbate	Precursor	Activator	Other reagents	C ₀ (mg/L)	Optimum adsorption conditions			q (mg/g)	Regeneration	References
					pH	t (h)	Dose (g/L)			
Ni ²⁺	Pyrophyllite	NaOH	–	10–50	7.8	1.5	2.5	7.28 ^b	n.d.	Panda et al. (2018)
Ni ²⁺	MK	NaOH, (Na ₂ SiO ₂) _n O	–	≈ 0–590	≥ 4	50	3.2	42.61	n.d.	Kara et al. (2017)
Ni ²⁺	BFS	NaOH, (Na ₂ SiO ₂) _n O	–	2.17 ^d	6–10	0.5	1	4.42 ^b	n.d.	Luukkonen et al. (2016a)
Sr ²⁺	MK, FA	NaOH	–	175	> 5	≈ 1	n.d. (2)	154.32 ^b	0.1 M HCl	Chen et al. (2013)
Pb ²⁺	Pyrophyllite	NaOH	–	10–50	7.8	1.5	2.5	7.54 ^b	n.d.	Panda et al. (2018)
Pb ²⁺	MK, CL	NaOH, (Na ₂ SiO ₂) _n O	–	20–3000	6	8	n.d. (≈ 10)	261.22	n.d.	Andrejkovicová et al. (2016)
Pb ²⁺	FA	NaOH	–	100	5–6	1	2	174.34 ^b	n.d.	Al-Zboon et al. (2011)
Pb ²⁺	MK	NaOH, (Na ₂ SiO ₂) _n O	–	50–300	≥ 4	n.r.	n.r.	147 ^b	2 M HCl	Cheng et al. (2012)
Pb ²⁺	FA	NaOH, (Na ₂ SiO ₂) _n O	–	100–1000	3–6	2.5	n.d. (4)	118.6 ^a	n.d.	Liu et al. (2016b)
Pb ²⁺	MK	NaOH	K12, PEG-600	100	n.d. (5)	50–60	n.d. (1.5)	45.1 ^a	n.d.	Tang et al. (2015)
Pb ²⁺	MK	NaOH	–	50–500	n.d. (5)	n.r.	n.d. (1.25)	35 ^{b, c}	n.d.	López et al. (2014b)
Pb ²⁺	FA	NaOH, (Na ₂ SiO ₂) _n O	H ₂ O ₂	50	5	3	n.d.	6.34	0.1 M HCl	Novais et al. (2016b)
Sb(III)	BFS	NaOH, (Na ₂ SiO ₂) _n O	–	1.77 ^d	10	1	7	0.34 ^b	n.d.	Luukkonen et al. (2016a)
Zn ²⁺	LD slag	NaOH, (Na ₂ SiO ₂) _n O	–	50–150	≥ 8	1	1.5	86 ^a	n.d.	Sarkar et al. (2018)
Zn ²⁺	Volcanic tuff	NaOH	–	10–160	7	0.5	8	14.83 ^b	n.d.	Al-Zboon et al. (2016)
Zn ²⁺	MK, CL	NaOH, (Na ₂ SiO ₂) _n O	–	20–500	6	8	n.d. (≈ 10)	35.88	n.d.	Andrejkovicová et al. (2016)

CL clinoptilolite, BFS blast furnace slag, FA fly ash, MB methylene blue, MK metakaolin, RHA rice husk ash, CV crystal violet, K12 sodium dodecyl sulfate, PEG-600 polyethylene glycol, CTAB cetyl trimethylammonium bromide, n.d. not determined, values in parenthesis indicate non-optimized parameters, ZT zeolitic tuff

^aExperimental capacity

^bLangmuir isotherm maximum capacity

^cMulti-component solution

^dSpiked mine-effluent

than potassium-based activators in the case of NH_4^+ adsorption by metakaolin geopolymers. In addition, some studies involved additives and other reagents such as hydrogen peroxide (blowing agent), sodium dodecyl sulfate (surfactant), cetyl trimethylammonium bromide (surfactant), polyethylene glycol (plasticizer), oleic acid (hydrophobic modifier), or sodium alginate (providing carboxyl functional groups) (Table 1). Typically, aggregates have not been incorporated in AAM adsorbents, but in some cases, zeolite has been added as a filler.

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of AAM adsorbents (Table 1) has been in the range of 0.5–19. Low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios indicate that the network has more 3D structure instead of 2D chains and more negative charge. López et al. (2014b) showed that the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio significantly affected Pb^{2+} adsorption: almost no adsorption occurred at $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 0.5, optimum was reached at $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 1, and the adsorption amount fell again at $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 1.5–2.5. In another study, the optimum was at $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 5 in the case of Cs^+ adsorption. (López et al. 2014a)

The $\text{Na}_2\text{O}/\text{SiO}_2$ ratio should be sufficiently high to depolymerize aluminosilicate via the action of alkali. However, a too high $\text{Na}_2\text{O}/\text{SiO}_2$ ratio can inhibit the reaction (Granizo et al. 2007). The typical optimum of $\text{Na}_2\text{O}/\text{SiO}_2$ in terms of compressive strength is approximately 0.68 (when using metakaolin as precursor), but the resulting materials exhibited a low porosity (Gao et al. 2014). The parameter $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, on the other hand, describes how well the negative charge of the aluminosilicate network is balanced (for instance by Na^+); and consequently, a value of approximately one is an optimum. Higher $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios increase the instability of the AAM, which can be observed as disintegration when immersed in water (Pimraksa et al. 2011) and as formation of efflorescence. The $\text{Na}_2\text{O}/\text{SiO}_2$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios have varied between 0.01–1 and 0.02–2.4, respectively, in AAM adsorbents (Table 1). Finally, the $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio of AAM adsorbents has varied within the range 9–22. A large $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio increases channel formation in the material but decreases surface area: ratios of 18–19 and 21–22 resulted in approximately 37–39 and 3–9 m^2/g specific surface areas, respectively (Ge et al. 2015a).

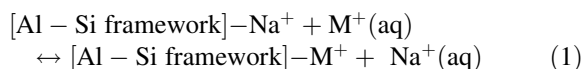
According to Landi et al. (2013), increasing the water amount increases total porosity and the average pore diameter of AAMs because water acts as pore-forming agent.

When AAM adsorbents are prepared using the fusion method, solid sodium hydroxide is reacted with fly ash (weight ratio 0.8–1.2) at 250–600 °C for 1–2 h and water is subsequently added at a liquid-to-solid weight ratio of 4.0–4.5 (Li et al. 2006; Javadian et al. 2013; Wang et al. 2007). Increasing the fusion temperature and the amount of NaOH up to a certain value increases the adsorption efficiency, possibly by increasing the structure porosity (Wang et al. 2007). However, the high temperature of the fusion method could decrease the environmental feasibility of the method. One interesting variant of the fusion method is the reaction of NaOH with kaolin (optimum at weight ratio of over 2.2) at elevated temperature (500–700 °C, at least 14 h) and subsequent rinsing with distilled water (800 mL/1 g of product) (Naghsh and Shams 2017). The benefit of this synthesis method was that kaolin did not need a separate dehydroxylation step into metakaolin.

Important physico-chemical characteristics of adsorbents and catalysts include specific surface area, pore size distribution, and zeta potential. Specific surface area AAMs is typically in the range of 17–56 m^2/g (Bortnovsky et al. 2008; Wang et al. 2007; Luukkonen et al. 2016b). However, specific surface areas up to 114 m^2/g have been reported (Lee et al. 2016a). With an addition of surfactant, the specific surface area can be further increased: for instance, from 137 to 216 m^2/g by using cetyl trimethylammonium bromide (Singhal et al. 2017). AAMs are usually mesoporous (i.e., pore size 2–50 nm), but also micro (< 2 nm) and macro pores (> 50 nm) are present (Bortnovsky et al. 2008; Luukkonen et al. 2016b). The zeta potential of AAMs is negative due to the negative charge of the aluminosilicate framework structure (Luukkonen et al. 2016b; López et al. 2014b). The point of zero charge for metakaolin geopolymers has been determined to be at pH 4.5 (Luukkonen et al. 2016b) and 8.0 for alkali-activated LD slag (which is a high-calcium system) (Sarkar et al. 2018).

Adsorption of alkaline earth metals, transition metals, metalloids, and rare earth elements

The main sorption mechanism of AAMs is thought to be ion exchange similar to zeolites (Bortnovsky et al. 2008) which occurs at both interlayer and surface sites (Provis et al. 2015). Ion exchange can be presented on a general level with Reaction 1, where M^+ is a cation with a higher affinity than Na^+ (in this example, Na is used as the charge-balancing cation). With high-calcium AAMs, the tobermorite-like phases have cation-exchange/adsorption properties as well (Guo and Shi 2017).



Due to the high alkalinity of AAMs and subsequent increase of pH, some transition metal cations can precipitate in addition to sorption (Novais et al. 2016b). However, the increase of pH is modest in well-buffered effluents: for example, municipal wastewater pH increased significantly only when over 5 g/L metakaolin geopolymer adsorbent powder doses were used (Luukkonen et al. 2017b). Furthermore, it has been shown that careful flushing with water decreases pH of AAMs to near neutral values (Ge et al. 2015a). Finally, the removal of some anionic impurities, for instance $H_2AsO_3^-$, has been explained by the formation of secondary mineral phases, such as hydroxalite (which is, as layered double hydroxide, anion exchanger), during alkali-activation (Luukkonen et al. 2016a).

AAMs have been studied for the removal of several potentially toxic elements: for instance, Co, Pb, Cu, Zn, Cr, Ni, As, and Sb (Table 1). Exposure to these metal(loid)s can be acutely toxic for humans and other organisms at elevated concentrations whereas a prolonged exposure to lower concentrations can cause cancers, for instance (Chowdhury et al. 2016; Järup 2003; Tchounwou et al. 2012). The origin of these metal(loid)s to the aquatic environment is from various industrial (point) sources and other human activities but also through dissolution of natural geological depositions. The World Health Organization guideline maximum concentrations for Cu, Ni, Cr (total), Sb, Pb, As, and Cd in drinking water are 2000, 70, 50, 20, 10, 10, and 3 $\mu\text{g/L}$, respectively (World Health Organization 2011a). For Co and Zn, there are

no established guideline values (World Health Organization 2011a; Kim et al. 2006). As can be seen from Table 1, AAMs represent promising removal efficiencies and regenerability for above-mentioned metal (loid)s in many reported cases. For instance, Ge et al. (2015b) prepared porous metakaolin-based geopolymeric spheres, which had higher capacity than commercial spherical molecular sieves (4 A zeolite) for Cu removal and acceptable stability in acidic conditions. However, as a large majority of the experiments in Table 1 is conducted with synthetic wastewaters, more research is needed before the practical potential of AAM adsorbents can be realistically evaluated.

Calcium and magnesium are essential minerals for human health but their presence at elevated concentrations causes the formation of scale in domestic and industrial water networks and heat exchangers (World Health Organization 2011b). Tang et al. (2015) used porous metakaolin-based geopolymer to adsorb Ca^{2+} but their material was characterized by a relatively low capacity (24 mg/g) and a long required contact time (equilibrium was reached after 50–60 h). Naghsh and Shams (2017) obtained regenerable water-softening geopolymer (for Mg and Ca removal) from kaolin using a novel fusion method: their material was comparable to commercial water softeners (for instance 4A zeolite) in terms of efficiency. Experiments were conducted in both synthetic and real groundwater (Naghsh and Shams 2017).

Rare earth elements (REEs) are critical resources for several high technology applications and thus their demand is increasing. REEs are typically present as relatively low concentrations within minerals, which requires efficient extracting technologies. Furthermore, the recycling of REEs from various end-of-life products is challenging. Fiket et al. (2018) reported a preliminary study in which they adsorbed Ce, La, Nd, Pm, Dy, Er, Eu, Gd, Ho, Lu, Sc, Sm, Tb, Tm, Y, and Yb from multi-element solution (total concentration of REEs was 1 mg/L) on coal fly ash-geopolymer. Their results demonstrate that all studied REEs were adsorbed quite effectively when using contact time of 120 min and that the geopolymer SiO_2/Na_2O ratio of 0.7–0.8 was more efficient than 1.1–1.3.

The selectivity of metakaolin-based geopolymer adsorbents has been studied in several publications with the following results: $Cs^+ > Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Cd^{2+}$ (López et al. 2014b); $Pb^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Cr^{3+}$ (Andrejkovicová

et al. 2016); $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Cr}^{3+}$ (Cheng et al. 2012); and $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ca}^{2+}$ (Tang et al. 2015). The results seem rather consistent although the structure of geopolymers is nonordered: the main differences are the selectivity towards Cd^{2+} and the order of Cu^{2+} and Zn^{2+} . However, El-Eswed et al. (2012) obtained deviating results for kaolin/zeolite-based geopolymer: $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+}$. The selectivity of alkali-activated blast furnace slag was shown to be $\text{Ni}^{2+} > \text{As(III)} > \text{Sb(III)}$ in mine effluent (Luukkonen et al. 2016a). Ge et al. (2017) showed that the presence of Na^+ , Ca^{2+} , and Mg^{2+} decreased the adsorption efficiency of spherical metakaolin/alginate geopolymer towards Cu^{2+} . This demonstrates that the removal efficiency in real wastewaters with a multicomponent composition and varying ionic strength is likely to be lower than those reported in Table 1.

It has been suggested that the adsorption properties of AAMs could be utilized in construction materials such as water tanks, pipes, and dams (Alshaaer et al. 2012; Yousef et al. 2009; Alshaaer et al. 2010; Hamaideh et al. 2014). Good mechanical properties combined with adsorption capacity could be obtained if zeolitic tuff is used as fine aggregate in AAM binder (Andrejkovicová et al. 2016; Huang et al. 2012). However, regeneration of such permanent installations represents a challenge.

Adsorption of radioisotopes

AAMs have been used to adsorb several elements that have radioisotopes: cesium, strontium, radium, and cobalt (Table 1). The removal of radioisotopes from water has become increasingly important since the Fukushima nuclear accident in Japan in 2011 (Kinoshita et al. 2011; Liu et al. 2014). Cesium occurs as Cs^+ in the aqueous environment and is highly soluble and stable (Lima 2010). Radioactive ^{137}Cs is of special concern due to its long half-life of 30.2 years. Strontium (present primarily as Sr^{2+} in the aqueous environment) has several radioactive isotopes, of which ^{90}Sr (half-life 28.9 years) is the most significant (Guillén et al. 2010). All isotopes of radium (commonly present as Ra^{2+} in low salinity conditions) are radioactive (half-lives vary from a few days up to 1600 years) (International Atomic Energy Agency 2014). AAM from metakaolin was potentially effective in adsorbing Cs: it was selective over Pb^{2+} , Cu^{2+} ,

Cd^{2+} , Ni^{2+} , and Zn^{2+} and the adsorption efficiency was not affected by the presence of NaCl up to 10 weight-% concentration (López et al. 2014a, b). Chuang and Liao (Chuang and Liao 2015) adsorbed Cs^+ on phosphate geopolymer containing potassium zinc ferrocyanide. Lee et al. (2017) used porous AAM blocks prepared from fly ash and blast furnace slag to remove Cs^+ . AAMs compare favorably to many other adsorbents that have been used to remove Cs^+ in terms of, for instance, maximum adsorption capacity (Liu et al. 2014). Chen et al. (2013) studied the removal of Cs^+ , Sr^{2+} , and Co^{2+} with AAM prepared of metakaolin and fly ash and obtained very high adsorption capacities (see Table 1). It was also possible to desorb these ions with 0.1 M HCl indicating that adsorbent could be regenerated (Chen et al. 2013). Also fly ash-based AAMs are potentially effective in removing Co^{2+} (it should be noted that radioisotopes and non-radioactive isotopes have similar aqueous chemistry) (Mužek et al. 2016a, b). Finally, radium isotopes were removed with foamed AAM in which BaSO_4 was incorporated: the material was suggested for use as a passive filtration material (Kunze et al. 2002).

Adsorption of dyes

Several AAMs have been used for the removal of the basic cationic dyes methylene blue and crystal violet (Table 1). Khan et al. (2015) adsorbed methylene blue on phosphoric acid-activated metakaolin (Langmuir capacity, 4.26 mg/g). It was possible to regenerate the adsorbent multiple times by calcination at 400 °C for 2 h, and the adsorption capacity in fact improved upon regeneration (Khan et al. 2015). An approximately similarly effective methylene blue adsorbent (Langmuir capacity, 4.75 mg/g) was prepared by Yousef et al. (2009) via the NaOH activation of kaolin and using zeolite as filler. Li et al. (2006) prepared fly ash-based AAM via a solid-state fusion method with NaOH and obtained somewhat higher capacities: 18.3 and 17.2 mg/g for methylene blue and crystal violet, respectively. The most efficient AAM to date for methylene blue was prepared by Liu et al. (2016c), who obtained an experimental adsorption capacity of 50.7 mg/g: their adsorbent also showed improved porosity and was floatable due to the addition of H_2O_2 . Although AAMs show some promising features for dye removal, such as the ability to be regenerated,

their currently reported adsorption capacities are clearly inferior to that of commercially available activated carbons or several other experimental adsorbents (Rafatullah et al. 2010). However, Barbosa et al. (2018) prepared AAM from metakaolin, rice husk ash, and soybean oil (as mesostructured directing agent), used it for the adsorption of crystal violet, and obtained relatively high maximum capacity of 276.9 mg/g.

Adsorption of ammonium and sulfate

Ammonium (NH_4^+) is the commonly occurring nitrogen species in, for instance, untreated municipal wastewater. Its removal has been studied extensively via ion-exchange on natural and synthetic zeolites as an alternative to the traditionally used microbial nitrification–denitrification (Couto et al. 2016; Hedström 2001; He et al. 2016; Leyva-Ramos et al. 2010; Niu et al. 2012; Zhang et al. 2011; Ye et al. 2015; Sarioglu 2005; Ji et al. 2007). In fact, anaerobic digestion followed by natural zeolite-based ion exchange had potential for the recovery of nitrogen, lower operational costs, and better nitrogen-removal performance in comparison to the conventional nitrification–denitrification or the Anammox processes (Lin et al. 2016). Luukkonen et al. (2016b) used metakaolin-based geopolymer and obtained 21.07 mg/g ammonium adsorption capacity in model solutions, which was higher than that obtained with typical natural zeolites. They also demonstrated that the removal was based on ion exchange, material could be regenerated with a solution containing 0.2 M NaCl and 0.1 M NaOH, and the adsorbent was effective for on-site treatment of landfill leachate (initial $\text{NH}_4^+ \approx 55$ mg/L) at low temperatures (Luukkonen et al. 2016b). In another study, Luukkonen et al. (2017a) used a central composite design technique to optimize the preparation of metakaolin geopolymer to maximize ammonium adsorption capacity. Using higher amounts of silicate and hydroxide, lower amounts of metakaolin, and sodium as the charge balancing cation instead of potassium during the preparation resulted in the best capacity (Luukkonen et al. 2017a). With the aforementioned optimization, it was possible to increase the maximum adsorption capacity from 21.07 to 31.70 mg/g (Luukkonen et al. 2017a). Luukkonen et al. (2017b) also prepared metakaolin geopolymer with the

granulation-geopolymerization method to be used as a filter media. In a continuous small-scale pilot (Fig. 2), it was possible to consistently obtain less than 4 mg/L ammonium concentration in municipal wastewater (initial $\text{NH}_4^+ \approx 23$ mg/L) at low temperature (approximately 10 °C) and regenerate material multiple times with NaCl/NaOH. Bai and Colombo (2017) studied metakaolin-based geopolymer foams in the form of monolithic porous filters, which could be prepared by 3D printing using the direct ink writing technique. The filter was able to remove up to 95.3% of ammonium from the initial concentration of 3 mg/L NH_4^+ (Bai and Colombo 2017).

Sulfate (SO_4^{2-}) is a ubiquitous naturally occurring anion that is not considered toxic as such, but it can cause salinization of water bodies. Therefore, sulfate removal must be managed in several industries, such as mining (acid mine drainage) (De La Torre et al. 2011) and desalination plants (reverse osmosis reject water) (Pérez-González et al. 2012). Runtti et al.



Fig. 2 Small pilot-scale set-up for ammonium removal from municipal wastewater using granulated metakaolin geopolymer (Luukkonen et al. 2017b). With this set-up, it was possible to reach < 4 mg/L NH_4^+ in cold wastewater (≈ 10 °C)

(2016) modified alkali-activated blast furnace slag by exchanging charge-balancing sodium cations into barium and used the obtained material to remove sulfate from synthetic wastewater ($\text{SO}_4^{2-} \approx 1000 \text{ mg/L}$) and mine effluents ($\text{SO}_4^{2-} \approx 900 \text{ mg/L}$). The observed adsorption capacity was relatively high, approximately 119 mg/g , and it was possible to achieve very low sulfate concentrations ($< 2 \text{ mg/L}$) (Runtti et al. 2016). The proposed removal mechanism was the surface complexation or precipitation of extremely low solubility BaSO_4 (Runtti et al. 2016). Zhang et al. (2018) showed by molecular dynamics simulation that cations such as Na^+ or Mg^{2+} are adsorbed on the surface hydroxyls of the NASH gel and attract SO_4^{2-} ions.

Thermodynamics of adsorption

Thermodynamic parameters, standard enthalpy change (ΔH^0), standard entropy change (ΔS^0), and standard free energy change (ΔG^0), provide information about the nature and thermodynamic feasibility of the adsorption process. The reported ΔH^0 values of adsorption on AAMs have been generally positive (Runtti et al. 2016; Javadian et al. 2013; Al-Harashsheh et al. 2015; Duan et al. 2016; Sarkar et al. 2017; Liu et al. 2016b; Al-Zboon et al. 2011, 2016), which indicates that the adsorption efficiency increases at higher temperatures. However, one deviating result ($\Delta H^0 < 0 \text{ kJ/mol}$) was obtained by Li et al. (2006) for methylene blue removal by fly-ash based geopolymer. Further support is provided by the fact that the values of ΔS^0 are consistently positive indicating that the system entropy increases after adsorption process (Runtti et al. 2016; Javadian et al. 2013; Al-Harashsheh et al. 2015; Duan et al. 2016; Sarkar et al. 2017; Liu et al. 2016b; Al-Zboon et al. 2011, 2016). This has been explained by the separation of hydrated water molecules from the metal ion (i.e., inner-sphere complexes are formed and specific adsorption occurs) before attachment to the surface sites of AAMs, which is an energy-requiring process (Al-Zboon et al. 2011; Al-Harashsheh et al. 2015). Finally, the negative ΔG^0 (numerical values approx. -6 to -27 kJ/mol) indicate that adsorption on geopolymers is an overall spontaneous process through physical and reversible interactions (Runtti et al. 2016; Javadian et al. 2013; Al-Harashsheh et al. 2015; Duan et al. 2016; Sarkar

et al. 2017; Liu et al. 2016b; Al-Zboon et al. 2011, 2016).

Membranes and filters

Alkali-activation technology allows the production of highly porous ceramic-like inorganic self-supporting membranes and filters without sintering (Bai and Colombo 2018) and subsequently could lower the production costs compared to the conventional ceramic materials. In fact, ceramic filters and membranes have many beneficial features over organic polymers but their high price has prevented more widespread use in industrial water treatment (Ciora and Liu 2003). The existing laboratory-scale studies have pointed out, as discussed below, that the performance of AAMs in membrane separation is promising and in some cases already comparable to commercially available materials. However, the majority of the published articles is so far more concentrated on the material science aspects than on the applications. This section summarizes the AAM materials for external pressure-driven membranes and gravity filtration media.

Pressure-driven membranes

Pressure-driven membranes are classified as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, based on the separation capacity. Of these classes, AAM membranes have been typically in the micro or ultrafiltration range (pore sizes $20\text{--}100 \text{ nm}$) (Ge et al. 2015a; Xu et al. 2015). The inherent porosity of AAM materials can be utilized for membrane application, which means that the preparation process does not necessarily require any specific additives or foaming processes. However, one of the first geopolymer membranes was prepared using the sacrificial filler method: self-assembled layers from nano-sized polystyrene spheres were prepared, covered with metakaolin-alkali silicate slurry, 200 MPa pressure was applied for 1 h , and curing was conducted at 50°C for 24 h and the polystyrene template was dissolved with a solvent (Mallicoat et al. 2005). Ge et al. (2015a) prepared an AAM membrane via directly mixing metakaolin with sodium silicate and curing at 60°C : the membrane had a total porosity of 62.64% and water flux values (at steady state) between

approximately 21 and 237 kg/(m² × h) at 0.1 MPa depending on the H₂O/Na₂O ratio. Furthermore, the membrane could adsorb Ni²⁺ with a capacity of 43.36 mg/g (Ge et al. 2015a). Xu et al. (2015) prepared a similar membrane from metakaolin with an optimum H₂O/Na₂O ratio of 18: the membrane had water flux of 185 kg/(m² × h) at 0.3 MPa (membrane thickness, 5.0 mm) and 100% rejection rate for nanosized Al₂O₃ particles. In addition, an AAM membrane with potential to remove Ca²⁺ and Mg²⁺ has been reported (Li et al. 2017). Alkali-activated blast furnace slag membranes were prepared by the hydraulic pressing method: the optimum conditions for preparation were 400 bar pressure, 6 h drying time, and 5 min pressing time and 225 bar pressure, 8 h drying time, and 30 min pressing time for chemical oxygen demand (COD) removal (100%) and permeation flux optimization (1960 kg/(m² × h), respectively (Mohammadi and Mohammadi 2017).

Another method to utilize the alkali-activation technology for membrane preparation is to first prepare amorphous AAM material and convert it into crystalline zeolite membrane using hydrothermal aging process. For instance, self-supporting NaA zeolite membranes have been prepared of AAM material by submerging them into water or dilute NaOH solution at approximately 90 °C for 6–48 h (Yan et al. 2012; Xuemin et al. 2011; He et al. 2013; Zhang et al. 2014, 2016). Furthermore, if the Na/Si ratio is increased up to 1.25, the transformation from amorphous AAM into zeolite can occur via a simple heat curing (at 60 °C) without hydrothermal treatment (Xu et al. 2017). AAMs can also be cured into a faujasite-type zeolite by optionally adding oleic acid and aluminum powder to promote permeability (Liu et al. 2016a, 2017). Although the aforementioned membranes were used for the water–ethanol separation, it has been demonstrated that zeolite membranes also have potential in water treatment applications (Kazemimoghadam 2010; Cui et al. 2008).

Filtration media

In addition to the high pressure-driven membrane filtration, AAM materials could also be used as filtration media in sand filters, permeable reactive barriers, or point-of-use water treatment filters, as an example. In these uses, AAMs could serve as adsorptive (see Sect. 2) and/or catalytically active (see

Sect. 3) media in addition to simple physical filtration. This application requires, however, pores in the range of micro or millimeters, in addition to micro and mesoporosity, to have sufficiently high permeability. The preparation methods of highly porous AAM materials have been classified as direct foaming, sacrificial filler method, replica method, additive manufacturing, and other methods (such as granulation) (Bai and Colombo 2018). The direct foaming is the most widely used method and it involves mechanical mixing or blowing agents to introduce gas bubbles into the fresh AAM paste (Bai and Colombo 2018). When surfactants are used, they stabilize the formed foam and resulting materials have highly interconnected pores and permeability similar to that of granular filters (Strozi Cilla et al. 2014b). Surfactants can also be produced in situ by adding, for example, vegetable oils (triacylglycerols) to the alkaline AAM suspension, which results in the saponification reaction (decomposition into glycerol and soaps) due to high pH (Cilla et al. 2017; Bai et al. 2016). In addition, albumin powder (from chicken egg white) has been studied as a surfactant for foaming AAMs with hydrogen peroxide (Bai and Colombo 2017). AAM foam was able to adsorb 95% and 87% of ammonium and copper, respectively, from synthetic wastewater when the initial concentration was 3 mg/L for each (Bai and Colombo 2017). The total and open porosities of the aforementioned foams were in the ranges of 67–88 and 60–85 vol%, respectively (Bai and Colombo 2017; Strozi Cilla et al. 2014a; Bai et al. 2017; Cilla et al. 2017). Landi et al. (2013) prepared geopolymer filter material from metakaolin, potassium silicate, and fumed silica with highly interconnected macropores by using elemental silicon as blowing agent. The filter had NH₄⁺ exchange capacity, although it was concluded that only a small portion of the inner volume pores were accessible due to cavity dimensions. Pervious alkali-activated concrete (prepared of fly ash, nanosized silica, and ordinary Portland cement) could be used for phosphorus and fecal coliform removal from wastewater due to leaching of calcium and increase of pH, respectively (Jo et al. 2015). Finally, additive manufacturing, or 3D-printing, of AAM materials is a method to produce carefully controlled pore sizes, shapes, and amounts (Bai and Colombo 2018). Examples of porous materials prepared by direct foaming, 3D printing, and geopolymerization-granulation are shown in Fig. 3.

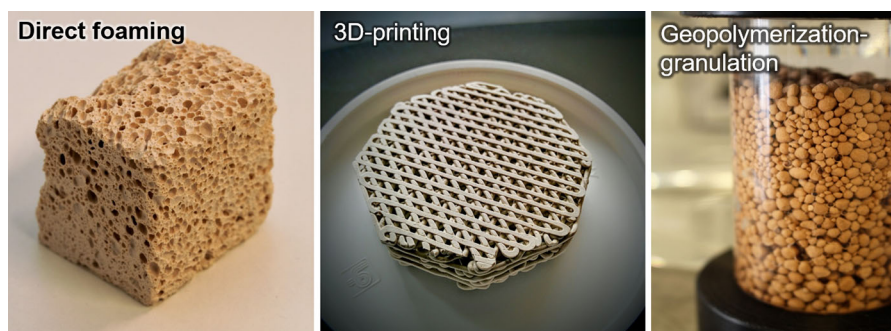


Fig. 3 Approaches for preparing porous filters by alkali-activation: direct foaming, 3D-printing and geopolymerization-granulation (pictures are from experimental work conducted at the Fibre and Particle Engineering Research Unit,

University of Oulu (Finland); the Department of Industrial Engineering, University of Padova (Italy); and Kajaani University of Applied Sciences, Kajaani (Finland), respectively). Photograph credits Tero Luukkonen and Kimmo Kempainen

Catalysts

AAMs have been studied as catalysts or catalyst supports for pollutant degradation in both gas and liquid phase reactions (Asim et al. 2019). In water and wastewater treatment, they have been so far applied as photocatalysts (i.e., reactive radicals are produced when the catalyst is exposed to irradiation with energy equal to or larger than the bandgap) for degradation of various dyes. AAM catalysts could be also used in other types of advanced oxidation processes and for other recalcitrant organic pollutants as well but such studies are still lacking. AAMs are interesting materials for catalysts as they can be designed to have high permeability, surface area, chemical durability, and mechanical strength together with a simple, low-cost, and low-energy synthesis, as already discussed earlier. In this section, the preparation of AAM catalysts and studies in which they have been used for wastewater treatment are outlined.

The preparation of AAM catalysts and catalyst supports is largely similar to the preparation of adsorbents (see Sect. 2.1) or porous materials (see Sect. 3.2). An example of mesoporous microstructure of an AAM catalyst is shown in Fig. 4. Catalytically active metals can be introduced to the structure by mixing them into the fresh-state AAM paste in the form of salts or nanoparticles or to the cured material via ion exchange either directly or by first converting the geopolymer into NH_4^+ form (MacKenzie 2014). The advantage of carrying out the Na^+ to NH_4^+ ion exchange step first is that the subsequent ion exchange with catalytically active metal is more efficient (Gasca-Tirado et al. 2012). Moreover, wet

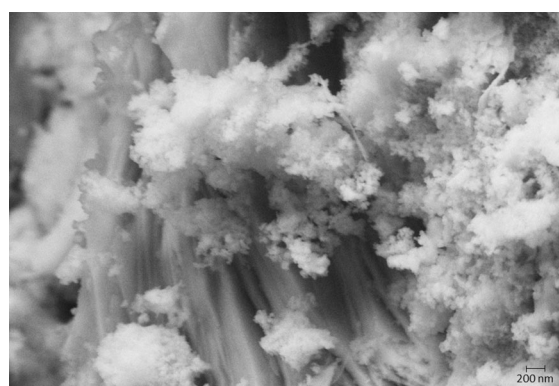


Fig. 4 Micrograph of a mesoporous AAM catalyst support prepared by mixing metakaolin and KOH

and incipient wetness impregnation techniques have been used for the addition of catalytically active components to geopolymers. Furthermore, some waste-based raw materials can already contain catalytically active metals as in a study by Zhang and Liu (2013) in which fly ash was used as an AAM precursor. It already contained a sufficient amount of metal oxide semiconductors, Fe_2O_3 (4.78 weight-%) and TiO_2 (0.94 weight-%), to provide photocatalytic activity for dye degradation (Zhang and Liu 2013).

The photocatalytic degradation of methyl orange was performed with Cd suspension geopolymer spheres (CdS-GS), which were prepared by the suspension-solidification method together with the photochemical synthesis process (i.e., the growth of CdS crystals was promoted by UV irradiation) (Li et al. 2016a). The methyl orange solutions (concentration 5 mg/L) were treated continuously (0.4 mL/min) at 25 °C in a quartz tube reactor packed with

CdS-GS catalysts under UV light. Methyl orange could be removed up to 93% (39% adsorption and 54% photo degradation) using a bed of 5 g of CdS-GS and 2 h contact time. Moreover, the resistance against catalyst poisoning was tested by repeating five cycles: the abatement of methyl orange was still over 90%, indicating that the CdS geopolymer spheres had relatively stable photocatalytic performance.

Another dye, methylene blue, was photocatalytically degraded using geopolymers based on metakaolin (Gasca-Tirado et al. 2012; Fallah et al. 2015) or fly ash (Zhang and Liu 2013). Gasca-Tirado et al. (2012) incorporated the active component, TiO_2 , into the metakaolin-based geopolymers via ion exchange. The geopolymers treated with ion exchange had a larger surface area than those without the active component. The highest Ti content was achieved with the geopolymer cured at 90 °C. After 90 min of reaction, the color of the methylene blue disappeared completely. Zhang and Liu (2013) used their fly ash-based photocatalyst (without addition of active metals) with a contact time of six hours and obtained 93% abatement of methylene blue. However, adsorption was responsible for 89% of the methylene blue removal. In the study of Fallah et al. (2015), most of the methylene blue degradation was also caused by adsorption of the dye onto the Cu_2O nanoparticle-modified metakaolin-based geopolymer, and UV-induced degradation was a minor mechanism.

Zhang et al. (2017) prepared a composite material from alkali-activated bottom ash and graphene containing Mn^{2+} and CuO as active metals. Metals were introduced by performing first ion-exchange of Na^+ to NH_4^+ and submerging the material into solutions of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2$. Then, calcination at 400 °C for 4 h was performed to convert copper into oxide. The catalyst was tested successfully for photocatalytic degradation of aqueous direct sky blue 5B dye and hydrogen gas production.

Solidification/stabilization of wastewaters and water treatment residues

Water and wastewater treatment processes produce various sludges, spent ion-exchangers, catalysts, and highly concentrated effluents, which pose frequently disposal problems due to the hazardous components and chemical instability. One option for treating these

water treatment residues (WTR) is the solidification/stabilization (S/S), which allows safe landfilling or utilizing obtained solid materials.

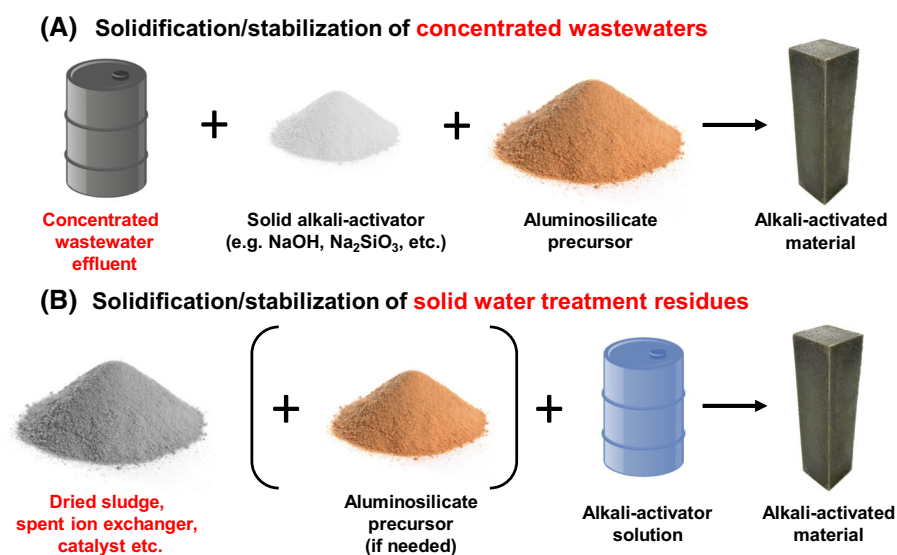
The definition of S/S is the process of mixing waste with binder to convert it into a monolithic solid and thus reduce the likelihood of release of hazardous components to the environment (Bernal 2014). Typically, S/S mechanisms are divided into two categories: (1) physical encapsulation and (2) chemical stabilization. However, a clear-cut separation is not meaningful as these mechanisms can work in conjunction and the exact determination of mechanism is difficult (Glasser 1997). Furthermore, El-Eswed (2018) defined the immobilization of solid and liquid wastes into an AAM matrix as “intra-solidification” and “inter-solidification”, respectively. Typically, AAMs are able to decrease the mobility of cationic species effectively, whereas transition metals, which form oxanionic species, remain less effectively stabilized (Bernal et al. 2014a, b). Both solid and liquid WTR fractions have been immobilized into the AAM matrixes as illustrated in Fig. 5.

Physical encapsulation occurs on a micrometer scale. The zeolite-type cage structures can trap hazardous components if their size is suitable. Other types of physical encapsulation can take place when a physical barrier prevents the leaching medium (water) from contacting the hazardous components, thus preventing leaching.

Chemical stabilization occurs on the nanoscale. Metal(loid)s can react with other reactive compounds in the mixture and become part of the aluminosilicate structure, for example by replacing silicon atoms (Schoenung 2008). It was recently demonstrated that the immobilization of metals does not occur with ion exchange but rather through isomorphous substitution (Zheng et al. 2016), which is a major difference from the above-discussed application as adsorbents (see Sect. 3). Transition metals could also precipitate as non-soluble compounds (e.g., as hydroxide) (Bernal et al. 2014a, b) and subsequently become trapped inside the geopolymer.

The studies concerning the S/S treatment of wastewaters (i.e., inter-solidification) have been mostly conducted with synthetic wastewaters (i.e., metal salts dissolved in water) (see Table 2). The S/S treatment method could also be potentially applied to extremely concentrated effluents such as reverse osmosis reject water (brine). Some water treatment

Fig. 5 Schematic presentation solidification/stabilization of **a** concentrated wastewaters and **b** solid water treatment residues. The need for aluminosilicate in **b** is determined by the reactivity of the solid water treatment residue. Obtained alkali-activated material can be safely disposed to landfill or utilized as, for instance, construction material. Photograph credits Simon A. Eugster and Tero Luukkonen



sludges, on the other hand, are suitable raw materials for AAMs as they contain alumina and/or silicate and the resulting products can be used as masonry units, for instance (Belmokhtar et al. 2016; Xu et al. 2013; Yang et al. 2009, 2010, 2013a, b; Guo and Shi 2012; Antunes Boca Santa et al. 2013; Chen et al. 2009, 2011; Choi et al. 2010; Yan et al. 2016; Nimwinya et al. 2016; Poowancum et al. 2015; Suksiripattanapong et al. 2015a, b, c; Horpibulsuk et al. 2015).

Table 2 compiles studies related to S/S of wastewater and solid WTRs. Studies in which hazardous components were added as solid are excluded from this survey, whereas the studies discussing S/S of WTRs, wastewaters, or synthetic wastewaters (i.e., model solutions) are included. As can be seen, most studies have used synthetic wastewater, such as lead and copper nitrates dissolved in water, to simulate immobilization of wastewater into AAMs. The suggested stabilization mechanism for most heavy metals is a combination of physical encapsulation, chemical bonding, and/or charge balancing of the negative aluminate group. The immobilization efficiency was not typically reported, although there are numerous suitable leaching procedures as described in Sect. 7. Sullivan et al. (2010) reviewed arsenic-containing water treatment waste disposal methods and suggested alkali-activation/geopolymerization as a potential approach, although no published studies were available.

Leaching tests and regulatory guidelines

As the primary goal of S/S is to reduce the release of contaminants into the environment, chemical leaching tests provide the most useful information regarding the successfulness of S/S treatments. Experimental conditions such as pH, type and amount of leachant, leaching time, and particle size of the studied material affect the concentration of contaminants in the leachate. Consequently, the purpose of this section is to provide a general overview of the regulatory requirements for stabilized materials and introduce some of the most commonly used leaching tests.

Leaching tests can be roughly divided into three groups: (1) regulatory tests, (2) predictive tests, and (3) investigatory tests (LaGrega et al. 1994). The first group of tests are used in regulatory decision-making processes, where the result of the test is compared to the limit values determined by the authorities. Predictive tests are used for modeling real-world contaminant migration in the long term. Investigatory tests are used to study the binding mechanisms of contaminants.

European leaching limits for landfilling

According to the European waste hierarchy, landfilling is the least preferable option for waste management (European Council 2008). However, where landfilling of waste is required, it is regulated with the Landfill Directive (European Council 1999), which

Table 2 Solidification/stabilization studies of wastewater and water treatment residues into alkali-activated matrix

Precursor	Activator	Curing conditions		Waste	Hazardous components	Haz. component dosage (wt%)	Suggested stabilization mechanism	Refs.
		T (°C)	t (d)					
Metakaolin	NaOH, (Na ₂ SiO ₂) _n O	22	15–540	Chromium liquid waste	Cr ³⁺ , Cr ⁶⁺	3–20 ^a	–	Ponzoni et al. (2015)
Metakaolin	NaOH, (Na ₂ SiO ₂) _n O	90, 60, 22	1	K ₂ Cr ₂ O ₇ solution	Cr ⁶⁺	0.1	Redox-reaction with Fe ²⁺ , charge balancing	Chen et al. (2016)
Metakaolin	NaOH, (Na ₂ SiO ₂) _n O	23	7	Pb(NO ₃) ₂ and Cu(NO ₃) ₂ solutions	Pb ²⁺ , Cu ²⁺	0.5	Physical and chemical	Phair et al. (2004)
Metakaolin	NaOH or KOH, (Na ₂ SiO ₂) _n O or (K ₂ SiO ₂) _n O	45	1	Pb(NO ₃) ₂ and Cu(NO ₃) ₂ solutions	Pb ²⁺ , Cu ²⁺	0.5	Physical	Phair and Van Deventer (2001)
Class F fly ash	NaOH, (Na ₂ SiO ₂) _n O	40	28	CsNO ₃ dissolved in Na silicate	Cs ⁺	2	–	Deng et al. (2015)
Fly ash	NaOH, (Na ₂ SiO ₂) _n O	60	28	CsNO ₃ dissolved in water or Na silicate	Cs ⁺	2	Chemical bonding	Li et al. (2013)
Fly ash	NaOH, (Na ₂ SiO ₂) _n O, NaAlO ₂	70, 22	1, 7	Pb(NO ₃) ₂ solution	Pb ²⁺	0.5, 1	Charge balancing	Lee et al. (2016b)
Fly ash	NaOH, (Na ₂ SiO ₂) _n O	20	1, 28	Pb(NO ₃) ₂ solution	Pb ²⁺	0.5, 1	Physical and charge balancing	Nikolić et al. (2014)
Fly ash, BFS	NaOH, (Na ₂ SiO ₂) _n O	60, 20	1, 28	CsCl and SrCl ₂ ·6H ₂ O dissolved in water or Na silicate	Cs ⁺ , Sr ²⁺	10 ^b	Physical	Jang et al. (2016)
Kaolin, zeolitic tuff	NaOH	80, 22	1, > 30	Pb(NO ₃) ₂ , Cu(NO ₃) ₂ , Cd(NO ₃) ₂ and Cr(NO ₃) ₃ solutions	Pb ²⁺ , Cu ²⁺ , Cd ²⁺ , Cr ³⁺	0.0014 ^c	Charge balancing	El-Eswed et al. (2015)
Metakaolin, GGBFS	NaOH, (Na ₂ SiO ₂) _n O	150, 80, 20	1, 6	Pb(NO ₃) ₂ and Cu(NO ₃) ₂ solutions	Pb ²⁺ , Cu ²⁺	0.1, 0.2, 0.3	–	Yunsheng et al. (2007)
Fly ash, kaolin, metakaolin	KOH, NaOH	30, 20	7, 14, 28, 60	Pb(NO ₃) ₂ and Cu(NO ₃) ₂ solutions	Pb ²⁺ , Cu ²⁺	0.1, 0.2	Physical, chemical bonding	Van Jaarsveld et al. (1999)
WTR, calcined WTR	NaOH	28	7	Electroplating sludge from wastewater treatment plant	Zn, Cr	–	–	Wajjarean et al. (2014)

Table 2 continued

Precursor	Activator	Curing conditions		Waste	Hazardous components	Haz. component dosage (wt%)	Suggested stabilization mechanism	Refs.
		T (°C)	t (d)					
Paper sludge ash	NaOH, (Na ₂ SiO ₂) _n O	20	28	Sr(NO ₃), Cs(NO ₃) added to geopolymer slurry	Sr ²⁺ , Cs ⁺	1 (as nitrate)	Ion exchange into faujasite or geopolymer gel	Li et al. (2016b)
Coal fly ash	Na ₂ CO ₃ , (Na ₂ SiO ₂) _n O	20	1, 6	Electroplating sludge from wastewater treatment plant	Pb, Cr, Cd, Zn, Cu	–	–	Asavapit and Chotklang (2004)

^a = weight-% of waste, ^b = g/L of volume of waste simulant, ^c = as nitrate salt

defines different waste categories (municipal waste, hazardous waste, non-hazardous waste, and inert waste) and landfill types (inert waste, non-hazardous waste, and hazardous waste). Exact criteria for different waste classes and landfill types are given in the 2003/33/EC (European Council 2003). Leaching limit values for the different types of landfills are given in Table 3. Leaching of different components must be determined using either standards EN 12457/1-4 (EN 12457-1 2002; EN 12457-2 2002; EN 12457-3 2002; EN 12457-4 2002) or CEN/TS 14405 (2004). Member states can determine which of the test methods and corresponding limit values should be used.

Regulatory leaching tests

The four-part EN 12457 standard is a compliance tests used to determine whether the waste complies with specific reference values (see Table 3). The tests include one or two extraction batches on different L/S ratios (2–10) and different particle sizes (< 4 or < 10 mm). In all phases, a sample is shaken with distilled water for a total of 24 h. These tests have also been used for AAM samples (Kourti et al. 2011; Pereira et al. 2009; Izquierdo et al. 2009, 2010; Lancellotti et al. 2010; Galiano et al. 2011; Ogundiran et al. 2013; Onisei et al. 2012; Nikolić et al. 2013).

Percolation test CEN/TS 14405 (2004) is used to study the leaching of inorganic constituents from granular wastes. The studied sample (particle size < 4 mm or < 10 mm) is packed into a column and demineralized water is percolated through it (15 ± 2 cm/day). Samples from the eluate are collected with cumulative L/S ratios of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, and 10.0.

United States Environmental Protection Agency method EPA 1311 (Toxicity Characteristic Leaching Procedure, TCLP) is meant to study the leaching of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes (SW-846 Test Method 1311 1992). Liquid wastes are filtered and the extract is analyzed. Solid wastes (particle size < 9.5 mm) are agitated with extraction fluid for 18 h (L/S = 20). The extraction fluid is an aqueous solution of either acid (pH 2.88) or acid and NaOH (pH 4.93). This test has been widely used for AAM samples (Galiano et al. 2011; Nikolić et al. 2013; Ogundiran et al. 2013; Onisei et al. 2012; Pereira et al. 2009; Fernández-

Table 3 Leaching limit values for different types of landfills according to the European Council Decision 2003/33/EC (2003)

Component	Inert waste			Non-hazardous waste/Hazardous waste acceptable at non-hazardous waste landfill			Hazardous waste		
	L/S = 2	L/S = 10	C ₀	L/S = 2	L/S = 10	C ₀	L/S = 2	L/S = 10	C ₀
	L/kg	L/kg	(percolation test) mg/L	L/kg	L/kg	(percolation test) mg/L	L/kg	L/kg	(percolation test) mg/L
	mg/kg dry substance			mg/kg dry substance			mg/kg dry substance		
As	0.1	0.5	0.06	0.4	2	0.3	6	25	3
Ba	7	20	4	30	100	20	100	300	60
Cd	0.03	0.04	0.02	0.6	1	0.3	3	5	1.7
Cr total	0.2	0.5	0.1	4	10	2.5	25	70	15
Cu	0.9	2	0.6	25	50	30	50	100	60
Hg	0.003	0.01	0.002	0.05	0.2	0.03	0.5	2	0.3
Mo	0.3	0.5	0.2	5	10	3.5	20	30	10
Ni	0.2	0.4	0.12	5	10	3	20	40	12
Pb	0.2	0.5	0.15	5	10	3	25	50	15
Sb	0.02	0.06	0.1	0.2	0.7	0.15	2	5	1
Se	0.06	0.1	0.04	0.3	0.5	0.2	4	7	3
Zn	2	4	1.2	25	50	15	90	200	60
Cl [−]	550	800	460	10,000	15,000	8500	17,000	25,000	15,000
F [−]	4	10	2.5	60	150	40	200	500	120
SO ₄ ^{2−}	560 ^a	1000 ^a	1500	10,000	20,000	7000	25,000	50,000	17,000
Phenol index	0.5	500	0.3	–	–	–	–	–	–
DOC ^b	240	1	160	380	800	250	480	1000	320
TDS ^c	2500	4000	–	40,000	60,000	–	70,000	100,000	–

^aIf the these values are not met, alternative requirements are: 1500 mg/L as C₀ at L/S = 0,1 L/kg (percolation test) and 6 000 mg/kg at L/S = 10 L/kg (batch leaching or percolation test)

^bIf these values are not met (at pH of waste), alternative testing conditions are L/S = 10 L/kg and a pH between 7.5 and 8.0: the results should be ≤ 500 mg/kg (inert waste) or ≤ 800 mg/kg (non-hazardous waste and hazardous waste)

^cThe values for total dissolved solids (TDS) can be used alternatively to the values for sulfate and chloride

Jiménez et al. 2005; Bankowski et al. 2004a, b; Kumar and Kumar 2013; Phair et al. 2004).

Other tests that can be applied for AAMs include batch tests EPA 1313 (SW-846 Test Method 1313) and EPA 1312 (SW-846 Test Method 1312 1994). The first is used to study the leaching of inorganic constituents as a function of pH and the latter (The Synthetic Precipitation Leaching Procedure, SPLP) is similar to the TCLP test (SW-846 Test Method 1311 1992) but the extraction fluids are different (mixture of sulfuric and nitric acids; pH 4.2 or 5.0). Diffusion tests ANS 16.1 (2008) and MCC-1 (1981), also usable for AAMs, were originally designed for nuclear wastes. Finally, batch leaching test NEN 7341 (1995) is used to

measure the maximum solubility of harmful substances from granulated waste material.

Predictive leaching tests

Diffusion test NEN 7345 (1995) has been used especially in Europe to study the solubility of waste materials. However, this test has been replaced with static diffusion test NEN 7375 (2004), which is used to simulate the leaching of inorganic components into water from monolithic materials under aerobic conditions as a function of time. With this test, it is possible to determine the leaching mechanism (diffusion, dissolution, depletion, or surface wash-off) of

inorganic components. In the test, solid cubic mortar samples are subjected to leaching in closed tanks using deionized water as the leachant. The water is replaced eight times during the test (at 0.25, 1, 2.25, 6, 9, 16, 35, and 65 days). The eluates are filtered, and the filtrates are analyzed. These standards have been used in some studies for geopolymer samples (Pereira et al. 2009; Izquierdo et al. 2010; Ogundiran et al. 2013; Álvarez-Ayuso et al. 2008).

Investigatory leaching tests

There are several sequential leaching methods in the literature, but the two most widely used are the Tessier et al. (1979) method and BCR (Rauret et al. 1999) method. In sequential leaching, various types of chemical reagents are applied to the samples in a series, with each successive treatment being more drastic than the previous one. Typical fractions of sequential leaching are (1) a water-soluble fraction, (2) an acid-soluble fraction, (3) a reducible fraction, and (4) an oxidizable fraction. In theory, the first fraction should contain water-soluble ions, while the second fraction should contain metals bonded electrostatically, metals bonded with weak covalent bonds, or metals bonded to carbonates. The third fraction should contain metals bonded to Mn and Fe oxides, while the fourth fraction should contain metals bonded to organic matter or to different sulfides and oxides. However, sequential leaching was originally designed for fractionating sediments. Therefore, the bonding of different metals that originate from matrixes that differ notably from sediments, such as geopolymers, cannot be precisely deduced from sequential extraction results. Still, even when the bonding of metals cannot be deduced from sequential extraction data, it nevertheless provides a good estimate of the solubility of metals in real environmental conditions. Sequential leaching has been used for geopolymer samples (Yliniemi et al. 2015; Pesonen et al. 2016).

Conclusions

The amount of studies about water and wastewater treatment with alkali-activated materials (AAMs) has significantly increased during the last decade. One of the main drivers for this interest is that AAMs have many beneficial characteristics (e.g., mechanical

strength, durability, porosity, and ion-exchange capacity) similar to competing materials (e.g., conventional ceramics, synthetic zeolites, or organic polymers) but the preparation process is simple and low-energy. Moreover, AAMs can be prepared of several industrial by-products, which makes them consistent with the circular economy.

As adsorbents or ion-exchangers, AAMs have shown promising potential for the removal and possible recovery of different metal(loid)s, rare earth elements, ammonium, sulfate, and organic dyes. Studies related to the use of AAMs as catalysts or catalyst supports indicate that these materials have a great potential for photocatalytic degradation of recalcitrant organic compounds (micropollutants). AAM-based membranes utilize the intrinsic mesoporosity of the materials and thus could be used in micro or ultrafiltration applications. However, if larger pore sizes are generated, AAMs can be used as lower pressure filtration media as well. The ability of AAMs to solidify/stabilize various potentially toxic elements can be taken advantage of in the management and utilization of water treatment residues such as sludges and spent adsorbents. Some other innovative uses for AAMs in water treatment include pH buffering materials, antimicrobial materials, and carrier media for biological treatment processes. As a final remark, it can be concluded that although the performance in the reviewed applications is promising, more research is needed in larger scale and longer duration to demonstrate the technological readiness of these materials.

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