

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Geopolymers and Alkali-Activated Materials for Wastewater Treatment Applications and Valorization of Industrial Side Streams

Tatiana Samarina, Esther Takaluoma and Outi Laatikainen

Abstract

The EU has the ambitious goal to transition from linear to circular economy. In circular economy, the old saying of “one’s waste is the other’s treasure” is being implemented. In this chapter, valorisation of industrial side streams, traditionally branded as waste, is discussed with respect to their applications as raw materials for new adsorptive products – geopolymers (GP) and alkali-activated materials (AAM) – as adsorbents in wastewater treatment. The chemical nature and structure of materials generally have great influence on GP/AAM adsorption capability. The approaches used for the raw materials preparation (chemical or physical) prior geopolymerization to increase the adsorption capacity of the final products will be discussed. Adsorption properties and performance of GPs/AAMs towards various contaminants are described, and the latest research on testing those materials as water remediation are reviewed. Special attention is paid to regeneration of exhausted materials and available resource recovery options that the regeneration approach opens. New forms of geopolymer adsorbent such as foams or core-shell structures are described and in the last part of the chapter, a short economic evaluation of resource recovery models is provided.

Keywords: adsorption, metal removal, nutrient recovery, geopolymer composite, wastewater treatment

1. Introduction

The United Nations have ratified 17 goals of sustainable development, of which responsible consumption and production is directly, while economy, innovative industry, infrastructure, and climate action are indirectly related to circular economy and the need of sustainable production [1]. Sustainability in the processing industries can be applied along the main value chain, e.g. from metal extraction to metal recycling, but can also be applied to the associated waste materials. Copper and iron mining alone are estimated to generate yearly about 5 bn tons of tailings [2], i.e. the fraction of the processed ore, after extraction of the valuable minerals. Finding a way to successfully reuse vast amount of this material and other waste sources is a great step towards circular economy.

While recycling an initial waste or side-stream, the material can be upcycled, meaning the newly derived product is of higher intrinsic value and properties or downcycled, where the new material has lower value. A prominent example for downcycling is the reuse of plastic bottles as fleece and carpet material. The material has less intrinsic value, because the carbon chains of the plastic polymer are shortened. Geopolymerization of industrial side streams is an upcycling process, as the geopolymer (GP), utilized as concrete and binder, has a higher value than the initial industrial by-products. To obtain upcycling, energy is put into the system, however, since tailings have usually been milled, the material has already undergone energy intensive steps and can therefore readily be used as starting blocks for geopolymerization. Utilizing tailings for upcycling into GPs, is therefore beneficially in terms of waste management, process energy, and emission of greenhouse gases, as the energy used in the beneficiation process is passed onwards into the geopolymerization process. Upcycling often requires further energy sources to achieve higher valuable material. In geopolymerization or alkaline activation this means the addition of chemicals, and in some occasions, such as analcime tailings, the addition of thermal energy [3].

In this chapter the valorization of high volume, inorganic side streams from mining, chemical industries, steel processing, and waste incineration into new adsorbents useable for water treatment is discussed. The purpose is to show how the material undergoes value change from side stream to potentially highly functional material.

As every tailing and every ash has a different chemical and mineral composition, tailoring of the properties of resulting adsorbents is possible by careful choosing of precursor materials. Aluminosilicates form the backbone of the geopolymer structure, but ion exchange, channel size, and physical properties are affected by the minerals used for geopolymerization [4–6]. Lastly, by controlling of the geopolymerization conditions, also the macroscopic structures can be developed by using various manufacturing methods from foaming to granulation.

The ultimate goal of using GPs/AAMs in water purification is to be able to recover valuable materials such as nutrients or battery chemical metals from contaminant-rich wastewater streams. In other words, the target is to use one industrial side stream to recovery of valuable material from another side stream or waste water in order to multiply circular economy potential.

2. Raw materials and preparation of GP/AAM materials for water treatment applications

This section summarizes different types of aluminosilicate precursors, occurring naturally or derived from industrial processes. Materials, which are currently abundant and/or urgent to dispose of, fall within the ambit of the section, but cover only water treatment applications not geopolymer production for construction industry, e.g. substitutes for Portland cement or as tailings' covering.

2.1 Conventional and new sources of aluminosilicate precursors for GP/AAM preparation

Ashes. *Fly ashes (FA)* are prominent materials used as alkaline-activation binders. FAs are abundant yet complex materials, the composition of which is affected by co-incinerated material. Produced mostly by coal-fired electric and steam generating plants, coal FAs represent the greater part of generated FAs with the estimated flow of approximately 750 Mt. in 2015. The utilization rates of FAs

differ greatly worldwide. Thus, rates in the developed countries equal 96%, 85%, 50% and 65% from produced streams for Japan, Germany, UK and USA, respectively [7]. For the developing countries with growing economics such India and China, the utilization rates are 38% and 45%, yet rate 66% for Asia in general are reported. Russian Federation and Africa implement FA as secondary resource less than 20% [7].

The composition of FA varies widely as it is derived initially from various primary sources: municipal waste/sludge co-incineration, different coal types, or subspecialized byproducts from industrial treatment plant (paper, forestry industry or agriculture). The combustion and cooling processes have profound impact on the characteristics of FA (particles size, shape, surface area, uniformity, etc.) as well as its composition and impurities' inclusion.

Mainly, ASTM C 618 specification is applied to indicate the class of FA used for geopolymer preparation; however, a local/field or an unspecified labelling is also common. Coal FA (class F [8, 9] and C [10]) has been extensively considered as an aluminosilicate source for GP production, while the exploitation of biomass and co-incinerated FAs is less common [11, 12]. On the other hand, the utilization of these FAs particularly in the GP production for water treatment sector might be also beneficial. It would reduce the FA accumulation in landfills, and improve adsorbents' LCA in comparison with metakaolin-based GPs.

Although FAs were studied as adsorptive materials previously [7, 13, 14], concerns on potential toxicity of impurities and convenience of use have encouraged to seek more suitable forms of FA-based materials for water treatment sector.

Municipal waste incineration bottom ash (IBA) has been traditionally considered as solid waste [15, 16]. IBA is mainly composed of Si, Al, Ca, and Na oxides, and could be classified as a hazardous or non-hazardous waste depending on the amount of toxic metal(oid)s. IBA's main applications are in the engineering field as secondary materials in form of weathered bottom ash (after outdoor ageing for 2–3 months for pH stabilization). However, new applications of IBA have emerged in recent years as use as an aluminosilicate source for GPs/AAMs [17] including adsorbents [15, 18–20]. IBA by itself also was investigated as an adsorptive material for metal removal [21, 22]. In most of the studies, mixtures of IBA with various aluminosilicate precursors (BFS, FA, metakaolin) are used in order to obtain desired mechanical characteristics [23]. For the water treatment applications, IBA as raw material for GPs could have hidden benefits as the aluminum presented in it reacts with the alkaline activator and forms hydrogen gas, which leads to an increase in porosity [24]. Moreover, since a compressive strength of the resulting materials could be lower than for construction applications, the high porosity of materials and *in situ* stabilization of concomitant hazardous impurities via encapsulation could be attractive options [9, 19].

Pre-treatment of FAs and IBAs with various chemicals were suggested in order to reduce their toxicity and to meet the environment requirements of pristine materials or/and GPs/AAMs based on them [14, 25–27].

Steel industry waste. *Blast furnace slag (BFS), dust, and sludge.* BFS is another copious industrial nonmetallic by-product that is used widely as GP precursor in civil engineering [28]. Similar to ashes, steel industry wastes are mainly composed of Si and Al oxides, while Mg and Ca oxides could consist up to 35–60% of the material by weight [29]. Iron and sulfur are the major impurities in BFS, derived from the iron-smelting process. Ground granulated BFS has a high specific area due to the small particle size distribution, which makes it an excellent candidate as adsorptive material [13, 30]. However, in order to avoid the leaching of heavy metals from BFS during deployment of these materials in water remediation techniques, alkaline activation were suggested for entrapment/binding impurities

within the GPs' matrix [31–34]. The presence of significant amounts of silica, aluminosilicates, and calcium-alumina-silicates in a pristine material makes the geopolymerization process rapid and effective resulting in rigid and enduring compositions. Thus, BFS was used to enhance the stability of metakaolin- and FA-based GPs [35].

Basic oxygen and electric arc furnace slag. These materials are sub-categorized, depending on the process of their formation. Both basic oxygen furnace slag (BOFS) and electric arc furnace slag (EAFS) are formed during the steelmaking process [36, 37]. These types of slags are similar in composition to BFS, except for their iron, manganese, chromium and sulfur contents, which are higher in BOFS and EAFS. EAFS was modified by alkali activation [38] and its adsorption properties towards copper were compared to raw EAFS. Significant amount of posnjakite were detected in the crystalline phase after adsorption of copper that could explain the drastically high removal efficiency of this AAM.

The accumulation of BOFS has become a significant issue due to its generation in large quantity, high disposal costs, and unsuitableness in cement industry due to high iron oxide content. Sarkar et al. adopted BOFS as a raw material for obtaining of GPs and investigated Ni^{2+} [39], Zn^{2+} [40], and F^- [41] removal. BOFS was used by Sithole et al. as a precursor for AAM preparation [42, 43]. In order to achieve highly porous structures for percolation column tests, a foaming agent (hydrogen peroxide) was added.

Red mud, silica fume and ore materials. *Bauxite* is a sedimentary rock, rich in aluminum oxide minerals and accompanied by kaolinite, quartz, and iron oxides. The amount of impurities varies depending on the place of origin. Bauxite itself has recently been tested in water treatment applications for purification of fluor- and arsenic-contaminated waters [44, 45]. However, even keener interest is observed in the valorization of bauxite residues, rich in iron and aluminum, as GPs/AAMs [46] and their water purification applications [47, 48].

Alumina manufactured through Bayer process from bauxite mainly goes to aluminum metal production. The rest (up to 10% of the whole production flow) is used as fillers in construction, in glass production, abrasive materials, and catalysts. Depending on the field of application, aluminum oxide could be called alumina, aloxide, aloxite, or alundum, and their respective waste materials would conform to these terms. Aloxite, for instance, is used as catalyst and/or catalyst support in organic chemistry due to its physicochemical stability and unique surface properties. As waste material, it could be accumulated in immense amounts from gas purification, decolorization, and catalytic processes as well as refining and desulfurization of petroleum oils and waxes. One of the ways of its valorization is in the design of eco-friendly GPs [49] and adsorbents for wastewater treatment [50, 51]. Thus, the addition of aloxite to analcime before geopolymerization showed an increase in the specific surface area and pore volume [50].

Silica fume is an amorphous form of silicon dioxide, collected as a by-product of the silicon and ferrosilicon alloy production. Historically, the main field of application is as pozzolanic material for high performance concrete of high strength and low porosity, though its applications for designing of foamed GPs and immobilization of cesium are reported [52, 53].

Mine tailings are mining and mineral wastes. The proper disposal of tailings has gotten under strong scrutiny for environmental preservation during the last decades. In many cases, the tailings are fine particles, containing silica together with iron oxides, alumina, and other minor minerals. This constitution makes tailings an excellent source of material for GPs. Iron ore tailings were mixed with FA to produce GP for copper removal [54], while gold mine tailings with Al_2O_3 additive were the source for GP production used for lead removal [51]. Prophylite waste

materials obtained from mine were converted torophyllite GPs by Panda et al. [55], and tested as adsorbent for Co, Cd, Ni, and Pb removal from model solutions. Magnesite tailings from talcum mines show a reactivity dependent on the calcination temperature: light burnt (700 – 1000°C), hard burnt (1000 – 1500°C), and dead burnt (1500 – 2000°C). For use in water treatment and as a GP precursor, a light burnt magnesite in the form of periclase MgO is suitable.

Natural materials: zeolites, clays, sedimentary rocks. Kaolin is a rock rich in kaolinite, a clay mineral, and the source of production for the most widely used GP precursor called metakaolin. Metakaolin, a disordered, activated, and dehydroxylated form of kaolinite, is obtained through calcination of kaolinite over 600°C. The temperature of calcination has direct impact on reactivity of metakaolin, and as a consequence, on the crystallinity of the produced GPs [56]. However, raw kaolin/kaolinite were also used in GP production [57], yet for water treatment applications just recently [58]. Moreover, valorization of spent metakaolin could be beneficial and decline the cost of metakaolin-based GP [59]. Other clay materials have also been utilized recently for GP design [60]. Thus, bentonite clay calcined at 700–800°C were used by Maleki et al. [61] for obtaining a magnetic GP for heavy metal removal. Laterite clay-based GP were proposed by Ghani et al. [62] as a promising adsorptive material for Ni and Co removal. Laterite was activated at 900°C prior the geopolymerization. Volcanic tuff is another naturally available material with high porosity and with a high potential for ion-exchange. It was used in [63, 64] as an abundant yet low-cost material for GP production, and subsequent Zn removal from water.

Zeolites and zeolitic materials are well-known microporous materials. Found in nature or obtained through synthetic procedure, they are considered to be selective adsorbents [65–67], catalysts [68], carriers in biotreatment [69] due to their unique structure. Although, naturally occurred zeolites are readily available, they generally show lower surface area than synthetic ones.

Recently, much attention has also been paid on how zeolite could be synthesized from low-cost materials [70]. GP-zeolite composites and zeolite-like GPs are two different categories of adsorptive materials, which have recently attracted increased interest [71]. GP-zeolite composites are hybrid materials, unite the advantages of both constituents. The GP here serves as a durable support, while the zeolite provides a high surface area, porosity, and adsorption capacity. For instance, metakaolinite-zeolitic tuff GPs have been proposed in [72]. The report clearly showed the beneficial influence of the zeolitic tuff addition into a starting mixture on the microstructure and the adsorption potential of GPs. Andrejkovičová et al. [4] prepared metakaolin-based GPs blended with by 25, 50 and 75% of Nižný Hrabovec zeolite. It was shown that the zeolite particles are responsible for the higher amount of crystalline phases, producing a more compact and firm microstructure of blended GPs. The amount of blender has significant influence on the order of adsorbed metals and on the adsorption capacities of the formulations. Hayashi et al. [63] incorporated clinoptilolite into GPs though sol-gel protocol in order to further use of the resulting coatings for heavy metal ion adsorption.

It should be noted that zeolitic phase could be incorporated into GPs' structures not only externally. Zeolite-like crystalline phases could be derived from synthesis routes through fusion method or even at moderate temperatures leading to zeolite-like GP structures. Javadian et al. [64] converted FA into a mesoporous aluminosilicate adsorbent through a fusion method at 600°C. Deng et al. showed that a hydrothermal synthesis of zeolite-like materials from IBA with higher crystallinity than through a fusion method is possible [73]. Similarly, Visa [74] converted FA into zeolite through a hydrothermal process. Rios et al. synthesized zeolite-like GPs from metakaoline at 100°C through the hydrothermal procedure [75]. Studies reported

indicate that such materials have higher surface area and porosity than GPs/AAMs obtained through simple alkaline activation. Although the ultimate set of preferable conditions to form a GP instead of a zeolite are still under discussion, ratios Si:Al > 1.5 have been empirically established as providing more amorphous structures [60].

α -Analcime is a reject from spodumene refining at a Finnish lithium hydroxide plant, currently in piloting stage, and estimated to start the production in 2024, but is also found as a natural zeolite [3]. The small cavity size of analcime facilitates ion-exchange only for small mono- and divalent cations such as ammonium and Cu^{2+} , and also K^+ , Ag^+ , Tl^+ , Rb^+ (at elevated temperatures), and with low adsorption capacity. Raw analcime is inert to alkaline activation and analcime requires either chemical activation by 3–5 M H_2SO_4 or thermal activation above 700°C [3].

Not infrequently, industrial side streams cannot be used alone for geopolymerisation due to disharmonious Si/Al molar ratios. Therefore, by-products are commonly used as mixtures of aluminosilicate sources [76]. **Table 1** summarizes the studies on different compositions of GPs/AAM that have been proposed for water and wastewater treatment applications. An effort was made to collect and match the precursors, synthetic protocol specificity, and distinctive characteristics resulting materials.

2.2 Forms and manufacturing techniques of GPs/AAMs for water treatment

Originally, a basic composition applied for manufacturing GP/AAM adsorbents consisted of an aluminosilicate precursor, an alkali, and an additional source of silicate in a form of water glass. Initially, both sodium and potassium forms of alkaline activators were used to induce geopolymerization. In the vast majority of the research reviewed, sodium alkaline and water glass are used in the activation process. It was shown by Bakharev that dissolution rates of the minerals was higher when a sodium form is used [148]. Luukkonen et al. [149] found that adsorption characteristics of metakaolin-based GP prepared with NaOH is better than with KOH in case of ammonium removal. An in-depth discussion of G chemistry and vivid explanations could be found in the latest reviews [57, 150, 151].

Forms and manufacturing techniques of GPs/AAMs for water treatment application are emerging and evolving constantly. In the first instance, *powdered forms* were mostly used for gaining of adsorption characteristics of materials. At first, GPs/AAMs were manufactured in bulk forms to be crashed to powder or rubbles after curing procedures. However, these materials have relatively low porosity, and addition of foaming agents were appealing for increasing surface area, pore volume, and porosity. In **Table 1** forms of GPs/AAMs reported and specific additives listed along aside with their synthetic procedures and properties gained. For bulk samples, species are usually sealed with plastic films to prevent moisture evaporation since the presence of water increases porosity. Curing and aging are usually carried out at temperatures ranging from 20 to 105°C. Commonly, an industrial application of powdered forms requires instance pressure filtration and an additional separation step after adsorbent exhaustion. Both these processes increase a cost of treatment, its complexity, limiting a regeneration ability causing sludge accumulation.

Granular forms of GPs/AAMs are more preferable for large-scale applications. FA-based GPs supported on inert substrate were proposed with the aim of overcome these limitations [107]. A simple technique similar to the conventional GP preparation was applied to design floatable light granules for phosphorous removal. Moreover, spherical granules could be produced by *in situ* geopolymerization during granulation by a high-shear granulator, where a liquid alkaline activator acts as a binding liquid [59, 152]. A granule size distribution is a function of a liquid to solid ratio, granulation time, and a rotation speed. While the amount of liquid required

GP/AAM	Precursor/additives	Preparation method, prime oxide ratios	Surface Area/Pore Volume/Pore size	Type/form of GP	Ref.
MK-GP with TiO ₂	MK	HT	27.21 m ² /g 0.207cm ³ /g 2.19 nm	Bulk	[77]
MK-GP	MK	SSM	53.95 m ² /g 0.061 mL/g 5.38 nm	Porous/Spheres, 2–4 mm	[78]
MK-GP	MK	AA Si/Al = 1.7	–	Bulk	[79]
MK/Z-GP	MK Zeolitic tuff	AA SiO ₂ /Al ₂ O ₃ = 1	–	Bulk/Discs	[72]
MK-GP	MK	AA Si/Al =	12.21 m ² /g 0.037cm ³ /g	Bulk	[80]
MK-GP	MK SDS 0.06 wt%	SSM SiO ₂ /Al ₂ O ₃ = 1.6	53.95 m ² /g 1.29 cm ³ /g 15 nm	Porous/spheres 2–4 mm	[81]
MK/FA-GP	2/3 MK 1/3 bioFA (w/w)	AA SiO ₂ /Al ₂ O ₃ H ₂ O ₂	–	Porous/Monolith	[11]
MK-GP	MK	AA foaming, SiO ₂ /Al ₂ O ₃ = 5	–	Foam/Powder <100 µm	[82]
MK-GP/alginate hybrid	MK sodium alginate	AA + SSM SiO ₂ /Al ₂ O ₃ = 1.6	16.2 m ² /g 0.05 mL/g 11.5 nm	Bulk/Spheres 2–4 mm	[83]
MK-GP	MK	AA SiO ₂ /Al ₂ O ₃ = 3.2	39.24 m ² /g	Bulk/Powder 150 µm	[84]
MK-GP functionalized with CTAB	MK silica fume	AA CTAB	216 m ² /g 0.22 cm ³ /g	Bulk/rubbles, 1.5 mm	[85]
MK/FA-GP	MK:FA 2:1 wt	AA	7.9 m ² /g	Porous/discs	[86]

GP/AAM	Precursor/additives	Preparation method, prime oxide ratios	Surface Area/Pore Volume/Pore size	Type/form of GP	Ref.
MK-GP	waste MK	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.5$	–	Bulk/Powder, granules	[59]
MK-GP	MK	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.2$	39.24 m ² /g	Bulk/Powder, 150 µm	[87]
MK-GP activated with hull ash	MK BioFA TiO ₂	SSM $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.18^*$	–	Porous/Spheres 2–3 mm	[88]
MK/FA-GP	MK:FA 50:50 wt%	SSM SDS	–	Foam/ Spheres	[89]
MK-GP/alginate-chitosan hybrid	MK alginate/chitosan	SSM AA 0.5 wt% H ₂ O ₂ , 1.5 wt% SDS	230 m ² /g 0.99 mL/g 35 µm	Porous/Spheres	[90]
MK/FA-GP	MK FA class C 60:40 wt%	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.7$	–	Bulk/Powder 63–125 µm	[91]
MK/BFS-GP	MK BFS 60:40 wt%	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.1$	–	Bulk/Powder 63–125 µm	[91]
MK-GP	MK	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.31^{**}$	–	Bulk/Powder, 200 µm	[92]
MK-GP/ coal gangue hybrid	MK gangue 50/50 wt%	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.0$	26.41 m ² /g 0.330 cm ³ /g	Bulk	[93]
MK-GP	MK	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2–8$	–	Bulk/Pervious	[94]
MK-GP	Waste MK Aluminum scrap recycling waste 1:1 (w/w)	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.25^{**}$	15.95 m ² /g	Bulk/Granules 4–11.2 mm	[95]

GP/AAM	Precursor/additives	Preparation method, prime oxide ratios	Surface Area/Pore Volume/Pore size	Type/form of GP	Ref.
MK-GP	MK	AA	8.16 m ² /g 0.021 cm ³ /g 10.5 nm	Bulk/ Granules 0.5 mm	[96]
MK-GP functionalized with HDTMABr	MK	AA HDTMABr	–	Bulk/Powder, 53 µm	[97]
MK-GP MK/aloxid ANA-GP ANA/aloxid-GP	MK analcime aluminum oxide	AA** MK-GP SiO ₂ /Al ₂ O ₃ = 3.96 MK/aloxid GP SiO ₂ /Al ₂ O ₃ = 2.13 ANA-GP SiO ₂ /Al ₂ O ₃ = 7.01 ANA/aloxid-GP SiO ₂ /Al ₂ O ₃ = 3.60	MK-GP 19.97 m ² /g 0.131 cm ³ /g 26.24 nm MK/aloxid GP 6.36 m ² /g 0.036 cm ³ /g 23.18 nm ANA-GP 0.69 m ² /g 0.003 cm ³ /g 21.69 nm ANA/aloxid-GP 38.29 m ² /g 0.125 cm ³ /g 13.07 nm	Bulk/Powder, 63–125 µm	[50]
MK/Z-GP	25% MK 75% zeolite	AA SiO ₂ /Al ₂ O ₃ = 1	57.5 m ² /g	Bulk	[4]
MK-GP functionalized CTAB	Calcinated halloysite clay	Precipitation SiO ₂ /Al ₂ O ₃ = 2.91 CTAB/Cu ₂ O/TiO ₂	34.8 m ² /g 29.7 nm	Bulk	[98]
MK-GP functionalized with CTAB	MK	AA CTAB	26.45 m ² /g 0.121 cm ³ /g 9.12 nm	Bulk/Powder, 125 µm	[99]
MK-GP, magnetic hybride	MK Magnetite 5 wt%	AA SiO ₂ /Al ₂ O ₃ = 4.55* H ₂ O ₂	19.5 m ² /g 0.045cm ³ /g 10.4 nm	Porous	[100]

GP/AAM	Precursor/additives	Preparation method, prime oxide ratios	Surface Area/Pore Volume/Pore size	Type/form of GP	Ref.
MK/Silica-GP functionalized with Cr	MK silica fume 9:1 (w/w)	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.90^{**}$	30 nm	Bulk/Membrane	[101]
MK-GP	MK	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.14^{**}$	–	Bulk/Powder, 355 μm	[102]
MK/FA-GP	MK FA	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.45^{**}$	27 m^2/g	Bulk/rubbl 1.0–0.3 mm	[103]
MK-GP	MK	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.0$	21 m^2/g 1252 mm^3/g 0.32 μm	Bulk/Granules, 3 mm	[104]
MK-GP alginate hybrid	MK sodium alginate TiO_2	SSM $\text{SiO}_2:\text{Al}_2\text{O}_3 = 4$	20 m^2/g 714 mm^3/g 0.11 μm	Bulk/Spheres, 2 mm	[105]
MK-GP/ magnetic hybrid	MK	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.55$ H_2O_2	42.92 m^2/g 0.052 cm^3/g 4.88 nm	Porous	[106]
MK-GP/LECA	MK LECA support	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.5$	–	Bulk/Granules, 4–8 mm	[107]
MK/Biochar-GP	MK Biochar	AA H_2O_2	37.46 m^2/g	Foam/membrane	[108]
MK-GP functionalized with $\text{K}_4\text{Fe}(\text{CN})_6$	MK	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.60$ H_2O_2	35 m^2/g 55 cm^3/g	Foam	[109]
MK-GP/graphene oxide hybrid	MK graphene oxide 10 wt%	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 0.45$	–	Bulk/ Particles, < 0.5 mm	[110]
FA-GP	Fly ash	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.03$	–	Bulk	[111]

GP/AAM	Precursor/additives	Preparation method, prime oxide ratios	Surface Area/Pore Volume/Pore size	Type/form of GP	Ref.
FA-GP	Fly ash, 75 µm	FM SiO ₂ /Al ₂ O ₃ = 1.98 [*]	8.22 m ² /g 2.9 nm	Bulk/Powder	[64]
FA-GP Iron-enriched	Calcinated FA, < 70 µm	FM SiO ₂ /Al ₂ O ₃ = 1.00 Fe ₂ O ₃ /Al ₂ O ₃ = 0.151	–	Bulk	[112]
FA-GP modified with iron	Coal fly ash	AA SiO ₂ /Al ₂ O ₃ = 1.43 [*]	162.38 m ² /g 0.126 cm ³ /g 3.90 nm	Bulk/Powder	[113]
FA-GP	Fly ash	AA SiO ₂ /Al ₂ O ₃ = 4.61	–	Bulk/Powder, 71–90 µm	[9]
FA/IOT -GP	Fly ash IOT 70:30 (w/w)	AA H ₂ O ₂	6 nm - 360 µm	Porous/Cubes	[54]
FA-GP	Fly ash	AA SiO ₂ /Al ₂ O ₃ = 1.12 ^{**}	20.48 m ² /g 19.62 nm 0.070 cm ³ /g	Bulk/Powder, 74 µm	[114]
FA/Z-GP	Fly ash Fajustite	HT SiO ₂ /Al ₂ O ₃ = 0.69 ^{**}	174.35 m ² /g 0.14 cm ³ /g 9.69 nm	Bulk/Powder, 74 µm	[114]
FA-GP	Fly ash C	AA SiO ₂ /Al ₂ O ₃ = 3	–	Bulk/Powder	[115]
FA-GP/LECA	Fly ash C LECA support	AA SiO ₂ /Al ₂ O ₃ = 1.5	–	Bulk/Granules, 4–8 mm	[107]
FA-GP	Fly ash	AA SiO ₂ /Al ₂ O ₃ = 5.36	–	Bulk/Powder, 71–90 µm	[116]
FA-GP	Fly ash	HT	–	Bulk	[117]
FA/Z-GP	Fly ash BFS 4:1 (w/w)	HT SiO ₂ /Al ₂ O ₃ = 3.49 [*]	–	Bulk/Powder	[118]

GP/AAM	Precursor/additives	Preparation method, prime oxide ratios	Surface Area/Pore Volume/Pore size	Type/form of GP	Ref.
Fly ash/ iron oxide hybrid	Fly ash Fe ₂ O ₃ 5 wt%	AA SiO ₂ /Al ₂ O ₃ = 3.30 ^{**}	60.75 m ² /g	Bulk/Powder, 50 µm	[119]
FA-GP/Graphene hybrid	Fly ash graphene (1 wt%)	AA SiO ₂ /Al ₂ O ₃ = 3.41 ^{**}	20.41 m ² /g 0.047 mL/g 9.73 nm	Bulk	[120]
FA/BFS-GP	Fly ash BFS	HT SiO ₂ /Al ₂ O ₃ = 3.23 [*]	76.6 m ² /g 0.24 cm ³ /g 12.5 nm	Bulk	[35]
FA-GP	Boiler fly ash < 80 mesh	HT SiO ₂ /Al ₂ O ₃ = 2.75 ^{**}	27.51 m ² /g 0.032 mL/g	Bulk	[121]
FA-GP	Fly ash	AA SiO ₂ /Al ₂ O ₃ = 3	29 m ² /g 0.134 cm ³ /g	Bulk/Powder, < 74 µm	[122]
FA-GP/Polyethersulfone hybrid	Fly ash	AA SiO ₂ /Al ₂ O ₃ = 3.05	168.3 m ² /g	Bulk/Powder, 150 µm	[123]
FA/Z-GP	Calcinated fly ash	SiO ₂ /Al ₂ O ₃ = 1.61 ^{**}	–	Bulk/Powder	[124]
FA-GP	Fly ash	AA	131.4 m ² /g	Bulk/Powder, <105 µm	[125]
FA-GP	Coal Fly ash	FM SiO ₂ /Al ₂ O ₃ = 1.25 [*]	93.8 m ² /g 0.62 cm ³ /g	Bulk	[8]
FA-GP	Fly ash silica	AA Si/Al = 2.2	31.87 m ² /g 0.12 cm ³ /g 15.45 nm	Bulk/Powder, 125–212 µm	[126]
FA-GP	Fly ash F, ≤ 177 µm	AA SiO ₂ /Al ₂ O ₃ = 2.97 ^{**}	30 m ² /g 0.076 cm ³ /g	Bulk	[127]
FA/analcime-GP	Fly ash analcime	AA SiO ₂ /Al ₂ O ₃ = 2.10 ^{**}	–	Bulk/Membrane	[128]
FA-GP	Fly ash	AA SiO ₂ /Al ₂ O ₃ = 5.42	35.97 m ² /g 124 cm ³ /kg 9 nm	Bulk/Powder, 150 µm	[31]

GP/AAM	Precursor/additives	Preparation method, prime oxide ratios	Surface Area/Pore Volume/Pore size	Type/form of GP	Ref.
FA-GP	Rice husk ash, waste alum cans	HT $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.82^*$	36.15 m ² /g 0.097 mL/g 5.4 nm	Bulk	[129]
FA-GP	Fly ash class C and F	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 6.6^{**}$ (class C) $\text{SiO}_2/\text{Al}_2\text{O}_3 = 10.9^{**}$ (class F)	2463.64 mm ² /g	–	[130]
FA/MK-GP	bioFA MK 70:30 (w/w)	AA aluminum powder, anionic surfactant	46.3 m ² /g	Foam/Membrane	[131]
IBA-GP/Graphene hybrid	Bottom ash graphene	AA 0.15 wt% Mn ²⁺ 19.5 wt% CuO	29.28 m ² /g 0.1078 mL/g 14.77 nm	Bulk/ Particles, 0.180–0.315 mm	[132]
BFS –GP	BFS	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.40^*$	64.5 m ² /g 0.095 cm ³ /g 5.93 nm	Bulk/Powder, 63–125 µm	[32]
BFS –GP	BFS	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.2$	–	Bulk/Powder, 63–125 µm	[115]
BFS –GP/graphene hybrid	BFS graphene 0.01 wt%	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.61^*$	146.17 m ² /g 0.161 mL/g 4.40 nm	Bulk/Powder, 250–315 µm	[133]
BFS –GP/barium modified	BFS	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.00^{**}$	63.1 m ² /g 0.070 cm ³ /g	Bulk/Powder, 63–125 µm	[134]
BOFS-GP	BOFS	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 11.5^{**}$	30.84 m ² /g 0.091 cm ³ /g 11.8 nm	Bulk/Particles, ~0.1 mm	[39, 40]
Slag-based GP	Slag	SSM $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.02^*$ 0.3 wt% SDS	100.9 m ² /g 7 nm	Porous/Spheres, d ≈ 100 µm	[33]

GP/AAM	Precursor/additives	Preparation method, prime oxide ratios	Surface Area/Pore Volume/Pore size	Type/form of GP	Ref.
Silicomanganese slag-GP	Silicomanganese slag (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	AA SiO ₂ /Al ₂ O ₃ = 1.44 ^{**}	51.79 m ² /g 0.192 mL/g 10.30 nm	Bulk/Particles, 0.16– 0.315 mm	[135]
BOFS-GP modified with Ni(II) or Zn(II)	BOFS-GP	AA	Zn/LDS-GP 58.14 m ² /g Ni/LDS-GP 53.42 m ² /g LDS-GP 30.84 m ² /g	Porous/Powder, ~0.1 mm	[41]
Slag-based GP	Slag	SSM SiO ₂ /Al ₂ O ₃ = 3.08 [*]	87.74 m ² /g	Bulk/Spheres	[34]
Slag-based GP/ Fe ₂ O ₃ -hybride	Slag	SSM SiO ₂ /Al ₂ O ₃ = 70.65 ^{**} Fe ₂ O ₃ /Al ₂ O ₃ = 188 Fe ₂ O ₃ /SiO ₂ = 2.66	233.8 m ² /g	Bulk/Microspheres, 75– 300 µm	[136]
Steel slag/fly ash/analcime-GP	Steel slag fly ash	HT SiO ₂ /Al ₂ O ₃ = 2.01 ^{**}	27.25 m ² /g 0.050 cm ³ /g 8.12 nm	Bulk	[137]
BFS –GP	BFS	AA SiO ₂ /Al ₂ O ₃ = 5.26	23.56 m ² /g 73 cm ³ /kg 7.8 nm	Bulk/Powder, 150 µm	[31]
EAFS-GP	electric arc furnace slag	AA SiO ₂ /Al ₂ O ₃ = 2.02 [*]	6.5 m ² /g 0.014 cm ³ /g 8.7 nm	Bulk/Powder	[38]
BOFS-GP	Basic Oxygen furnace slag	AA H ₂ O ₂	–	Porous	[43]
Slag-GP/CeO loaded	Slag	SSM SiO ₂ /Al ₂ O ₃ = 3.31 ^{**}	186.40 m ² /g 0.352 cm ³ /g 7.56 nm	Bulk/Sphere, 75–300 µm	[138]

GP/AAM	Precursor/additives	Preparation method, prime oxide ratios	Surface Area/Pore Volume/Pore size	Type/form of GP	Ref.
Clay-based GP	Kaolin	FM $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.88^{**}$	51.3 m ² /g 0.324 cm ³ /g 25.25 nm	Bulk/Powder	[58]
clay/gangue microsphere -GP	Kaolin coal gangue 50/50 wt%	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.0$	39.74 m ² /g 52.00 nm	Bulk/rubbles, 0.45– 0.15 mm	[139]
Clay-GP/Fe ₃ O ₄ hybride	Calcined bentonite clay	AA	2.32 m ² /g 0.008 cm ³ /g 13.76 nm	Bulk/Powder	[61]
Clay-GP	Lateritic clay, 58 µm	AA	17.441 m ² /g 0.005 cm ³ /g 1,4 nm	Bulk/Powder, 58 µm	[62]
Natural tuff-GP	Volcanic tuff	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.74^{**}$	–	Bulk/Powder, < 200 µm	[140]
Alumino silicate-GP	Alumino silicate powder	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4$	50.1 m ² /g 0.36 cm ³ /g 0.04 µm	Bulk/Monoliths or granules	[141]
Synthetic GP	Chemosynthetic Al ₂ O ₃ -SiO ₂ powder	SSM $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2$	–	Bulk/Spheres	[142]
Chitosan modified geopolymer	Aluminum salt and silica solution, chitosan	Precipitation $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.06^{**}$	–	Bulk/Powder	[143]
OTB-GP	Pyrophyllite mine waste samples	AA $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.39^{**}$	–	Bulk/Powder, < 45 µm	[55]
OTB-GP	Gold mine waste	FM	74.92 m ² /g	Bulk	[144]
OTB-GP	Gold mine tailings Al ₂ O ₃	FM	74.916 m ² /g	Bulk	[51]
Municipal solid waste-GP	Sludges	FM $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.12^{**}$	0.496 m ² /g 9.98 nm	Bulk	[145]

GP/AAM	Precursor/additives	Preparation method, prime oxide ratios	Surface Area/Pore Volume/Pore size	Type/form of GP	Ref.
Municipal solid waste-GP	Municipal solid waste biochar	AA	6.5 m ² /g - -	Bulk	[146]
Dolochar ash based geopolymer	Dolochar < 100 mesh	AA SiO ₂ /Al ₂ O ₃ = 4.97**	49.91 m ² /g 0.087 cm ³ /g 8,9 nm	Bulk/Particles, ≈ 0.1 mm	[147]
<p>Materials: GP – geopolymer; MK – Metakaolin; FA – fly ash; IBA – incineration bottom ash; BFS – blast furnace slag; BOFS – basic oxygen furnace slag; EAFS – electric arc furnace slag; Z – zeolite; IOT – iron ore tailing; OTB-ore/tailings based; Procedure: AA – alkaline activation at moderate temperature; SSM – suspension-solidification method; FM-fusion method; HT- Hydrothermal method; Additives: SDS – sodium dodecyl sulfate; CTAB – cetyltrimethylammonium bromide; HDTMABr -hexadecyltrimethylammonium bromide.</p> <p>*Calculated using the amounts of raw materials in the slurry.</p> <p>**Calculated using the XRF of product.</p>					

Table 1.
GP/AAMs compositions for water and wastewater treatment reported in literature.

depends on the wetting behavior and particle size of the precursors, a good starting point is L/S of 1/3. The production method is easy to upscale that makes feasible large-scale water treatment applications with granular GPs. A more complicated procedure enables the development of granular adsorbents through a suspension and solidification method, resulting in microspheres ($<100\text{ }\mu\text{m}$) [33, 34] or highly porous GPs [93]. Composites of GPs with biopolymers, for instance alginate that possesses the ability to solidification in presence of calcium ions, were also obtained in granulated form [83, 93].

Porous GP/AAM adsorbents contain relatively high volume of voids or pores. The pore sizes usually range from nanometers up to millimeters with the total pore volume ranging from 30 to 90% [153]. Direct foaming, either chemically or mechanically, is seen as the most widely applied foaming approach. The common additives that have been used in the direct foaming methods are hydrogen peroxide [11, 33, 43, 54, 78, 93], Al [131, 154] or Si [155] powders along aside with stabilization agents such surfactants or oils.

Pervious GP/AAM is another promising form of an adsorptive material for water purification. Thus, AAM-based membranes with potential to remove alkaline earth metals [156], and nickel [157] have been reported. Development of porous/pervious GPs/AAMs led to variety of fabricated adsorptive forms such as monoliths, membranes, granules, and self-supported filters. That is opening the versatility of approaches, conventional in water and wastewater treatment practice, yet challenging if the powdered forms used. Separation, regeneration, and surface modification are no longer restricted by the form of production. Porous/pervious materials can be used directly in packed bed adsorbers, and be easily regenerated or retrieved after adsorbent saturation with target substances or contaminants.

3. Properties and performance of GPs/AAMs towards various contaminants

Despite the fact that the first identification of GPs as unconventional construction materials was in 1979 [158], broader applications of GPs/AAMs started in late 90s. Although GPs/AAMs are to be considered by some authors as an economic alternative to zeolites or activated carbons for water purification, the lack of real cases reported is obvious. To urge commercial importance, GP/AAM adsorbents should be readily available, economically feasible, steady in characteristics, and easily regenerated. Several comprehensive reviews on the GP/AAM materials for the water treatment sector have been published just recently [57, 150, 151, 153]. Therefore, in this section the bright and promising works will be highlighted as well as challenges and trends for future studies revealed.

GPs/AAMs for metal(oid)s removal. The adsorption characteristics of individual species and particular conditions of adsorption could be found elsewhere [57, 150, 151, 153]. Here, we would like to emphasize some challenges and gaps, which might be addressed in future studies. There are only several articles discussing selectivity of adsorption on GPs/AAMs alongside the matrix effects. In most of the studies pure mono-element aqueous solutions were implied, and the adsorption characteristics for individual substances- without possible influence of matrix macro-elements have been established. However, GPs/AAMs that are considered as a replacement of zeolites have to demonstrate selectivity under complex matrices in order to have opportunities to promote the implementations in various industrial applications.

In order to obtain adequate adsorption parameters, an excessive alkaline residue in GP/AAM should be washed out properly ($\text{pH } 7 \pm 0.5$ within 24 h required) [159].

Otherwise, the increment of pH of aqueous solutions containing heavy metals will favor the hydroxide precipitation process, leading to wrong result interpretation. For porous GPs, washing away the excessive alkalis resulted in the increment of total porosity [11], which led to better performance. Moreover, excessive alkalis were used intentionally to neutralize AMD [42] and remove metal ions. However, a strict protocol must be followed to characterize newly designed materials.

Selective adsorption relies on several factors such as a metal ion activity, hydration radius and free energy of hydration, and a pore size distribution of GP.

Geopolymerisation by itself could lead to the formation of new ion-exchange sites at the GP surface, but additives in composite formulations could have even higher influence the adsorption characteristics.

An ionic exchange reaction between the heavy metal ions and sodium ions has resulted in heavy metal removal by the metakaolin GP [159]. The adsorption selectivity of heavy metal ions by the GPs at pH 4 in multi-component solution was in the following order: $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Cr}^{3+}$, while q_e [mg/g]: $100 > 76 > 55 > 10$. The order of adsorption was in accordance with the hydrated radius and free energy of hydration for selected ions. However, the free energy of hydration and the activity for Cr^{3+} are all higher compared to those of other metals, though its adsorption rate does not correspond to the assumed order. The selectivity towards Cr^{3+} was explained through its ionic status. When the pH exceeded 4, Cr^{3+} transforms to $\text{Cr}(\text{OH})^{2+}$, which might lead to its lower adsorption ability. It is also noted that at lower pH, the balancing ions present on the GP surface tend to be replaced by the hydrogen ions instead of the metal ions that lead to lower capacity at acidic pH.

Lopez et al. [5] investigated the selectivity of metakaolin-based GPs in multicomponent solutions (Pb^{2+} , Cu^{2+} , Cd^{2+} , Ni^{2+} , Zn^{2+} and Cs^+). For a composition with Si/Al ratio 2, the best capacities and selectivity towards Pb^{2+} and Cs^+ were observed. The adsorption selectivity for the mixture of metal ions was in the following order $\text{Cs}^+ > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$, while q_m [mg/g]: $43 > 35 > 15 > 3 > 1 > 2$. The adsorption capacity for individual elements were higher: $57 \text{ mg Pb}^{2+}/\text{g} > 52 \text{ mg Cs}^+/\text{g} > 46 \text{ mg Cu}^{2+}/\text{g} > 14 \text{ mg Cd}^{2+}/\text{g} > 9 \text{ mg Zn}^{2+}/\text{g} > 4 \text{ mg Ni}^{2+}/\text{g}$. Moreover, the effect of solution salinity (NaCl, 5% and 10%, wt) was studied, and no considerable effect on the adsorption order of metal ions or GP capacity in multi-composition solution was found. The authors presumed the existence of at least two types of binding sites with different affinities toward the metal ions to explain such a tolerance.

Selectivity of GP composites with zeolite filler was studied by Andrejkovičová et al. [4]. The highest adsorption was observed for Pb^{2+} for all the GPs obtained, while an adsorption order was as follows: $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Cr}^{3+}$. The adsorption of Cu^{2+} and Cr^{3+} increased as the amount of metakaolin in the GP increased, whereas the composite with 25% zeolite doping had higher adsorption characteristics towards Pb^{2+} , Cd^{2+} and Zn^{2+} . GPs prepared from zeolitic tuff and kaolinitic soil by El-Eswed et al. [160] showed totally different order of adsorption: $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$. Moreover, the adsorption order strongly depended on the GP composition, although Cu^{2+} and Pb^{2+} adsorption has always prevailed.

The ability of BFS- and metakaolin-based GPs to remove Ni^{2+} and metalloids (As and Sb) in form of oxyanions was shown in [32]. Both adsorbents completely removed Ni^{2+} that most likely was associated with precipitation of its hydroxides on the GPs, while both metalloid oxyanions were adsorbed by BFS-GP equally. Another remarkable merit is that the adsorption capacities were obtained with real matrixes (spiked mine effluents), and were 4.42 mg/g, 0.52 mg/g, and 0.34 mg/g for Ni^{2+} , As^{3+} , and Sb^{3+} , respectively. It is specified by the authors that the low capacities could be a result of competition of some matrix ions (Sr, Ca, Mg, Mn) with the target ions for binding sites.

Researches with increasing frequency pay attention to this problem and try to demonstrate the removal efficiencies with real samples. Removal of Ca^{2+} and Mg^{2+} from intact groundwater was examined in [58] on kaolin-based GP. With adsorbent dose of 1 g/L, the removal rate were 37.5% and 16.2% for Ca^{2+} and Mg^{2+} , respectively. Metakaolin-based GP was tested by Kara et al. [87] for Mn^{2+} and Co^{2+} removal from real wastewater. The removal rates in real wastewater decreased from 97.5% to 53.01% and 94.6% to 39.12% for Co^{2+} and Mn^{2+} , respectively. The results demonstrated that the adsorption performance affected negatively by the coexistence of some other cations and/or anions in the adsorption medium. Bentonite-based GPs were used for heavy metals removal from synthetic wastewater [61]. Porous biomass FA-based GPs were used in [129] for simultaneous removal of heavy metals from wastewater samples. Mixed FA/metakaoline-based GPs were used in [103] for Cu^{2+} removal from real wastewater. In the showcase, the adsorption capacity of GPs towards Cu^{2+} decreased by 27% as compared to synthetic samples. Sithole et al. treated acidic industrial effluents by FA/BOFS-based GPs [42, 43]. New GPs containing hollow gangue microsphere were applied for Zn^{2+} removal from smelting plant wastewater in [93]. At an adsorbent dose of 30 g/L, a complete Zn removal was observed. The distinctive aspect of the reported cases was that a complex composition of treated solutions is likely to decrease substantially capacity of the GP. Thus, the adsorption capacities obtained for the ideal laboratory conditions should be primary used as the guiding not decision-making parameters.

GPs/AAMs for removal of other inorganic ions. Besides metal(oid)s, GPs/AAMs were examined for removal of ammonium and various anions. Luukkonen et al. [149, 152, 161] showed potential of metakaolin-based GPs to remove ammonium. The optimized GP composition was proposed and manufactured in both powder and granular forms. The efficiency of removal was demonstrated in municipal wastewaters (primary and secondary effluents) as well as landfill leachates. Metakaolin-based GPs prepared from commercial and waste metakaolin were able to effectively remove ammonium from synthetic and wastewater samples [59]. In fact, GPs prepared from paper mill fiber sludge showed better selectivity in the presence of competing ions under real matrix conditions. Bai and Colombo prepared metakaolin-based GP foams in the form of monolithic porous filters [162, 163]. The filter was able to remove up to 95.3% of ammonium from runoff waters at the initial concentration of 3 mg/L.

The removal of phosphorus was attempted in [10] with a pervious FA-based GP. The removal rate increased with the increase of pH. Up to 85% of phosphorus were removed from a treated wastewater. Simultaneous removal of ammonium and phosphate by composite metakaolin/BFS-based GPs was demonstrated in [91]. Phosphate removal was enhanced in presence of ammonium. At slightly alkaline conditions (pH 7–8), the removal rate towards phosphate ions was relatively high (>86%), whereas the ammonium removal up to 35% was also achieved. FA-, BFS- and fiber sludge GPs were investigated as promising adsorbents for phosphorous removal from diluted solutions. The capacities at initial phosphate concentration of 100 mg/L are 26 mg PO_4/g for BFS-GP, 36 mg PO_4/g for FAF-GP, and 43 mg PO_4/g for FSHCa-GP [115].

Sulfate ions were removed by barium-modified BFS-based GPs [134]. Adsorption capacities were 91.1 and 119.0 mg SO_4/g for model solution and mine effluent, respectively. The surface complexation or precipitation of barium sulfate were suggested as probable removal mechanisms.

Removal of halides by GPs/AAMs is an emerging topic. For this end, composite or functionalized materials are designed. Removal of F^- was demonstrated by slag-based GP microspheres modified with CeO [138], Fe_2O_3 [136], and bivalent metallic species [41] with capacities towards the contaminant 127.7 mg/g, 59.8 mg/g, and 60 mg/g (zinc impregnated BOFS-GP), respectively. A metakaolin-based GP functionalized

by surfactant was developed for efficient removal of radioactive iodide [97]. High concentrations of competitive anions had limited influence on the adsorption process.

GPs/AAMs for removal of organic substances. In fact, GPs contained residual metal oxides could have potential catalytic performance. Thus, GPs based on industrial by-products such as FA, BFS, or their mixtures with silica fume and aloxite demonstrated catalytic activity under visible light irradiation. The descriptive list of organic substances removed by GPs could be found in reviews [57, 150, 151, 153]. Mainly, cationic and neutral dyes were investigated as targets in recent studies, although removal of fecal coliforms [10], volatile organic compound [77], and tetracycline [164] was reported.

Oxidative degradation or photodegradation after adsorption have been specified by authors as primary mechanisms of organic pollutants' removal. Although conventional GPs have been reported for these purposes [86, 89, 104, 126, 139], they would rather have had low adsorption/degradation characteristics. Hybrid or composite materials were proposed to improve the removal efficiency of organic pollutants. Thus, graphene [120, 132, 133, 165], TiO₂ [88, 98, 105], CdS [142], various metal oxides [101, 106, 135] were introduced in GP matrix in order to enhance degradation abilities of resulting materials.

4. Regeneration of GPs/AAMs and further resource recovery options

In last a few decades, significant improvements were made in both efficiency and economy in removal of metal(oid)s and other substances by adsorbents. Nevertheless, regeneration and recycling of used adsorbents, or recovery of the removed species from the desorbing agents are still rarely reported. For regeneration and reuse of GPs/AAMs, various possible regenerating agents such as acids, alkalis and chelating agents could be used. Only a few of the reported studies were focused on recovery of adsorbed (from saturated adsorbents) and desorbed (from regenerating agents) metals [11, 87, 96, 131]. However, for industrial application and success completion of new GP/AAM adsorbents on the market, research studies on number of adsorption–desorption cycles are in high demand. Moreover, revenues gathered from resource recovery options will have a decisive role in further technology implementation.

The regeneration of metakaolin-based GP by sodium chloride under alkaline conditions after ammonium adsorption for the first time were demonstrated in [152]. Three adsorption–desorption cycles were carried out with a steady removal efficiency. Sodium chloride and sulfate, potassium sulfate and phosphate were studied in [59] as regenerating agents for saturated metakaolin-based GPs. Sodium sulfate showed better results during five cycles under continuous sorption–desorption experiment, only 34% of an initial overall capacity of the GP were lost. Sodium chloride regenerant was also efficient, but only 55% of ammonium could be removed after 5th desorption cycle. The same adsorbents were used to test a nitrogen recovery option in a laboratory-scale demonstration setup [166]. The layout consisted of an adsorption/desorption unit and Liqui-Cel® membrane. A liquid phase obtained during adsorbent regeneration was purified in the membrane contactor in order to recover ammonium nitrogen as ammonium sulfate or phosphate. The purified regeneration solution was used repeatedly for further adsorbent regeneration. Several regeneration-purification cycles were conducted to estimate system sustainability and chemical consumption demand. Operational conditions of a membrane process such as shellside and lumenside feed flows, temperature, and pH were adjusted to gain maximal capacity of the setup. One membrane contactor (2.5 × 8-inch Liqui-Cel) was used under following operational conditions: 100 L/h shellside and 60 L/h lumenside feed flows, 40°C working temperature, pH ≥ 10.

Technical sulfuric or phosphoric acids, up to 5%, were used as lumenside phases. The concentration of ammonium-content salt in a resulting received phase were 17% and 22% for phosphate and sulfate salt, respectively.

Metal recovery from GPs/AMMs via ion-exchange mechanism can only take place if physical adsorption occurred and the pH was low enough to prevent precipitation of metal hydroxide during adsorption process. Acids of over 0.1 M strength affect the structure of the GPs, and while metals are regenerated by acid washing, the reuse of adsorbents are diminished both in batch [11] as also in continuous mode [87, 167] experiments. Mild acid washing with 0.01 M H_2SO_4 or HNO_3 removed metals from GPs efficiently in short time (1–2 h). It has also been shown that the adsorption capacity after mild acid washing could increase [131], which could be explained by exchange of Na^+ with easier replaceable H^+ cations. Selective desorption of copper has been observed by ammonia. A linear desorption ability with respect to ammonia concentration was observed, and complete desorption being possible by 10% ammonia solution [50, 61].

Sequential desorption tests of Cd^{2+} have been conducted on a loaded metakaolin GP, establishing the percentages of physically adsorbed, ion-exchangeable, EDTA extractable, and residual forms of metal [96]. The authors showed that physical adsorption is negligible, and ion-exchange with MgCl_2 constituted to only 2–8% of adsorbed Cd^{2+} . The bulk amount of Cd^{2+} adsorbed by the metakaolin GP was EDTA extractable, and the adsorbent remained 85% of its adsorption capacity after EDTA desorption for 5 cycles. Luukkonen [32] and Naghsh [58] suggested the efficient metal desorption by 5% NaCl. However, care must be taken since the balancing ions can form a positively charged film on the adsorbent surfaces. El Esweed et al. have achieved ion-exchange based desorption of Cu^{2+} by 0.1 M NaCl [160]. From all the studies reported, only Cd^{2+} has been shown to be desorbed at $\text{pH} > 8$ with NaOH solution, achieving 24–84% desorption [64].

5. Environmental impact and costs of treatment with GPs/AAMs

An efficient use of GPs/AAMs in real wastewater treatment practices including economic evaluation is little investigated. Above all, these adsorbents show rather low selectivity, and therefore the ubiquitous metal ions (Na^+ , Ca^{2+} , Mg^{2+} , Fe^{3+}) present in wastewater solutions demonstrate either competing interaction with the target ions, or the interaction has not been studied [57]. Additionally, for economic and ecological assessment is essential that the adsorbent would be regenerable [168]. To be economically successful, exhausted adsorbents need to pass the non-hazardous leaching criteria of the adsorbed materials, while the amount of waste regenerated should be as little as possible. This means that the adsorption-regeneration cycle needs to be performed as often as possible. And yet, afterwards the adsorbent needs to find end storage place, e.g. in tailing pond, or further use, e.g. as binder, filler, or soil amendment.

Adsorption capacity of a powdered GP is usually higher, but technical implementation of powdered forms requires precise dosing, contact vessel with stirring, solid–liquid separation step, and transfer of exhausted adsorbent to regeneration vessel. The powder can then be regenerated by addition of suitable regenerant, e.g. mild acid, separated, and dried prior to the next adsorption cycle.

Technically, the use of granular forms is an easier option. However, the size of the column vs. wastewater stream can easily become very large, as granules per se, are larger particles and adsorption is a surface process. This puts additional burden on geopolymer production as the overall capacity should be sufficient, and the granules will need to show suitable compressive strength to withstand the

gravimetric pressure in the purification column. Conversely, regeneration is technically easily realized by counter flow of regeneration liquid through the column.

Economic evaluation therefore needs to take these considerations into account during CAPEX estimation. OPEX, in turn, is not only the ongoing replacement of exhausted adsorbent, electricity consumed, maintenance, staff, and regeneration chemicals, but also the transportation costs of adsorbents, which can be high at low adsorption capacity.

As a thought experiment, an example of 55 mg/g adsorption capacity of copper adsorbent, with 85% cycling capacity has a 47 mg/g adsorption capacity after desorption cycle, shall be considered. For a mine effluent or process water with 5 mg/L Cu^{2+} and a flow of 200 m³/h requires about 21 kg adsorbent per hour. The price of GPs is given as 1–1.5 € per kg [103], and as such the treatment costs of merely 1 h would be between 10 and 21 €. Regeneration up to 20 times gives more realistic cost factors, of 0.5–1 € per h, only for adsorbent costs. It becomes quickly clear that without regeneration, high efficiency, and selectivity GPs/AAMs will be too expensive for wastewater treatment.

6. Conclusions

Much work has been done on the adsorption properties of GPs/AAMs towards a wide variety of inorganic pollutants during the last decade. While the effect of competing ions in real water samples remain an issue, the incorporation of new composite materials and the tailoring of reaction conditions have a high potential to increase their selectivity as adsorbents. However, more and more authors have understood the need to regenerate adsorbents and research are being conducted on the recovery of valuable materials, such as metals or nutrients. The recovery of high energy products from side streams utilizing adsorbents made from industrial side streams, will bring circular economy towards the next level. It is also of interest, to cover the costs of water treatment by the revenue of removed materials. While still much work needs to be done, the authors remain confident, that GPs/AAMs will continue to have a prominent place in wastewater treatment.

Acknowledgements


The research was partially funded by European Regional Development Fund (Leverage from the EU, WaterPro project № A74635; Keski-Pohjanmaan liitto/Kainuun liitto/Pohjois-Pohjanmaan liitto) and by Maa- ja vesitekniikan tuki (№ 13-8271-17).

Author details

Tatiana Samarina*, Esther Takaluoma and Outi Laatikainen
KAMK Kajaani University of Applied Sciences, Kajaani, Finland

*Address all correspondence to: tatiana.samarina@kamk.fi

IntechOpen

© 2021 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

References

- [1] Bennich T, Weitz N, Carlsen H. Deciphering the scientific literature on SDG interactions: A review and reading guide. *Science of The Total Environment* 2020;728:138405. DOI: 10.1016/j.scitotenv.2020.138405.
- [2] World Bank Group. The Growing Role of Minerals and Metals for a Low Carbon Future. World Bank, Washington, DC; 2017. DOI: 10.1596/28312.
- [3] Takaluoma E, Samarina T. Valorisation of Sidestream from lithium Refining - Activation of Analcime. Proceedings of the 6th World Congress on New Technologies (NewTech'20), Virtual: AVESTIA; 2020. DOI: 10.11159/icepr20.149.
- [4] Andrejkovičová S, Sudagar A, Rocha J, Patinha C, Hajjaji W, da Silva EF, et al. The effect of natural zeolite on microstructure, mechanical and heavy metals adsorption properties of metakaolin based geopolymers. *Applied Clay Science* 2016;126:141–152. DOI: 10.1016/j.clay.2016.03.009.
- [5] López FJ, Sugita S, Tagaya M, Kobayashi T. Metakaolin-Based Geopolymers for Targeted Adsorbents to Heavy Metal Ion Separation. *Journal of Materials Science and Chemical Engineering* 2014;2:16–27. DOI: 10.4236/msce.2014.27002.
- [6] Ariffin N, Abdullah MMAB, Zainol MRRMA, Baltatu MS, Jamaludin L. Effect of Solid to Liquid Ratio on Heavy Metal Removal by Geopolymer-Based Adsorbent. *IOP Conf Ser: Mater Sci Eng* 2018;374:012045. DOI: 10.1088/1757-899X/374/1/012045.
- [7] Gollakota ARK, Volli V, Shu C-M. Progressive utilisation prospects of coal fly ash: A review. *Sci Total Environ* 2019;672:951–989. DOI: 10.1016/j.scitotenv.2019.03.337.
- [8] Tian Q, Sasaki K. Structural characterizations of fly ash-based geopolymer after adsorption of various metal ions. *Environmental Technology* 2019;0:1–11. DOI: 10.1080/09593330.2019.1649469.
- [9] Mužek MN, Svilović S, Ugrina M, Zelić J. Removal of copper and cobalt ions by fly ash-based geopolymer from solutions-equilibrium study. *Desalination and Water Treatment* 2016;57:10689–10699. DOI: 10.1080/19443994.2015.1040077.
- [10] Jo M, Soto L, Arocho M, St John J, Hwang S. Optimum mix design of fly ash geopolymer paste and its use in pervious concrete for removal of fecal coliforms and phosphorus in water. *Construction and Building Materials* 2015;93:1097–1104. DOI: 10.1016/j.conbuildmat.2015.05.034.
- [11] Novais RM, Buruberri LH, Seabra MP, Labrincha JA. Novel porous fly-ash containing geopolymer monoliths for lead adsorption from wastewaters. *J Hazard Mater* 2016;318: 631–640. DOI: 10.1016/j.jhazmat.2016.07.059.
- [12] Yao Z. Fly Ash: Sources, Applications and Potential Environmental Impacts. 2014.
- [13] De Gisi S, Lofrano G, Grassi M, Notarnicola M. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review. *Sustainable Materials and Technologies* 2016;9:10–40. DOI: 10.1016/j.susmat.2016.06.002.
- [14] Ahmaruzzaman M. A review on the utilization of fly ash. *Progress in Energy and Combustion Science* 2010;36:327–363. DOI: 10.1016/j.pecs.2009.11.003.
- [15] Ji Z, Pei Y. Geopolymers produced from drinking water treatment residue

- and bottom ash for the immobilization of heavy metals. *Chemosphere* 2019;225: 579–587. DOI: 10.1016/j.chemosphere.2019.03.056.
- [16] Ji Z, Pei Y. Bibliographic and visualized analysis of geopolymer research and its application in heavy metal immobilization: A review. *Journal of Environmental Management* 2019; 231:256–267. DOI: 10.1016/j.jenvman.2018.10.041.
- [17] Maldonado-Alameda À, Giro-Paloma J, Alfocea-Roig A, Formosa J, Chimenos JM. Municipal Solid Waste Incineration Bottom Ash as Sole Precursor in the Alkali-Activated Binder Formulation. *Applied Sciences* 2020;10: 4129. DOI: 10.3390/app10124129.
- [18] Al-Ghouti MA, Khan M, Nasser MS, Saad KA, Heng OE. Application of geopolymers synthesized from incinerated municipal solid waste ashes for the removal of cationic dye from water. *PLOS ONE* 2020;15:e0239095. DOI: 10.1371/journal.pone.0239095.
- [19] Silva RV, de Brito J, Lynn CJ, Dhir RK. Use of municipal solid waste incineration bottom ashes in alkali-activated materials, ceramics and granular applications: A review. *Waste Management* 2017;68:207–220. DOI: 10.1016/j.wasman.2017.06.043.
- [20] Chiang YW, Ghyselbrecht K, Santos RM, Meesschaert B, Martens JA. Synthesis of zeolitic-type adsorbent material from municipal solid waste incinerator bottom ash and its application in heavy metal adsorption. *Catalysis Today* 2012;190:23–30. DOI: 10.1016/j.cattod.2011.11.002.
- [21] Hong S-H, Shin M-C, Lee J, Lee C-G, Song D-S, Um B-H, et al. Recycling of bottom ash derived from combustion of cattle manure and its adsorption behaviors for Cd(II), Cu(II), Pb(II), and Ni(II). *Environ Sci Pollut Res* 2020. DOI: 10.1007/s11356-020-11719-7.
- [22] Zhang HY, Zheng Y, Hu HT, Qi JY. Use of Municipal Solid Waste Incineration Bottom Ash in Adsorption of Heavy Metals. *Key Engineering Materials* 2011;474–476:1099–1102. DOI: 10.4028/www.scientific.net/KEM.474-476.1099.
- [23] Joseph A, Snellings R, Van den Heede P, Matthys S, De Belie N. The Use of Municipal Solid Waste Incineration Ash in Various Building Materials: A Belgian Point of View. *Materials* 2018; 11:141. DOI: 10.3390/ma11010141.
- [24] Zhu W, Rao XH, Liu Y, Yang E-H. Lightweight aerated metakaolin-based geopolymer incorporating municipal solid waste incineration bottom ash as gas-forming agent. *Journal of Cleaner Production* 2018;177:775–781. DOI: 10.1016/j.jclepro.2017.12.267.
- [25] Fabricius A-L, Renner M, Voss M, Funk M, Perfol A, Gehring F, et al. Municipal waste incineration fly ashes: from a multi-element approach to market potential evaluation. *Environmental Sciences Europe* 2020;32: 88. DOI: 10.1186/s12302-020-00365-y.
- [26] Quina MJ, Bontempi E, Bogush A, Schlumberger S, Weibel G, Braga R, et al. Technologies for the management of MSW incineration ashes from gas cleaning: New perspectives on recovery of secondary raw materials and circular economy. *Science of The Total Environment* 2018;635:526–542. DOI: 10.1016/j.scitotenv.2018.04.150.
- [27] Zhuang XY, Chen L, Komarneni S, Zhou CH, Tong DS, Yang HM, et al. Fly ash-based geopolymer: clean production, properties and applications. *Journal of Cleaner Production* 2016;125: 253–267. DOI: 10.1016/j.jclepro.2016.03.019.
- [28] Wang GC. 11 - Slag use as an aggregate in concrete and cement-based materials. In: Wang GC, editor. *The Utilization of Slag in Civil Infrastructure*

Construction, Woodhead Publishing; 2016, p. 239–74. DOI: 10.1016/B978-0-08-100381-7.00011-2.

[29] Siddique R, Iqbal Khan M. Ground Granulated Blast Furnace Slag. In: Siddique R, Khan MI, editors. *Supplementary Cementing Materials*, Berlin, Heidelberg: Springer; 2011, p. 121–173. DOI: 10.1007/978-3-642-17866-5_3.

[30] Gupta VK, Carrott PJM, Carrott MMLR, Suhas. Low-Cost Adsorbents: Growing Approach to Wastewater Treatment—a Review. *Critical Reviews in Environmental Science and Technology* 2009;39:783–842. DOI: 10.1080/10643380801977610.

[31] Medina TJ, Arredondo SP, Corral R, Jacobo A, Zarraga RA, Rosas CA, et al. Microstructure and Pb(2+) Adsorption Properties of Blast Furnace Slag and Fly Ash based Geopolymers. *Minerals* 2020;10:808. DOI: 10.3390/min10090808.

[32] Luukkonen T, Runtti H, Niskanen M, Tolonen E-T, Sarkkinen M, Kemppainen K, et al. Simultaneous removal of Ni(II), As(III), and Sb(III) from spiked mine effluent with metakaolin and blast-furnace-slag geopolymers. *Journal of Environmental Management* 2016;166:579–588. DOI: 10.1016/j.jenvman.2015.11.007.

[33] Tang Q, Wang K, Yaseen M, Tong Z, Cui X. Synthesis of highly efficient porous inorganic polymer microspheres for the adsorptive removal of Pb²⁺ from wastewater. *J Clean Prod* 2018;193:351–362. DOI: 10.1016/j.jclepro.2018.05.094.

[34] Tang Q, Wang K, Su J, Shen Y, Yang S, Ge Y, et al. Facile fabrication of inorganic polymer microspheres as adsorbents for removing heavy metal ions. *Mater Res Bull* 2019;113:202–208. DOI: 10.1016/j.materresbull.2019.02.009.

[35] Khalid HR, Lee NK, Park SM, Abbas N, Lee HK. Synthesis of geopolymer-supported zeolites via robust one-step method and their adsorption potential. *Journal of Hazardous Materials* 2018;353:522–533. DOI: 10.1016/j.jhazmat.2018.04.049.

[36] Manchisi J, Matinde E, Rowson NA, Simmons MJH, Simate GS, Ndlovu S, et al. Ironmaking and Steelmaking Slags as Sustainable Adsorbents for Industrial Effluents and Wastewater Treatment: A Critical Review of Properties, Performance, Challenges and Opportunities. *Sustainability* 2020;12:2118. DOI: 10.3390/su12052118.

[37] Naidu TS, Sheridan CM, van Dyk LD. Basic oxygen furnace slag: Review of current and potential uses. *Minerals Engineering* 2020;149:106234. DOI: 10.1016/j.mineng.2020.106234.

[38] Nikolić I, Đurović D, Tadić M, Radmilović VV, Radmilović VR. Adsorption kinetics, equilibrium, and thermodynamics of Cu²⁺ on pristine and alkali activated steel slag. *Chemical Engineering Communications* 2020;207:1278–1297. DOI: 10.1080/00986445.2019.1685986.

[39] Sarkar C, Basu JK, Samanta AN. Removal of Ni²⁺ ion from waste water by Geopolymeric Adsorbent derived from LD Slag. *Journal of Water Process Engineering* 2017;17:237–244. DOI: 10.1016/j.jwpe.2017.04.012.

[40] Sarkar C, Basu JK, Samanta AN. Synthesis of mesoporous geopolymeric powder from LD slag as superior adsorbent for Zinc (II) removal. *Advanced Powder Technology* 2018;29:1142–1152. DOI: 10.1016/j.apr.2018.02.005.

[41] Sarkar C, Basu JK, Samanta AN. Experimental and kinetic study of fluoride adsorption by Ni and Zn modified LD slag based geopolymer. *Chemical Engineering Research and*

Design 2019;142:165–175. DOI: 10.1016/j.cherd.2018.12.006.

[42] Sithole NT, Ntuli F, Okonta F. Fixed bed column studies for decontamination of acidic mineral effluent using porous fly ash-basic oxygen furnace slag based geopolymers. *Miner Eng* 2020;154: 106397. DOI: 10.1016/j.mineng.2020.106397.

[43] Sithole NT, Ntuli F, Okonta F. Synthesis and evaluation of basic oxygen furnace slag based geopolymers for removal of metals and sulphates from acidic industrial effluent-column study. *J Water Process Eng* 2020;37: 101518. DOI: 10.1016/j.jwpe.2020.101518.

[44] Alhassan SI, He Y, Huang L, Wu B, Yan L, Deng H, et al. A review on fluoride adsorption using modified bauxite: Surface modification and sorption mechanisms perspectives. *Journal of Environmental Chemical Engineering* 2020;8:104532. DOI: 10.1016/j.jece.2020.104532.

[45] Alshaebi F, Yaacob WZ, Samsudin A, Esmail A. Arsenic Adsorption on Bauxite Mineral Using Batch Equilibrium Test. *American Journal of Applied Sciences* 2009;6. DOI: 10.3844/ajassp.2009.1826.1830.

[46] Hertel T, Pontikes Y. Geopolymers, inorganic polymers, alkali-activated materials and hybrid binders from bauxite residue (red mud) – Putting things in perspective. *Journal of Cleaner Production* 2020;258:120610. DOI: 10.1016/j.jclepro.2020.120610.

[47] Norouzi S, Badii K, Doulati Ardejani F. Activated bauxite waste as an adsorbent for removal of Acid Blue 92 from aqueous solutions. *Water Sci Technol* 2010;62:2491–2500. DOI: 10.2166/wst.2010.514.

[48] Taneez M, Hurel C, Marmier N, Lefèvre G. Adsorption of inorganic

pollutants on bauxite residues: An example of methodology to simulate adsorption in complex solids mixtures. *Applied Geochemistry* 2017;78:272–278. DOI: 10.1016/j.apgeochem.2017.01.007.

[49] Ren B, Zhao Y, Bai H, Kang S, Zhang T, Song S. Eco-friendly geopolymer prepared from solid wastes: A critical review. *Chemosphere* 2020:128900. DOI: 10.1016/j.chemosphere.2020.128900.

[50] Khalid MK, Agarwal V, Wilson BP, Takaluoma E, Lundstrom M. Applicability of solid process residues as sorbents for the treatment of industrial wastewaters. *J Clean Prod* 2020;246: 118951. DOI: 10.1016/j.jclepro.2019.118951.

[51] Demir F, Derun EM. Modelling and optimization of gold mine tailings based geopolymer by using response surface method and its application in Pb²⁺ removal. *J Clean Prod* 2019;237:117766. DOI: 10.1016/j.jclepro.2019.117766.

[52] Tian Q, Nakama S, Sasaki K. Immobilization of cesium in fly ash-silica fume based geopolymers with different Si/Al molar ratios. *Sci Total Environ* 2019;687:1127–1137. DOI: 10.1016/j.scitotenv.2019.06.095.

[53] Shakouri S, Bayer O, Erdogan ST. Development of silica fume-based geopolymer foams. *Constr Build Mater* 2020;260:120442. DOI: 10.1016/j.conbuildmat.2020.120442.

[54] Duan P, Yan C, Zhou W, Ren D. Development of fly ash and iron ore tailing based porous geopolymer for removal of Cu(II) from wastewater. *Ceram Int* 2016;42:13507–13518. DOI: 10.1016/j.ceramint.2016.05.143.

[55] Panda L, Rath SS, Rao DS, Nayak BB, Das B, Misra PK. Thorough understanding of the kinetics and mechanism of heavy metal adsorption onto a pyrophyllite mine waste based geopolymer. *Journal of Molecular*

Liquids 2018;263:428–441. DOI: 10.1016/j.molliq.2018.05.016.

[56] Lemougna PN, Wang K, Tang Q, Melo UC, Cui X. Recent developments on inorganic polymers synthesis and applications. *Ceramics International* 2016;42:15142–15159. DOI: 10.1016/j.ceramint.2016.07.027.

[57] Rasaki SA, Bingxue Z, Guarecuco R, Thomas T, Minghui Y. Geopolymer for use in heavy metals adsorption, and advanced oxidative processes: A critical review. *Journal of Cleaner Production* 2019;213:42–58. DOI: 10.1016/j.jclepro.2018.12.145.

[58] Naghsh M, Shams K. Synthesis of a kaolin-based geopolymer using a novel fusion method and its application in effective water softening. *Applied Clay Science* 2017;146:238–245. DOI: 10.1016/j.clay.2017.06.008.

[59] Samarina T, Takaluoma E. Metakaolin-Based Geopolymers for Removal of Ammonium from Municipal Wastewater, 2019. DOI: 10.11159/icepr19.195.

[60] Khalifa AZ, Cizer Ö, Pontikes Y, Heath A, Patureau P, Bernal SA, et al. Advances in alkali-activation of clay minerals. *Cement and Concrete Research* 2020;132:106050. DOI: 10.1016/j.cemconres.2020.106050.

[61] Maleki A, Hajizadeh Z, Sharifi V, Emdadi Z. A green, porous and eco-friendly magnetic geopolymer adsorbent for heavy metals removal from aqueous solutions. *J Clean Prod* 2019;215:1233–1245. DOI: 10.1016/j.jclepro.2019.01.084.

[62] Ghani U, Hussain S, Noor-ul-Amin, Imtiaz M, Ali Khan S. Laterite clay-based geopolymer as a potential adsorbent for the heavy metals removal from aqueous solutions. *Journal of Saudi Chemical Society* 2020;24:874–884. DOI: 10.1016/j.jscs.2020.09.004.

[63] Hayashi S, Onuma T, Kagaya F. Fixing of electrophoretically deposited natural zeolite particles by geopolymer reaction for heavy metal ion adsorbents. *Journal of the Ceramic Society of Japan* 2017;125:894–898. DOI: 10.2109/jcersj2.17134.

[64] Javadian H, Ghorbani F, Tayebi H, Asl SH. Study of the adsorption of Cd (II) from aqueous solution using zeolite-based geopolymer, synthesized from coal fly ash; kinetic, isotherm and thermodynamic studies. *Arabian Journal of Chemistry* 2015;8:837–849. DOI: 10.1016/j.arabjc.2013.02.018.

[65] Wang S, Peng Y. Natural zeolites as effective adsorbents in water and wastewater treatment. *Chemical Engineering Journal* 2010;156:11–24. DOI: 10.1016/j.cej.2009.10.029.

[66] Li Y, Li L, Yu J. Applications of Zeolites in Sustainable Chemistry. *Chem* 2017;3:928–949. DOI: 10.1016/j.chempr.2017.10.009.

[67] Delkash M, Ebrazzi Bakhshayesh B, Kazemian H. Using zeolitic adsorbents to cleanup special wastewater streams: A review. *Microporous and Mesoporous Materials* 2015;214:224–241. DOI: 10.1016/j.micromeso.2015.04.039.

[68] Yilmaz B, Müller U. Catalytic Applications of Zeolites in Chemical Industry. *Top Catal* 2009;52:888–895. DOI: 10.1007/s11244-009-9226-0.

[69] Montalvo S, Huiliñir C, Borja R, Sánchez E, Herrmann C. Application of zeolites for biological treatment processes of solid wastes and wastewaters – A review. *Bioresource Technology* 2020;301:122808. DOI: 10.1016/j.biortech.2020.122808.

[70] Khaleque A, Alam MM, Hoque M, Mondal S, Haider JB, Xu B, et al. Zeolite synthesis from low-cost materials and environmental applications: A review. *Environmental Advances* 2020;2:

100019. DOI: 10.1016/j.envadv.2020.100019.

222–224. DOI: 10.1016/j.matlet.2014.07.090.

[71] Rožek P, Król M, Mozgawa W. Geopolymer-zeolite composites: A review. *Journal of Cleaner Production* 2019;230:557–579. DOI: 10.1016/j.jclepro.2019.05.152.

[78] Ge Y, Cui X, Kong Y, Li Z, He Y, Zhou Q. Porous geopolymeric spheres for removal of Cu(II) from aqueous solution: Synthesis and evaluation. *Journal of Hazardous Materials* 2015; 283:244–251. DOI: 10.1016/j.jhazmat.2014.09.038.

[72] Alshaaer M, Zaharaki D, Komnitsas K. Microstructural characteristics and adsorption potential of a zeolitic tuff–metakaolin geopolymer. *Desalination and Water Treatment* 2015;56:338–345. DOI: 10.1080/19443994.2014.938306.

[79] Zhang M, Zhao M, Zhang G, Nowak P, Coen A, Tao M. Calcium-free geopolymer as a stabilizer for sulfate-rich soils. *Applied Clay Science* 2015; 108:199–207. DOI: 10.1016/j.clay.2015.02.029.

[73] Deng L, Xu Q, Wu H. Synthesis of Zeolite-like Material by Hydrothermal and Fusion Methods Using Municipal Solid Waste Fly Ash. *Procedia Environmental Sciences* 2016;31: 662–667. DOI: 10.1016/j.proenv.2016.02.122.

[80] Duan J, Li J, Lu Z. One-step facile synthesis of bulk zeolite A through metakaolin-based geopolymer gels. *J Porous Mater* 2015;22:1519–1526. DOI: 10.1007/s10934-015-0034-6.

[74] Visa M. Synthesis and characterization of new zeolite materials obtained from fly ash for heavy metals removal in advanced wastewater treatment. *Powder Technology* 2016; 294:338–347. DOI: 10.1016/j.powtec.2016.02.019.

[81] Tang Q, Ge Y, Wang K, He Y, Cui X. Preparation and characterization of porous metakaolin-based inorganic polymer spheres as an adsorbent. *Materials & Design* 2015;88:1244–1249. DOI: 10.1016/j.matdes.2015.09.126.

[75] Rios C, Williams C, Castellanos OM. A comparative study on the use of zeolite-like materials in the removal of heavy metals and ammonium from wastewaters. *RP* 2020;18. DOI: 10.15665/rp.v18i2.2187.

[82] Kovářík T, Křenek T, Pola M, Rieger D, Kadlec J, Franče P. Ceramic-like open-celled geopolymer foam as a porous substrate for water treatment catalyst. *IOP Conf Ser: Mater Sci Eng* 2017;175:012044. DOI: 10.1088/1757-899X/175/1/012044.

[76] Toniolo N, Boccaccini AR. Fly ash-based geopolymers containing added silicate waste. A review. *Ceramics International* 2017;43:14545–14551. DOI: 10.1016/j.ceramint.2017.07.221.

[83] Ge Y, Cui X, Liao C, Li Z. Facile fabrication of green geopolymer/alginate hybrid spheres for efficient removal of Cu(II) in water: Batch and column studies. *Chemical Engineering Journal* 2017;311:126–134. DOI: 10.1016/j.cej.2016.11.079.

[77] Gasca-Tirado JR, Manzano-Ramírez A, Vazquez-Landaverde PA, Herrera-Díaz EI, Rodríguez-Ugarte ME, Rubio-Ávalos JC, et al. Ion-exchanged geopolymer for photocatalytic degradation of a volatile organic compound. *Materials Letters* 2014;134:

[84] Kara İ, Yilmazer D, Akar ST. Metakaolin based geopolymer as an effective adsorbent for adsorption of zinc(II) and nickel(II) ions from aqueous solutions. *Applied Clay Science*

2017;139:54–63. DOI: 10.1016/j.clay.2017.01.008.

[85] Singhal A, Gangwar BP, Gayathry JM. CTAB modified large surface area nanoporous geopolymer with high adsorption capacity for copper ion removal. *Applied Clay Science* 2017;150:106–114. DOI: 10.1016/j.clay.2017.09.013.

[86] Novais RM, Ascensão G, Tobaldi DM, Seabra MP, Labrincha JA. Biomass fly ash geopolymer monoliths for effective methylene blue removal from wastewaters. *Journal of Cleaner Production* 2018;171:783–794. DOI: 10.1016/j.jclepro.2017.10.078.

[87] Kara I, Tunc D, Sayin F, Akar ST. Study on the performance of metakaolin based geopolymer for Mn(II) and Co(II) removal. *Applied Clay Science* 2018;161:184–193. DOI: 10.1016/j.clay.2018.04.027.

[88] Bravo PI, Malenab RA, Shimizu E, Yu DE, Promentilla MA. Synthesis of geopolymer spheres with photocatalytic activity. *MATEC Web Conf* 2019;268:04007. DOI: 10.1051/mateconf/201926804007.

[89] Novais RM, Carvalheiras J, Tobaldi DM, Seabra MP, Pullar RC, Labrincha JA. Synthesis of porous biomass fly ash-based geopolymer spheres for efficient removal of methylene blue from wastewaters. *Journal of Cleaner Production* 2019;207:350–362. DOI: 10.1016/j.jclepro.2018.09.265.

[90] Yan C, Guo L, Ren D, Duan P. Novel composites based on geopolymer for removal of Pb(II). *Materials Letters* 2019;239:192–195. DOI: 10.1016/j.matlet.2018.12.105.

[91] Samarina T, Takaluoma E. Simultaneous Removal of Nutrients by Geopolymers Made From Industrial By-Products. *Proceedings of the 5th World*

Congress on New Technologies (NewTech'19), Lisbon: AVESTIA; 2019. DOI: 10.11159/ICEPR19.169.

[92] El Alouani M, Alehyen S, El Achouri M, Taibi M. Preparation, Characterization, and Application of Metakaolin-Based Geopolymer for Removal of Methylene Blue from Aqueous Solution. *Journal of Chemistry* 2019;2019:e4212901. DOI: <https://doi.org/10.1155/2019/4212901>.

[93] Yan S, Zhang F, Wang L, Rong Y, He P, Jia D, et al. A green and low-cost hollow gangue microsphere/geopolymer adsorbent for the effective removal of heavy metals from wastewaters. *Journal of Environmental Management* 2019;246:174–183. DOI: 10.1016/j.jenvman.2019.05.120.

[94] Chen X, Niu Z, Zhang H, Guo Y, Liu M, Zhou M. Study on the metakaolin-based geopolymer pervious concrete (MKGPC) and its removal capability of heavy metal ions. *International Journal of Pavement Engineering* 2019;0:1–12. DOI: 10.1080/10298436.2019.1667499.

[95] Bumanis G, Novais RM, Carvalheiras J, Bajare D, Labrincha JA. Metals removal from aqueous solutions by tailored porous waste-based granulated alkali-activated materials. *Appl Clay Sci* 2019;179:105147. DOI: 10.1016/j.clay.2019.105147.

[96] Lan T, Li P, Rehman FU, Li X, Yang W, Guo S. Efficient adsorption of Cd²⁺ from aqueous solution using metakaolin geopolymers. *Environ Sci Pollut Res* 2019;26:33555–33567. DOI: 10.1007/s11356-019-06362-w.

[97] Chen S, Qi Y, Cossa JJ, Deocleciano Salomao Dos SI. Efficient removal of radioactive iodide anions from simulated wastewater by HDTMA-geopolymer. *Progress in Nuclear Energy* 2019;117:103112. DOI: 10.1016/j.pnucene.2019.103112.

- [98] Falah M, MacKenzie KJD, Knibbe R, Page SJ, Hanna JV. New composites of nanoparticle Cu (I) oxide and titania in a novel inorganic polymer (geopolymer) matrix for destruction of dyes and hazardous organic pollutants. *Journal of Hazardous Materials* 2016;318:772–782. DOI: 10.1016/j.jhazmat.2016.06.016.
- [99] Yu Z, Song W, Li J, Li Q. Improved simultaneous adsorption of Cu(II) and Cr (VI) of organic modified metakaolin-based geopolymer. *Arab J Chem* 2020; 13:4811–4823. DOI: 10.1016/j.arabjc.2020.01.001.
- [100] Hua P, Sellaoui L, Franco D, Netto MS, Luiz Dotto G, Bajahzar A, et al. Adsorption of acid green and procion red on a magnetic geopolymer based adsorbent: Experiments, characterization and theoretical treatment. *Chemical Engineering Journal* 2020;383:123113. DOI: 10.1016/j.cej.2019.123113.
- [101] Chen H, Zhang YJ, He PY, Li CJ, Li H. Coupling of self-supporting geopolymer membrane with intercepted Cr(III) for dye wastewater treatment by hybrid photocatalysis and membrane separation. *Applied Surface Science* 2020;515:146024. DOI: 10.1016/j.apsusc.2020.146024.
- [102] Mladenovic N, Kljajevic L, Nenadovic S, Ivanovic M, Calija B, Gulicovski J, et al. The Applications of New Inorganic Polymer for Adsorption Cadmium from Waste Water. *J Inorg Organomet Polym Mater* 2020;30:554–563. DOI: 10.1007/s10904-019-01215-y.
- [103] da Costa Rocha AC, Scaratti G, Moura-Nickel CD, da Silva TL, Gurgel Adeodato Vieira M, Peralta RM, et al. Economical and Technological Aspects of Copper Removal from Water Using a Geopolymer and Natural Zeolite. *Water Air Soil Pollut* 2020;231:361. DOI: 10.1007/s11270-020-04722-8.
- [104] Papa E, Mor M, Natali Murri A, Landi E, Medri V. Ice-templated geopolymer beads for dye removal. *Journal of Colloid and Interface Science* 2020;572:364–373. DOI: 10.1016/j.jcis.2020.03.104.
- [105] Medri V, Papa E, Mor M, Vaccari A, Natali Murri A, Piotta L, et al. Mechanical strength and cationic dye adsorption ability of metakaolin-based geopolymer spheres. *Applied Clay Science* 2020;193:105678. DOI: 10.1016/j.clay.2020.105678.
- [106] Netto MS, Rossatto DL, Jahn SL, Mallmann ES, Dotto GL, Foletto EL. Preparation of a novel magnetic geopolymer/zero-valent iron composite with remarkable adsorption performance towards aqueous Acid Red 97. *Chemical Engineering Communications* 2020;207:1048–1061. DOI: 10.1080/00986445.2019.1635467.
- [107] Samarina T, Takaluoma E, Kazmaganbetova A. Geopolymers Supported on Inert Substrate for Phosphate Removal from Natural Waters. *Proceedings of the 6th World Congress on New Technologies (NewTech'20), Virtual: AVESTIA; 2020*. DOI: 10.11159/icepr20.119.
- [108] Huang J, Li Z, Zhang J, Zhang Y, Ge Y, Cui X. In-situ synchronous carbonation and self-activation of biochar/geopolymer composite membrane: Enhanced catalyst for oxidative degradation of tetracycline in water. *Chemical Engineering Journal* 2020;397:125528. DOI: 10.1016/j.cej.2020.125528.
- [109] Petlitckaia S, Barré Y, Piallat T, Grauby O, Ferry D, Poulesquen A. Functionalized geopolymer foams for cesium removal from liquid nuclear waste. *Journal of Cleaner Production* 2020;269:122400. DOI: 10.1016/j.jclepro.2020.122400.
- [110] Lertcumfu N, Jaita P, Thammarong S, Lamkhao S, Tandorn S, Randorn C, et al. Influence of graphene

- oxide additive on physical, microstructure, adsorption, and photocatalytic properties of calcined kaolinite-based geopolymer ceramic composites. *Colloid Surf A-Physicochem Eng Asp* 2020;602:125080. DOI: 10.1016/j.colsurfa.2020.125080.
- [111] Al-Harashsheh MS, Al Zboon K, Al-Makhadmeh L, Hararah M, Mahasneh M. Fly ash based geopolymer for heavy metal removal: A case study on copper removal. *Journal of Environmental Chemical Engineering* 2015;3:1669–1677. DOI: 10.1016/j.jece.2015.06.005.
- [112] Meher AK, Das S, Rayalu S, Bansiwala A. Enhanced arsenic removal from drinking water by iron-enriched aluminosilicate adsorbent prepared from fly ash. *Desalin Water Treat* 2015;57:20944–20956. DOI: 10.1080/19443994.2015.1112311.
- [113] Zhang K, Zhang D, Zhang K. Arsenic removal from water using a novel amorphous adsorbent developed from coal fly ash. *Water Sci Technol* 2016;73:1954–1962. DOI: 10.2166/wst.2016.028.
- [114] Liu Y, Yan C, Zhang Z, Wang H, Zhou S, Zhou W. A comparative study on fly ash, geopolymer and faujasite block for Pb removal from aqueous solution. *Fuel* 2016;185:181–189. DOI: 10.1016/j.fuel.2016.07.116.
- [115] Samarina T, Takaluoma E. New Geopolymer Adsorbents for Phosphate Removal from Diluted Solutions and their Applications. *Proceedings of the 5th World Congress on New Technologies (NewTech'19)*, Lisbon: AVESTIA; 2019. DOI: 10.11159/ICEPR19.158.
- [116] Mužek MN, Svilović S, Zelić J. Kinetic studies of cobalt ion removal from aqueous solutions using fly ash-based geopolymer and zeolite NaX as sorbents. *Separation Science and Technology* 2016;51:2868–2875. DOI: 10.1080/01496395.2016.1228675.
- [117] Qiu J, Zhao Y, Xing J, Sun X. Fly ash-based geopolymer as a potential adsorbent for Cr(VI) removal. *Desalin Water Treat* 2017;70:201–209. DOI: 10.5004/dwt.2017.20493.
- [118] Lee NK, Khalid HR, Lee HK. Adsorption characteristics of cesium onto mesoporous geopolymers containing nano-crystalline zeolites. *Microporous Mesoporous Mat* 2017;242:238–244. DOI: 10.1016/j.micromeso.2017.01.030.
- [119] Maiti M, Sarkar M, Malik MA, Xu S, Li Q, Mandal S. Iron Oxide NPs Facilitated a Smart Building Composite for Heavy-Metal Removal and Dye Degradation. *ACS Omega* 2018;3:1081–1089. DOI: 10.1021/acsomega.7b01545.
- [120] Zhang YJ, He PY, Zhang YX, Chen H. A novel electroconductive graphene/fly ash-based geopolymer composite and its photocatalytic performance. *Chemical Engineering Journal* 2018;334:2459–2466. DOI: 10.1016/j.cej.2017.11.171.
- [121] Samiullah M, Aslam Z, Rana AG, Abbas A, Ahmad W. Alkali-Activated Boiler Fly Ash for Ni(II) Removal: Characterization and Parametric Study. *Water Air Soil Pollut* 2018;229:113. DOI: 10.1007/s11270-018-3758-5.
- [122] Darmayanti L, Notodarmojo S, Damanhuri E, Kadja GTM, Mukti RR. Preparation of alkali-activated fly ash-based geopolymer and their application in the adsorption of copper (II) and zinc (II) ions. *MATEC Web Conf* 2019;276:06012. DOI: 10.1051/mateconf/201927606012.
- [123] Onutai S, Kobayashi T, Thavorniti P, Jiemsirilers S. Porous fly ash-based geopolymer composite fiber as an adsorbent for removal of heavy metal ions from wastewater. *Materials*

Letters 2019;236:30–33. DOI: 10.1016/j.matlet.2018.10.035.

[124] Soni R, Shukla DP. Synthesis of fly ash based zeolite-reduced graphene oxide composite and its evaluation as an adsorbent for arsenic removal. *Chemosphere* 2019;219:504–509. DOI: 10.1016/j.chemosphere.2018.11.203.

[125] Tian Q, Sasaki K. Application of fly ash-based geopolymer for removal of cesium, strontium and arsenate from aqueous solutions: kinetic, equilibrium and mechanism analysis. *Water Sci Technol* 2019;79:2116–2125. DOI: 10.2166/wst.2019.209.

[126] Siyal AA, Shamsuddin MR, Rabat NE, Zulfiqar M, Man Z, Low A. Fly ash based geopolymer for the adsorption of anionic surfactant from aqueous solution. *Journal of Cleaner Production* 2019;229:232–243. DOI: 10.1016/j.jclepro.2019.04.384.

[127] Darmayanti L, Kadja GTM, Notodarmojo S, Damanhuri E, Mukti RR. Structural alteration within fly ash-based geopolymers governing the adsorption of Cu²⁺ from aqueous environment: Effect of alkali activation. *J Hazard Mater* 2019;377:305–314. DOI: 10.1016/j.jhazmat.2019.05.086.

[128] Shao N, Tang S, Li S, Chen H, Zhang Z. Defective analcime/geopolymer composite membrane derived from fly ash for ultrafast and highly efficient filtration of organic pollutants. *Journal of Hazardous Materials* 2020;388:121736. DOI: 10.1016/j.jhazmat.2019.121736.

[129] Abdelrahman EA, Abou El-Reash YG, Youssef HM, Kotp YH, Hegazey RM. Utilization of rice husk and waste aluminum cans for the synthesis of some nanosized zeolite, zeolite/zeolite, and geopolymer/zeolite products for the efficient removal of Co (II), Cu(II), and Zn(II) ions from aqueous media. *Journal of Hazardous*

Materials 2021;401:123813. DOI: 10.1016/j.jhazmat.2020.123813.

[130] Mondal SK, Welz A, Rezaei F, Kumar A, Okoronkwo MU. Structure-Property Relationship of Geopolymers for Aqueous Pb Removal. *ACS Omega* 2020;5:21689–21699. DOI: 10.1021/acsomega.0c02591.

[131] Novais RM, Carvalheiras J, Seabra MP, Pullar RC, Labrincha JA. Highly efficient lead extraction from aqueous solutions using inorganic polymer foams derived from biomass fly ash and metakaolin. *J Environ Manage* 2020;272:111049. DOI: 10.1016/j.jenvman.2020.111049.

[132] Zhang YJ, He PY, Yang MY, Kang L. A new graphene bottom ash geopolymeric composite for photocatalytic H₂ production and degradation of dyeing wastewater. *International Journal of Hydrogen Energy* 2017;42:20589–20598. DOI: 10.1016/j.ijhydene.2017.06.156.

[133] Zhang YJ, Yang MY, Zhang L, Zhang K, Kang L. A new graphene/geopolymer nanocomposite for degradation of dye wastewater. *Integrated Ferroelectrics* 2016;171:38–45. DOI: 10.1080/10584587.2016.1171178.

[134] Runtti H, Luukkonen T, Niskanen M, Tuomikoski S, Kangas T, Tynjälä P, et al. Sulphate removal over barium-modified blast-furnace-slag geopolymer. *Journal of Hazardous Materials* 2016;317:373–384. DOI: 10.1016/j.jhazmat.2016.06.001.

[135] He PY, Zhang YJ, Chen H, Liu LC. Development of an eco-efficient CaMoO₄/electroconductive geopolymer composite for recycling silicomanganese slag and degradation of dye wastewater. *Journal of Cleaner Production* 2019;208:1476–1487. DOI: 10.1016/j.jclepro.2018.10.176.

[136] Chen F, Wang K, Shao L, Muhammad Y, Wei Y, Gao F, et al.

Synthesis of Fe₂O₃-modified porous geopolymer microspheres for highly selective adsorption and solidification of F⁻ from waste-water. *Composites Part B: Engineering* 2019;178:107497. DOI: 10.1016/j.compositesb.2019.107497.

[137] Liu Z, Li L, Shao N, Hu T, Han L, Wang D. Geopolymerization enhanced hydrothermal synthesis of analcime from steel slag and CFBC fly ash and heavy metal adsorption on analcime. *Environ Technol* 2020;41:1753–1765. DOI: 10.1080/09593330.2018.1545805.

[138] Wang K, Lei H, Muhammad Y, Chen F, Gao F, Wei Y, et al. Controlled preparation of cerium oxide loaded slag-based geopolymer microspheres (CeO₂@SGMs) for the adsorptive removal and solidification of F⁻ from acidic waste-water. *Journal of Hazardous Materials* 2020;400:123199. DOI: 10.1016/j.jhazmat.2020.123199.

[139] Yan S, He P, Jia D, Wang Q, Liu J, Yang J, et al. Synthesis of novel low-cost porous gangue microsphere/geopolymer composites and their adsorption properties for dyes. *International Journal of Applied Ceramic Technology* 2018;15:1602–14. DOI: <https://doi.org/10.1111/ijac.13045>.

[140] Al-Zboon KK, Al-smadi BM, Al-Khawaldh S. Natural Volcanic Tuff-Based Geopolymer for Zn Removal: Adsorption Isotherm, Kinetic, and Thermodynamic Study. *Water Air Soil Pollut* 2016;227:248. DOI: 10.1007/s11270-016-2937-5.

[141] Minelli M, Medri V, Papa E, Miccio F, Landi E, Doghieri F. Geopolymers as solid adsorbent for CO₂ capture. *Chemical Engineering Science* 2016;148:267–274. DOI: 10.1016/j.ces.2016.04.013.

[142] Li C, He Y, Tang Q, Wang K, Cui X. Study of the preparation of CdS on the surface of geopolymer spheres and photocatalyst performance.

Materials Chemistry and Physics 2016; 178:204–210. DOI: 10.1016/j.matchemphys.2016.05.013.

[143] Abdelrahman EA, Subaihi A. Application of Geopolymers Modified with Chitosan as Novel Composites for Efficient Removal of Hg(II), Cd(II), and Pb(II) Ions from Aqueous Media. *J Inorg Organomet Polym Mater* 2020;30:2440–2463. DOI: 10.1007/s10904-019-01380-0.

[144] Demir F, Moroydor Derun E. Usage of gold mine tailings based geopolymer on Cu²⁺ adsorption from water. *Main Group Chemistry* 2019;18: 467–476. DOI: 10.3233/MGC-190801.

[145] Wang J, Zhao Y, Zhang P, Yang L, Xu H, Xi G. Adsorption characteristics of a novel ceramsite for heavy metal removal from stormwater runoff. *Chinese Journal of Chemical Engineering* 2018;26:96–103. DOI: 10.1016/j.cjche.2017.04.011.

[146] Paranaque JEL, Maguyon-Detras MC, Migo VP, Alfafara CG. Chromium removal from chrome-tannery effluent after alkaline precipitation by adsorption using municipal solid waste-derived activated biochar. 26th Regional Symposium on Chemical Engineering (rsce 2019), vol. 778, Bristol: Iop Publishing Ltd; 2020, p. 012134. DOI: 10.1088/1757-899X/778/1/012134.

[147] Panda L, Jena SK, Rath SS, Misra PK. Heavy metal removal from water by adsorption using a low-cost geopolymer. *Environ Sci Pollut Res* 2020;27:24284–24298. DOI: 10.1007/s11356-020-08482-0.

[148] Bakharev T. Thermal behaviour of geopolymers prepared using class F fly ash and elevated temperature curing. *Cement and Concrete Research* 2006;36: 1134–1147. DOI: 10.1016/j.cemconres.2006.03.022.

[149] Luukkonen T, Tolonen E-T, Runtti H, Kemppainen K, Perämäki P,

- Rämö J, et al. Optimization of the metakaolin geopolymer preparation for maximized ammonium adsorption capacity. *J Mater Sci* 2017;52:9363–9376. DOI: 10.1007/s10853-017-1156-9.
- [150] Siyal AA, Shamsuddin MR, Khan MI, Rabat NE, Zulfiqar M, Man Z, et al. A review on geopolymers as emerging materials for the adsorption of heavy metals and dyes. *Journal of Environmental Management* 2018;224:327–339. DOI: 10.1016/j.jenvman.2018.07.046.
- [151] Luukkonen T, Heponiemi A, Runtti H, Pesonen J, Yliniemi J, Lassi U. Application of alkali-activated materials for water and wastewater treatment: a review. *Rev Environ Sci Biotechnol* 2019;18:271–297. DOI: 10.1007/s11157-019-09494-0.
- [152] Luukkonen T, Věžníková K, Tolonen E-T, Runtti H, Yliniemi J, Hu T, et al. Removal of ammonium from municipal wastewater with powdered and granulated metakaolin geopolymer. *Environmental Technology* 2018;39:414–423. DOI: 10.1080/09593330.2017.1301572.
- [153] Tan TH, Mo KH, Ling T-C, Lai SH. Current development of geopolymer as alternative adsorbent for heavy metal removal. *Environmental Technology & Innovation* 2020;18:100684. DOI: 10.1016/j.eti.2020.100684.
- [154] Ducman V, Korat L. Characterization of geopolymer fly-ash based foams obtained with the addition of Al powder or H₂O₂ as foaming agents. *Materials Characterization* 2016;113:207–213. DOI: 10.1016/j.matchar.2016.01.019.
- [155] Landi E, Medri V, Papa E, Dedeczek J, Klein P, Benito P, et al. Alkali-bonded ceramics with hierarchical tailored porosity. *Applied Clay Science* 2013;73:56–64. DOI: 10.1016/j.clay.2012.09.027.
- [156] Li Q, He Y, Xu M, Liu J, He M, Huang L, et al. Study on the removal of Ca²⁺ and Mg²⁺ in water by the geopolymer-based inorganic membrane 2017;48:01215–20. DOI: 10.3969/j.issn.1001-9731.2017.01.039.
- [157] Ge Y, Yuan Y, Wang K, He Y, Cui X. Preparation of geopolymer-based inorganic membrane for removing Ni²⁺ from wastewater. *Journal of Hazardous Materials* 2015;299:711–718. DOI: 10.1016/j.jhazmat.2015.08.006.
- [158] Davidovits J. 30 years of successes and failures in geopolymer applications. Market trends and potential breakthroughs. *Geopolymer 2002 Conference* 2002:1–16.
- [159] Cheng TW, Lee ML, Ko MS, Ueng TH, Yang SF. The heavy metal adsorption characteristics on metakaolin-based geopolymer. *Applied Clay Science* 2012;56:90–96. DOI: 10.1016/j.clay.2011.11.027.
- [160] El-Eswed B, Alshaaer M, Yousef RI, Hamadneh I, Khalili F. Adsorption of Cu(II), Ni(II), Zn(II), Cd (II) and Pb(II) onto Kaolin/Zeolite Based- Geopolymers. *Advances in Materials Physics and Chemistry* 2013;2:119–125. DOI: 10.4236/ampc.2012.24B032.
- [161] Luukkonen T, Sarkkinen M, Kemppainen K, Rämö J, Lassi U. Metakaolin geopolymer characterization and application for ammonium removal from model solutions and landfill leachate. *Applied Clay Science* 2016;119:266–276. DOI: 10.1016/j.clay.2015.10.027.
- [162] Bai C, Colombo P. Processing, properties and applications of highly porous geopolymers: A review. *Ceramics International* 2018;44:16103–16118. DOI: 10.1016/j.ceramint.2018.05.219.
- [163] Bai C, Franchin G, Elsayed H, Zaggia A, Conte L, Li H, et al. High-

porosity geopolymer foams with tailored porosity for thermal insulation and wastewater treatment. *Journal of Materials Research* 2017;32:3251–3259. DOI: 10.1557/jmr.2017.127.

[164] Huang X, Zhao H, Hu X, Liu F, Wang L, Zhao X, et al. Optimization of preparation technology for modified coal fly ash and its adsorption properties for Cd²⁺. *J Hazard Mater* 2020;392: 122461. DOI: 10.1016/j.jhazmat.2020.122461.

[165] Zhang YJ, Liu LC, Xu Y, Wang YC, Xu DL. A new alkali-activated steel slag-based cementitious material for photocatalytic degradation of organic pollutant from waste water. *Journal of Hazardous Materials* 2012;209–210: 146–150. DOI: 10.1016/j.jhazmat.2012.01.001.

[166] Samarina T, Takaluoma E. Ammonia Recovery from Wastewaters by Adsorption with subsequent Transmembrane Chemical Absorption. *Proceedings of the 6th World Congress on New Technologies (NewTech'20), Virtual: AVESTIA; 2020*. DOI: 10.11159/icepr20.146.

[167] Takaluoma E, Samarina T, Mwandila G, Kabondo Leonard L, Nyirenda Kawunga K, Mwaanga P. Selective Recovery of Copper and Cobalt from Mine Effluent. *IMWA 2020 Mine water solutions, New Zealand: IMWA; 2020*, p. 181186.

[168] Lata S, Singh PK, Samadder SR. Regeneration of adsorbents and recovery of heavy metals: a review. *Int J Environ Sci Technol* 2015;12:1461–1478. DOI: 10.1007/s13762-014-0714-9.