Recent Advances in Fly-Ash-Based Geopolymers: Potential on the Utilization for Sustainable Environmental Remediation

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**ABSTRACT:** This Mini-Review provides the fundamentals and the state-of-the-art overview on geopolymers, novel inorganic polymeric materials (also known as alkali-bounded ceramics), synthesized from aluminosilicate sources and explores their current and potential sustainable environmental applications. It summarizes and examines concisely the recent scientific advances on geopolymers widely synthesized from abundantly available fly-ash-based aluminosilicate materials via alkaline activation at relatively low temperatures. Although geopolymerization is not a new concept and has offered valuable solutions to some environmental challenges as a low-cost and environmentally benign alternative to conventional energy-intensive Portland cement-based construction materials and has also been used as a barrier in immobilizing toxic and radioactive metals, the application of this technology to produce effective adsorptive materials for mitigation of liquid- and gas-phase contaminants is relatively recent. The valorization of the fly-ash waste in the sustainable and cost-effective development of geopolymeric adsorbents and catalysts for the treatment and control of environmental contaminants and energy production and storage could lead to many economic benefits due to the low cost and resource recycling of this globally abundant raw material. Perspectives on the synthesis and utilization of new geopolymer-based adsorbents for environmental and energy applications with insights into future research directions, prospects, and challenges for economic large-scale production are addressed.

1. INTRODUCTION

Geopolymeric materials, which are synthesized from aluminosilicate sources, can offer valuable solutions to emerging environmental and energy challenges. Therefore, for several decades, they have attracted much more attention due to their cleaner production and greener technologies, excellent or favorable mechanical properties (e.g., high compressive strength without sintering), good chemical resistance especially to acidic media, thermal resistance and resistance to freeze–thaw cycles, low shrinkage and low permeability, long-term durability, and low cost and environmentally friendliness as it relates to the utilization of accessible and rather abundantly available solid wastes as raw materials for their production.¹⁻⁴ These attributes have afforded geopolymer its well-known advantage over other technologies for immobilizing toxic heavy or radioactive metals via the combination of physical encapsulation and chemical stabilization and/or physicochemical, electrostatic, and sorption mechanisms.⁻¹⁻⁴ In addition, the synthesis or fabrication often requires room- or low-temperature (<100 °C) methods, ensuring that the emissions of greenhouse gases such as CO₂ and also NOₓ, SOₓ, or CO are very low. The greenhouse or global warming potential of these gases is measured by the carbon dioxide equivalent, denoted by CO₂-e and which is used to compare the environmental footprint of various greenhouse gases.⁻¹⁻⁶ For instance, geopolymers are also easier to prepare than Portland cement, and geoplymer binders are low-CO₂ cementitious materials with a significant reduction in the CO₂ emission footprint compared to the cement industry. The comparison of estimated CO₂-e values for GP concrete (i.e., the substitution of OPC with GP binder) with OPC in earlier reports suggested significant differences, up to 80% less than OPC and a range of 20–45% lower than OPC concrete. However, more recent studies, which compared the CO₂-e footprint generated by concrete comprising GP binders and 100% OPC concrete, estimated the total emissions to be 320 CO₂-e/m³ and 354 kg CO₂-e/m³, respectively, suggesting a difference of only 9% per production of 1 m³ of concrete. To obtain more realistic estimates, these studies also took into account energy expended in other associated activities such as mining and transport of raw materials and in the manufacturing of the alkaline activators.⁶ Therefore, the GP technologies still provide alternative good solutions to the utilization of fly ash...
| Year | Raw Material/GP Type | Treatments | Physical Properties | Applications | Mode/Conditions | Significant Findings | Ref |
|------|----------------------|------------|---------------------|--------------|----------------|----------------------|----|
| 2020 | CFA-C and CFA-F      | NaOH, 10 M Na₂SiO₃, 1 M. Cured at 90 °C, 24 h | SA = 854.16–2463.64 cm²/g | Pb²⁺ sorption | Batch: C₀ = 100–200 ppm, 40 °C, pH 7 | Removal efficiency: 99.5% | 4 |
| 2019 | PES-NMP (60% FA)/GP fiber composite | NaSiO₂/NaOH, 10 M. Cured at 60 °C, 24 h | SA = 27.4/168.3 m² g⁻¹, ASV: 0.69/−0.52 | Pb²⁺, Cu²⁺, Ni²⁺ sorption | Batch: 25 mg/L of Pb²⁺, Cu²⁺, Cd²⁺, Ni²⁺; 25 °C, pH 5 | Maximum sorption: 49.8/118.6/143.3 mg/g | 23 |
| 2015 | FA-GP as photocatalyst, PC | alkaline activation, 30% H₂O₂ | Porosity (P): 74.6% | Cu²⁺ sorption | Batch: C₀ = 200 ppm, pH = 6, 45 °C | Removal efficiency 99.2% | 24 |
| 2016 | CFA + iron ore tailing | NaOH fusion treatment. Cured at 140 °C for 72 h | MPS = 17.2 μ, P = 198%, SA = 8.22 m² g⁻¹, APS = 29 Å | Cd²⁺ sorption | Batch: 0.08 g of ZFA in 25 mL of Cd²⁺, pH = 5, 45 °C, 7 h | 14.4 mg/g ³ removed (97.45%). Desorbed and reused | 37 |
| 2018 | FA-GP                | 12 M NaOH + Na₂SiO₃: 2.5 ratio. Cured at 40 °C for 24 h | Bath: C₀ = 5–60 ppm. GP: 0.05–0.15 g; pH = 2.5–11.2, 25 °C | Maximum capacity: 37 mg/g⁻¹, S | 30 |
| 2016 | 2/3 MK and 1/3 biomass FA | NaSiO₂/H₂O. Cured at 40 °C for 24 h | Monolith. Porosity: 41.0–78% | Pb²⁺ sorption | Batch: C₀ = 50 ppm, pH = 3, 25 °C | Uptake 0.95–6.34 mg/g (max) | 34 |
| 2011 | CFA GP               | 10 M NaOH, 30% H₂O₂, 200 μm size | 0.19 m² g⁻¹ | (Cu²⁺) sorption | Batch: C₀ = 100 ppm, pH = 6, 45 °C | 152.3 m² g⁻¹, 88.2% removal efficiency | 24 |
| 2011 | CFA GP               | 14 M NaOH. Cured at 105 °C for 24 h | 200 μm of SA/PG of GP = 7/14 × FA | Pb²⁺ sorption | Batch: C₀ = 100 ppm, pH = 6, 25 °C, 2 h | 1–90.66% with pH 1–5. GP 90% vs FA 40% | 36 |
| 2013 | FA-GP as photocatalyst, PC | alkaline activation | 50 nm size, PV = 387 nm | methylene blue dye | 0.02 g of PC; UV Dye: 4.0 × 10⁻⁶ M | 92.79% removal efficiency | 20 |
| 2011 | FA-GP + 5 wt % α-Al₂O₃ | NaOH + Na₂SiO₃ solution | 34.26 m² g⁻¹ | methylene blue cationic dye | Batch: C₀ = 5–60 ppm. GP: 0.05–0.15 g; pH = 2.5–11.2, 25 °C | Maximum capacity: 37 mg/g⁻¹, S | 30 |

Note: For detailed information on the applications and mode/conditions, please refer to the specific references.
with little negative impact on environment, as the FA-based geopolymer has emerged as a promising green cement to mix with aggregates to form concrete and other alternatives in the field of building and construction materials. These developments have demonstrated success in combining an easy and sustainable synthetic approach with the use of industrial byproducts for the realization of novel “eco-friendly” low-cost and sustainable technologies with reduced environmental footprint. However, some emerging applications of FA GPs are in the environmental (adsorption of contaminants in liquid and gas phases) and energy (photocatalysis—water splitting and \( \text{H}_2 \) production) arena.9–11

There are three common categories of aluminosilicate materials that can be used for geopolymer synthesis, namely, coal fly ash (CFA) and incineration ash, slags such as granulated blast (steel) or furnace (iron) slag, and clays such as metakaolinite (MK) or calcined clay.12,13 Also, there were other industrial wastes such as glass, melt-quenched aluminosilicates, and natural materials such as kaolinite and natural zeolite, volcanic ash, and industrial byproducts such as mine tailing, waste ceramics, and catalyst residues or mixtures of all these materials.8,9,14,15 These are all raw materials containing Si, Al, and O and other possible elements such as H, Na, K, Ca, and Mg. Calcined clay is favored due to its accessibility and hydrophilicity. The most common aluminosilicate or raw materials used by researchers to synthesize conventional geopolymeric adsorbents are fly ash and MK. CFA consists of substantial amounts of reactive silicon dioxide (\( \text{SiO}_2 \)), calcium oxide or lime (\( \text{CaO} \)), aluminum oxide (\( \text{Al}_2\text{O}_3 \)), and iron oxide (\( \text{Fe}_2\text{O}_3 \)), including glassy particles (e.g., quartz and mullite) as major portions of this raw material. Two classes of fly ashes are particularly useful for geopolymer synthesis, namely, Class F containing more than 70 wt % of SiO\(_2\) + Al\(_2\)O\(_3\) + Fe\(_2\)O\(_3\) and being low in lime, and Class C with a SiO\(_2\) + Al\(_2\)O\(_3\) + Fe\(_2\)O\(_3\) content between 50 and 70 wt % and high in lime.16 In general, fly ash has a hydrophilic surface and porous structure. The factors that affect the reactivity of fly ashes used for geopolymer synthesis also include the percentage of particles lower than 45 \( \mu \text{m} \), the amount of glassy phase, and the chemical and mineralogical compositions. Because of its massive production worldwide as a waste product, using CFA as a raw material for the production of different valued-added products has been the focus of research for many years to avoid landfills of large amounts (>50% of the world’s production) and subsequent mitigation of its harmful effects on the environment.16,17 In particular, a plethora of studies on the use of CFA for the sequestration of aqueous and gaseous pollutants have been reported.18,19 The problem of raw fly ash is the low adsorption capacity, which usually means proper physical and/or chemical treatments are required to improve its effectiveness. However, as an important aluminosilicate source material, these characteristics also make CFA a good composite for the fabrication of geopolymers with more effective adsorptive capabilities for sequestrating contaminants such as heavy metal cations (from CFA itself or external sources), organic compounds, and anionic contaminants in industrial and residential water.

This Mini-Review will provide a state-of-the-art overview on the fundamentals involved in the synthesis and applications of geopolymeric materials, focusing on the adsorption of pollutants in water and air, and evaluate the effectiveness against other adsorption technologies utilizing conventional materials such as activated carbon and zeolites. Unlike past reviews on the subject,9,10,20 this paper focuses mostly on fly-ash-based geopolymers and their emerging utilization for sustainable environmental remediation. It is intended to (1) advance our fundamental understanding and theoretical and applied research underpinnings of this field by combining the current chemistry knowledge base on the synthesis and reactivity of geopolymeric materials; (2) provide useful insights into current research gaps and outline future research directions and challenges for large-scale applications; (3) and serve as a meaningful guidance for further developments of sustainable geopolymer-based materials and technologies.

2. RESEARCH METHODOLOGY

The objective of this paper was to concisely provide a state-of-the-art overview of the most important aspects of geopolymers as they relate to synthesis chemistry and factors affecting performance. The main goal of this mini-review was to focus on recent published literature in the fields of chemistry, materials, and chemical, environmental, and energy engineering, which relate to adsorbents derived from fly-ash-based geopolymers and their emerging utilization for sustainable sequestration of water and air pollutants. The sources used to gather original research and review articles for this review include “Scopus”, “Researchgate”, “Academia”, and “Web of Science” databases. In addition, “Google” and publishers’ Web sites such as “Elsevier”, American Chemical Society (“ACS”), Royal Chemical Society (“RCS”), “Springer”, and “Wiley” were utilized to search selected journals using appropriate phrases and keywords relating to the objectives of this Mini-Review. The contents of the review were structured to include the fundamental aspects of geopolymerization, treatment conditions of the raw materials and factors affecting the physical properties, and adsorption effectiveness of the synthesized geopolymeric adsorbents for the removal of aqueous and gaseous contaminants, as summarized in Table 1.

3. FUNDAMENTALS AND THEORETICAL ASPECTS OF GEOPOLYMERIZATION

3.1. Geopolymer Types and Structures. Geopolymers, also called polysilicates, are amorphous to semicrystalline threedimensional aluminosilicate polymers considered as the analogues of certain zeolites. The term geopolymer was first coined by Joseph Davidovits in the 1970s to refer to a novel class of 3-D structured inorganic polymeric materials with high-performance cementitious properties, and the technology developed was then termed geopolymerization. These materials were synthesized from raw materials containing aluminosilicates by stepwise processes at low temperatures, involving alkaline or silicate activation followed by polycondensation and setting and hardening of the paste.1,14 In general, the reaction involves amorphous silica and alumina-rich solids (aluminosilicate oxides) and a highly concentrated alkaline solution to form amorphous to semicrystalline aluminosilicate inorganic materials with three-dimensional polymeric structures of Si–O–Al bonds, corresponding to different Si/Al ratios of 1, 2, and 3. The terminologies proposed to describe the common types of geopolymers are based on the structural chains in the aluminosilicate oligomers (polymeric building units) depending on the Si/Al ratio (which significantly determines the final structure of the geopolymer materials). The three types are poly(silicate) or PS (\(-\text{Si}–\text{O}–\text{Al}–\text{O}–\)), poly(silicate-siloxo) or PSS (\(-\text{Si}–\text{O}–\text{Al}–\text{Si}–\text{O}–\)), and poly(silicate-disiloxo) or PSDS type (\(-\text{Si}–\text{O}–\text{Al}–\text{Si}–\text{O}–\text{Si}–\text{O}–\)), corresponding to
Thus, geopolymers consist of a polymeric silicon-oxygen-aluminum framework with alternating silicon and aluminum tetrahedra joined together in three directions by sharing all the oxygen atoms. The fact that aluminum is four coordinated (i.e., Al$^{3+}$ in IV-fold coordination) with respect to oxygen creates a negative charge imbalance, and hence, the presence of cations is essential to maintain electric neutrality in the matrix. The process of geopolymerization starts with the dissolution of Al and Si from Al-Si source materials in alkaline solutions as hydrated reaction products or gel. The general or empirical formula describing the chemical composition of these mineral polymers is $M_n[(\text{SiO}_2)_{z}\text{AlO}_2]_n\cdot w\text{H}_2\text{O}$, where $z$ is 1, 2, and 3; $M$ is an alkali cation such as potassium ($K^+$), sodium ($Na^+$), or calcium ($Ca^{2+}$); $n$ is the degree of polymerization; and $w$ is the number of water molecules from the network.$^{1,2,22}$

It is noteworthy to mention also that zeolites are crystalline aluminosilicates with three-dimensional frameworks of SiO$_4$ and AlO$_4$ tetrahedral units. The negative charge is balanced by the interchangeable positive ions such as Na$^+$, K$^+$, Ca$^{2+}$, and Mg$^{2+}$. Therefore, geopolymers with frameworks of [SiO$_4$]$^{4-}$ and [AlO$_4$]$^{5-}$ tetrahedra linked alternatively by sharing all the oxygen atoms are generally amorphous aluminosilicates or semicrystalline zeolites depending on the alkaline activator used in their manufacture and reaction conditions. In an aluminosilicate monomer, Si$^{4+}$ is partially substituted by Al$^{3+}$, and the resultant negative charge in the aluminosilicate chains (i.e., the negative charge of Al$^{3+}$ in the IV-fold coordination or the

Figure 1. Schematic diagram of the geopolymerization process.
The formation of small coagulated structures by various activation procedures with highly concentrated alkaline solutions of NaOH or KOH and/or Na2SiO3 or K2SiO3 and involving sol–gel or diffusion methods at different temperatures. The activation is conducted by adding the solutions into fly ash together or individually. The reactive aluminosilicate content (alumina and silica) in the fly ash hydrolyzes in the highly alkaline solutions via breakage of the −Si–O–Si or Si–O–Al bonds to release active Al\(^{3+}\) and Si\(^{4+}\) species, which initially react to form SiO\(_4\) and AlO\(_4\) tetrahedra nuclei and subsequently lead to aluminosilicate oligomerization through a polymerization process. The formulation of a geopolymer or the geopolymerization process involves three main steps, which are dissolution, gelation, and polycondensation. These stages are further described as follows:

1. The rapid dissolution of aluminum and silicon species from the surface of the raw materials (aluminosilicate source) induced by the alkaline (or silicate) solution (as well as the surface hydration of undisolved particles) results in the formation of mobile precursors. The process occurs via complex and very reactive action of hydroxide ions from the alkaline activator, resulting in the breakage of Si/O/Si or Si/O/Al bonds to form SiO\(_4\)\(^-\) and AlO\(_4\)\(^-\) free units. The extent of the dissolution of the aluminum and silicon ions in the strong alkaline solutions is dependent on particle size, morphology, and the chemical composition of the raw material.

2. The formation of small coagulated structures by reorganization and internal restructuring and diffusion of dissolved ions, through which the SiO\(_4\) and AlO\(_4\) tetrahedral units are linked in an alternating manner by sharing oxygen atoms to yield amorphous geopolymers. Dissolution continues at this stage, while gelation occurs via the polymerization of active surface groups and soluble species, which could also hinder mass transfer if coatings are formed on particle surfaces.

3. The polycondensation and precipitation of species result in the formation of hydrated products, and the cross-linked 3-D network structures are formed as the solution system sets and hardens. As condensation between monoaloximates and monosilicates increases, so do the continuous gel network rearrangement and connectivity, resulting in increased Si–O–Si and Si–O–Al bond formations since they are more favored compared to Al–O–Al bonds.

The geopolymerization process schematized in Figure 1 involving the polycondensation of still hypothetical monomers, the orthosilicate ions, is exothermic, and there are many critical factors that affect the desired properties of any particular geopolymer product. Among these factors are the Si/Al ratios in the precursor material, type and amount of alkali solution, temperature, curing conditions, and any additives such as a foaming agent (e.g., H\(_2\)O\(_2\)). The metal cation in the alkaline activator plays an important role in the formation of the geopolymeric network. While the OH\(^-\) ion acts as the reaction catalyst, the alkaline metal cation acts as the structure-forming element. It balances the negative framework charge carried by the tetrahedral aluminum. While it might be expected that KOH, being a stronger alkaline than NaOH, would exhibit a greater dissolution ability, this is not the case in reality, and this apparent anomaly is attributed to the fact that the Na\(^+\) ion with smaller size relative to K\(^+\) and higher charge density could migrate faster and more easily through the gel network. As a result, these differences affect the mechanistic pathways and the eventual microstructure and the properties of the formed geopolymers. It has been found that NaOH promotes the formation of silicate monomers and enhances the reaction rate and dissolution of the solid aluminosilicate precursor. On the other hand, KOH is known to improve the degree of polymerization, resulting in stronger matrices. Also, H\(_2\)O\(_2\) is sometimes used as a foaming agent because it is thermodynamically unstable and easily decomposes to water and oxygen, releasing bubbles of gas which could be trapped within the paste to expand and increase its volume to produce more homogeneous pores in the matrix.

In addition, alternative energy sources such as ultrasound have been shown to improve the formation of polysialate species and enhance the ordering of the polysialate species for the formation of small-scale-ordered semicrystalline and highly regularly ordered crystalline materials. These positive results were attributed to acoustic cavitation events, known to produce highly localized temperatures and pressures (termed “hot spots”) and microstreaming which enhance reaction and mass transfer rates and the formation of high speed microjets capable of cleaning adsorbent or catalyst surfaces. Feng et al. studied the effects of ultrasound on the geopolimerization of mekaalalinite/sand and fly ash/metakaolinite mixtures and found it to improve the thermal stability of the geopolymeric products, including the compressive strength which increased with sonication up to a certain time. The dissolution of metakaolinite and fly ash in alkaline solutions was enhanced by ultrasonication, hence releasing more Al and Si into the gel phase for polycondensation. It was shown that ultrasonication largely improved the interlinkage between Al and Si species, increased the concentrations of the polysialate species, and enhanced the ordering of the Si and Al tetrahedra in the geopolymer. The improved performance was ascribed to the enhanced dissolution of the aluminosilicate raw materials. In addition, the strengthening of bonds at the solid particle/gel phase interfaces, accelerated polycondensation process, and improved formation of semicrystalline and crystalline phases were noted to contribute to the observed positive attributes.

Finally, it should be noted that the formation of geopolymeric materials follows routes similar to that of most zeolites. However, the fundamental difference is that with geopolym-
rization, once the aluminosilicate powder is mixed with the alkaline solution, a paste forms and quickly transforms into a hard geopolymer. As a result, there is no sufficient time and space for the gel or paste to grow into a well-crystallized structure as is the case in the formulation of zeolites. Due to the shorter setting and hardening time in the formulation of geopolymers, the resulting polycrystalline structures are more tightly packed with better mechanical properties than zeolites, which have lower density and cage-like crystalline structure usually with fixed-sized pores and paths with potential shape-selective characteristics for separation of certain heavy metals in a matrix-selective passage through the pores.

4. CURRENT AND EMERGING ENVIRONMENTAL AND ENERGY APPLICATIONS OF GEOPOLYMERS

Geopolymer technology provides an alternative good solution to the utilization of fly ash with little negative impact on environment. The waste valorization is related to the development of new building materials from fly ash by using alkaline treatment to produce inorganic polymers with properties similar to ordinary Portland cement. These geopolymer structures exhibit desirable properties, such as rapid compressive strength, low permeability, resistance to acid, resistance to freeze—thaw cycles, and a tendency to drastically decrease the mobility of most heavy metal ions. However, emerging environmental applications of geopolymers are in water treatment via adsorption processes to remove inorganic pollutants including toxic trace heavy metal ions and organic compounds such as dyes. Geopolymer surfaces tend to have photoactive sites, due to the presence of metal oxide moieties, that is, the transition metals (Fe₂O₃ or TiO₂) in the geopolymer network (originating from aluminosilicate source materials). This makes it directly relevant for disinfectant and as an antibacterial via photocatalysis. Fe₂O₄ could also induce magnetization of the geopolymeric adsorbent, making it easy to separate at the end of use. The presence of these transition metals is also being employed in energy production and storage applications, also including via photocatalysis, leading to water splitting and H₂ production. For instance, GP has been synthesized and functionalized with surface-coating materials, including a silver (Ag)−geopolymer composite, and used to mitigate bacterial growth. The bacterial inhibition worked by altering the surface properties of the substrate to make it more tractable to wetter and coastal organisms. The Ag-based antibacterial GP was successfully developed through a bioreduction phenomenon involving the incorporation of the nanoparticle onto the surface of the GP matrix. The method has been suggested to have great potential for fabricating devices to treat water effluents from wastewater plants, which are laden with microorganisms.

Recently, most studies have been devoted to the use of lab-synthesized GPs for the removal of trace toxic heavy metals (TTHMs) in aqueous solutions. Results of some recent representative studies involving environmental and/or sustainable applications are summarized in Table 1. Due to their inorganic structure and stability properties, heavy metals do not decompose in nature and pose the risk of accumulation in living species as highly toxic and carcinogenic elements, some even at very low concentrations. The removal of TTHMs from solutions has been commonly carried out by several processes such as adsorption, ion exchange, chemical precipitation, reverse osmosis, and solvent extraction. However, recently, adsorption is the one driving the most attention among these methods because of simpler equipment and smaller corrosiveness, lower energy consumption, high removal efficiency, reversible nature allowing regeneration of adsorbents, and flexibility in design. The geopolymeric adsorbent can be regarded as a sustainable material since it can be synthesized by utilizing abundant waste materials. However, it also has more economic incentives over other emerging sustainable adsorptive materials such as biochar, which has a higher energy footprint, resulting from its production via pyrolysis.

El Alouani et al. (2018) synthesized FA-based GP (FAG) formulated from CFA and alkali silicate activator obtained by mixing NaOH (12 M) and Na₂SiO₃ solution at mass ratio of 2.5, letting the paste cure at 60 °C for 24 h, and investigated its effectiveness for the removal of methylene blue (MB; cationic dye) from aqueous solution by batch adsorption at different process conditions (solution pH, adsorbent mass, contact time, initial MB concentration, and temperature). The amounts of dye adsorbed at equilibrium were found to be 19.39 mg/g (96.95%), 29.87 mg/g (99.56%), and 39.4 mg/g (98.5%) for 20 mg/L, 30 mg/L, and 40 mg/L, respectively. The adsorption capacity at equilibrium increased from 4.89 to 36.44 mg/g, with an increase in the initial MB concentration from 5 to 60 mg/L. The adsorption efficiency also increased from 50.45% to 98.25% as the solution pH increased from 2.5 to 11.2. The pHₚₑₚₙ of the FAG was determined to be 9.4, suggesting that at pH < 9.4 the surface becomes positively charged, while at pH > 9.4, it is negatively charged. The effect of temperature was studied at 20, 50, and 70 °C, and adsorption capacity was found to increase only slightly from 37.58 to 39.84 mg/g as the temperature increased from 20 to 70 °C, suggesting the influence of temperature was negligible. A comparative study with other adsorbents showed that the adsorption capacity for MB removal by an FA-based geopolymer (FAG) was higher (37.04 mg/g) versus natural zeolite (23.60 mg/g), fly ash (5.72 mg/g), and fly-ash-derived zeolites (12.64 mg/g). Zhang and Liu (2013) also synthesized GP by alkali-activated fly ash for use for the first time as a novel photocatalyst for degradation of methylene blue (MB) dye (in aqueous heterogeneous suspensions) from wastewater. The fly ash with low calcium and rich in SiO₂ and Al₂O₃ was employed as a starting material for production of GPs with an amorphous or a zeolite-like structure by alkali activation. In this study, they found that the Fe₂O₃ in the fly ash was sufficiently utilized as a photocatalyst, producing hydroxyl (OH⁺) and superoxide (O₂⁻) radicals in the aqueous solution as active oxidative species for the degradation of the dye waste. The capture efficiency of the FA-based geopolymeric catalyst for the MB dye in the presence of UV irradiation was significant, up to 92.79%, attributable to the synergistic effect of the combined adsorption process and semiconductor photocatalysis. Recently, geopolymers have been explored as cocatalyst and/or as catalyst support for photocatalytic degradation of organic compounds (OCs), due to the presence of various kinds of metal oxides (e.g., Fe₂O₃, TiO₂, Al₂O₃, and MgO) (which make them ceramic photocatalysts) formed in the Al—O—Si—O framework, resulting from geopolymerization. For instance, the photoexcitation of the semiconductor Fe₂O₃ in the GP leads to the formation of an electron (e⁻)−hole (h⁺) pair, and consequently, the reduction of Fe⁵⁺ to Fe³⁺ in the FA-based GP ensured rapid hydrolytic reaction between the hole (h⁺) and H₂O molecule to produce a hydroxyl radical (•OH) needed for the mineralization of the OCs. In the case of a GP functionalized by good electron conductors such as metal nitrides and carbides, a clean energy production scenario under visible light was also
Hypothesized to involve the splitting of water to generate $O_2$ and $H_2$.\(^{20}\)

Huang and Han (2011) synthesized a GP from FA and $\alpha$-$Al_2O_3$, which is the highly crystalline and most thermodynamically stable of the two main forms of crystalline alumina modifications: $\alpha$-$Al_2O_3$ and $\gamma$-$Al_2O_3$. They studied the microstructure and mechanical properties of the formed GP and its potential for the adsorptive removal of formaldehyde (HCHO) from indoor air. Due to its stability, the $\alpha$-$Al_2O_3$ is expected to be only slowly soluble in highly concentrated alkaline solution compared to the $\gamma$-$Al_2O_3$, which is much less crystalline and more likely be easily soluble in strong alkaline solution. The results showed that $\alpha$-$Al_2O_3$ addition with an appropriate amount (such as 5 wt%) increased the geopolymerization extent, resulting in the increase of surface area (SA). The test for the HCHO adsorption capacity demonstrated that the FA-based GP product exhibited much better property of adsorbing indoor HCHO physically and chemically than FA itself, and SA was a factor but not a unique factor influencing the adsorption capacity. Lower Si/Al ratio resulted in larger SA of GP, which resulted in an improved adsorption capacity. It was stated that 5 wt% of $\alpha$-$Al_2O_3$ was the most appropriate to reduce the Si/Al ratio in the activator solution in order to enhance the geopolymerization process and allow a larger extent of structural reorganization of GP gel.\(^{32}\)

Al-Harashsheh et al. (2015) evaluated the effectiveness of waste FA-based amorphous GP as a sorbent for copper ($Cu^{2+}$) removal from aqueous solutions using various initial concentrations ($C_0$: 10–160 ppm and pH 1–6). The FA sample was reacted with NaOH solution (14 M) at a mass ratio of 4 to 3, respectively. The obtained paste was shaken (5–10 min) and sonicated (30 s, 2×40 W, 120% US power, 40 kHz) to defoam it and improve the dissolution of alumina—silicate components in the FA. Much higher removal efficiency was observed for the GP compared with the raw FA. The result indicated that with 100 ppm of $Cu^{2+}$ at 45°C the sorption effectiveness was found to increase from 5.6 to 88.21% with an increase in pH from 1 to 6.\(^{53}\)

Duan et al. (2016) also studied the adsorptive removal of $Cu^{2+}$ in batch sorption tests using a porous geopolymer prepared from combined fly ash (FA) and iron ore tailing (IOT) as a precursor (with IOT as partial replacement of FA at a level of 30 wt%) and alkali silicate activation (10 M NaOH and Na$_2$SiO$_3$ with 14.51% Na$_2$O, 33.39% SiO$_2$, and 48.53% H$_2$O) and H$_2$O$_2$ as afoaming agent. Using 3 g of the synthetic porous GP, $Cu^{2+}$ concentration $C_0$ of 100 mg/L, pH = 5, contact time $t$ = 90 min, and at 20°C, the removal efficiency was 90.7% compared with only 33.9% for the reference GP. This improved efficiency was attributed to the superior physical properties of the porous GP, including its large total porosity and well-defined pore size distribution. It was indicated that the transformation of FA and IOT resulted in the formation of amorphous foaming GP with total porosity of about 74.6%. This superior pore structure contributed to the improved availability of sorption sites necessary for increased $Cu^{2+}$ uptake.\(^{24}\)

Novais et al. (2016) fabricated a novel biomass fly ash (BFA)-containing GP monolith exhibiting distinct total porosities (ranging from 41.0 to 78.4%) and low apparent density (between 1.21 and 0.44 g/cm$^3$) for the study of lead adsorption from wastewater. The aluminosilicate raw material for the synthesis of the GP consisted of a mixture of 2/3 MK and 1/3 FA (in wt.) activated by sodium silicate in the presence of a discrete amount of $H_2O_2$ (0.0, 0.30, 0.60, 0.90, and 1.2 wt%). The $H_2O_2$ was included in the formulation to determine its effects on the GP pore structure. The samples were cured at controlled conditions (40°C and 65% relative humidity) using a climate chamber for 24 h. The adsorption of $Pb^{2+}$ by the porous GP was studied as a function of porosity, contact time, and pH. The results indicated that lead adsorption ranged from 0.95 to a maximum of 6.34 mg/g (lead/GP) and that the adsorption capacity strongly depended on both the GP porosity and the pH of the $Pb^{2+}$ solution. The removal efficiency of $Pb^{2+}$ ions increased up to 68% when the total porosity rose from 52.0% to 78.4%, attributable to the higher number of adsorption sites.\(^{34}\)

Onutai et al. (2019) synthesized a GP—polymer composite fiber with porous structures by mixing GP powder with polyethersulfonic (PES)—N-methyl-2 pyrrolidone (NMP) solution, and the resulting slurry was extruded and transferred into the fiber by a phase inversion method. For comparison, the GP fiber particles were fabricated with PES-NMP (0% FA) and PES-NMP with 60 wt% of FA (FA-GP), with physical properties as follows: BET SA, 27.39 vs 168.30 m$^2$/g; apparent specific volume (ASV), 0.69 vs 0.52; and tensile strength (TS), 5.83 vs 1.40 MPa, indicating an increase in SA but a decrease in ASV and TS when FA-GP powder was added to PES fiber. The fiber was used to remove heavy metals ions in solution, and the adsorption capacity of the GP composite followed the order $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+}$.\(^{35}\) Al-Zboon et al. (2011) synthesized highly amorphous GP from waste CFA and 14 M NaOH using a mass ratio of 1.25 under sonication to defoam the GP body and enhance the Si—Al material (FA), and the paste was then cured at 105°C for 24 h in an oven. The sorbent was tested for lead ($Pb(II)$) removal from aqueous wastewater. The results using 50 mL of 100 ppm $Pb^{2+}$ solutions with 0.07 g of GP indicated that the adsorption efficiency (at 25°C and for 120 min) was pH-dependent, and it went from 1% to 90.66% with an increase in pH from 1 to 5. However, at pH 6, it fell slightly to 89.8%, indicating that the zero point of charge was reached at around pH 5. The results were consistent with the fact that at low pH there is an excess of $H_3O^+$ ions, resulting in the competition between two cations ($H_3O^+$ and $Pb^{2+}$) for available adsorption sites on the negatively charged GP surface, compared with the higher pH when $H_2O^+$ is less and $Pb^{2+}$ is the dominating species to be attracted to the GP surface by Coulombic forces. Comparing the raw CFA with the synthesized GP at pH = 5, $C_0$ = 100 ppm, and t = 120 min, the removal efficiency of the GP was found to be higher for the lead ions compared to the raw CFA (90.60 vs 39.87%), attributed to higher SA (7 times) and PV (14 times) of GP.\(^{36}\)

Javadian et al. (2015) synthesized a zeolite-based GP (ZFA) via fusion solid-state conversion of CFA at special conditions for the study of $Cd^{2+}$ adsorption from aqueous solutions. The synthesis procedure involved mixing 6 g of FA (sieved to uniform particle size of 75 $\mu$m) with 7.2 g of solid NaOH, after which the mixture was ground and kept at 600°C for 2 h, under a loose dark green light. The powder was then ground, mixed with deionized water, and heated to 95°C for about 75 h under constant stirring at 400 rpm, after which the slurry was cured at 140°C for 72 h. It was then filtered, washed with deionized water until filtrate solution became neutral (pH < 7), and finally dried for 12 h at 100°C. The BET surface areas were 130.45 and 8.22 m$^2$/g, respectively, for RFA and ZFA. The mean particle size of RFA and ZFA is 4.18 and 17.21 $\mu$m, respectively. The ZFA had a porosity of 19.82% and average pore size of 29 Å, and the pore size ranged from 18 to 530 Å. The effective removal of Cd(II) decreased in the initial pH range of 2–5, and at pH 5, the amount of Cd(II) removed was found to be 14.431 mg g$^{-1}$, with
experiments conducted in the pH 2–12 range. At the same conditions of pH 5, Cd(II) removal was 7 mg g⁻¹ using RFA, indicating ZFA was two times more effective than RFA. It was determined that the optimal sorption parameters were 0.08 g/dose of ZFA in 25 mL of Cd(II), 7 h contact time, and pH 5. With 0.08 g L⁻¹ of ZFA adsorbent and C₀ = 10–100 mg L⁻¹ at pH 5, the removal efficiency was determined to reach above 96% only with 10 mg L⁻¹. The improvement was ascribed to the porous structure of the surface of the ZFA. Batch desorption experiments were conducted by transferring the Cd(II)-loaded ZFA into 50 mL of distilled water, HCL, HNO₃, and NaOH solutions and stirring for 24 h. When NaOH solution was used at different concentrations (0.1–1 M), it was observed that desorption started at pH ≥ 8. The after-treatment sorption efficiency of Cd(II)-treated ZFA was dependent on the concentrations of the NaOH used for the regeneration process and ranged from 24% to 84% after three repeated cycles.⁴⁷

Mondal et al. (2020) studied the composition—structure—property relationships involved in the aqueous Pb removal and the effects of composition and microstructure on the Pb sorption kinetics and efficiency. Two different fly ash precursors, type C fly ash (FA-C) and type F fly ash (FA-F), were reacted with both 10 M NaOH and 1 M Na₂SiO₃ solutions to produce four GP samples (solution/solid mass ratio of 0.7) cured in an oven at 90 °C for 24 h. The synthesized GP samples were denoted as M1 (FA-C), M2 (FA-F), M3 (FA-C), and M4 (FA-F) with varying ratios of Ca/Si (1.065–1.016), Al/Si (0.303–0.183), Na₂Si (1.315–0.146), Ca/(Si + Al) (0.817–0.090), and (Na + Ca)/(Si + Al) (1.826–0.214). These pulverized GP samples, M1, M2, M3, and M4, with AVS of 0.733, 2.267, 1.813, and 0.923 μm and SA of 1244.63, 854.16, 1390.43, and 2463.64 cm²/g, respectively, were employed in batch sorption tests using 100 and 200 ppm Pb²⁺ solutions at 40 ± 0.5 °C and at pH 7 ± 1. It was shown that all the samples displayed very high removal efficiency of about 99.5%, the value decreasing slightly with increasing Ca/(Si + Al) and Al/Si ratios but increasing with increasing Na/Si and the mass percent of the amorphous content of the GP’s phase assemblage. It was also shown that composition and microstructure greatly affected the Pb sorption kinetics, which decreased exponentially with increasing Ca/(Si + Al) and Al/Si of the GP composition but increased with increasing percentage of the amorphous phase in the microstructure of the GPs. The high silica content, which enhanced the formation of amorphous GP phases, was also found to enhance the GP removal performance, while high Ca and Al favored the formation of more crystalline phases which were detrimental to the sorption process.⁴ Liu et al. (2016) examined the mineralogical features of raw FA, FA-based GP (FAG), and faujasite block transformed from the GP (FBG) and evaluated their sorption performances for Pb in aqueous solutions. FA was mixed with alkaline activator solution (mixture of NaOH and commercial water glass at a mass ratio of 1:4.15) to make GP paste, which was then air-cured for 12 h in an oven at 80 °C. The FBG sample was fabricated from the GP sample via HT treatment by mixing the GP with 20 mL of 1.0 M NaOH solution in a 100 mL Teflon bottle at 70 °C for 24 h. The BET SA of the FA was 16.45 m²/g, which increased to 20.48 and 174.35 m²/g for FAG and FBG, respectively. The maximum adsorption capacities (at 25 °C) of FA, FAG, and FBG at pH 7 were determined to be 49.8 mg/g (200 mg/L initial concentration [Pb²⁺]₀) saturation level where adsorption capacity remained constant (at about 50.0 mg/g of adsorbent), 118.6 mg/g (24.6 mg/g to 118.6 mg/g at [Pb²⁺]₀) of 100 mg/L to 600 mg/L), and 143.3 mg/g (24.9 mg/g to 143.3 mg/g at [Pb²⁺]₀) of 100 mg/L to 800 mg/L), respectively. Also, both the FAG and FBG reached adsorption equilibrium after 240 min compared to 150 min required for FA, showing improved efficiency of FAB over raw ash but still the superiority of the FBG.²³

He et al. (2020) synthesized a novel low-cost inorganic GP—zeolite composite membrane (GP-ZCM) using circulating fluidized bed fly ash (CFBFA) solid waste as the raw material through a cost-effective and facile geopolymerization combined with the HT process. The alkali-activator solution was composed of 5.04 g of LiOH in 50 mL of deionized water, 100 g of CFBFA, and 18 g of precipitated white carbon black precipitate, homogenized into a uniform paste by stirring. The paste was molded into a disk-like stainless steel with diameter and thickness of 40 mm and 6 mm, respectively, and cured at 80 °C for 24 h to produce the CFBFA-GP membrane. The CFBFA has a BET SA of 9.8304 m²·g⁻¹ and an APD of 11.5941 nm. The BET specific surface area (SSA), average pore size (APS), and pore volume (PV) of the GP membrane vs GP-ZCM were 13.36 vs 30.19 (m²·g⁻¹), 18.89 vs 15.99 (nm), and 0.0827 vs 0.1582 (cm³·g⁻¹), respectively. When the composite membrane was synthesized under optimal conditions, the Li-ABW zeolite phase was determined to be 51.86%. The GP-Li-ABW ZCM was utilized to study the adsorptive performance for Cr(VI) removal from aqueous solutions. With Cr(VI) concentration of 1000 mg L⁻¹ and at pH 7, the Cr(VI) rejection was up to 85.45% in the presence of 10 kPa TMP. They concluded that the HT process was effective in modifying the PV of GP by conversion of the GP into the GP-ZCM with higher BET SSA, higher PV, and smaller AVS. The formed sorbent was efficient in the removal of the extremely toxic hexavalent chromium from wastewater, with the capture mechanism determined to involve size exclusion and electrostatic interaction.³⁸

5. FUTURE RESEARCH NEEDS, CHALLENGES, AND OPPORTUNITIES

It is obvious from these discussions that geopolymers have great potential for further development of sustainable energy and environmental technologies. As discussed in section 4 and summarized in Table 1, fly-ash-based geopolymeric adsorbents are generally more effective compared with raw fly ash, natural zeolites, and fly-ash-derived zeolite adsorbents for the sequestration of aqueous and air contaminants. However, there are still a number of technical issues to be resolved before the realization of the ultimate goal of industrial applications. Geopolymers are well-known materials which often consist of high pore volume and large surface area. Adsorption has been regarded as the main interaction mechanism for GP in heavy metal removal investigations. Because the specific surface area is a primary factor in adsorption, geopolymeric nanoscale adsorbents with high surface/volume ratio and chemical activity are needed. Geopolymers have tunable physical properties (SA, porosity, PS, pore volume), which could be taken advantage of in synthesizing materials capable of higher adsorption performance with demonstrated applications similar to well-established adsorbents or even better. Synthesis methods play a significant role in fine-tuning surface properties to enhance photoactive sites. Alternative energy sources such as microwave and acoustic and/or hydrodynamic cavitation as green processes should be employed to improve mass transfer and chemical reaction in the synthesis of novel geopolymeric adsorptive and catalytic materials.
GPs have already been successively used in stabilizing heavy metals over a number of years as “green” sustainable technologies. However, their applications for heavy metal adsorption on an industrial scale have been hindered by leaching problems. The leaching of trace toxic metals could be problematic, especially when using industrial byproducts as raw materials. There is a scarcity of information on the environmental impact of fly ash as an ingredient in the preparation of materials or geopolymeric materials. Also, aluminosilicate precursors from which GPs are synthesized vary globally. These issues present critical challenges that require unified approaches in evaluating the impact of the variable compositions and properties on the GP for heavy metal adsorption. If geopolymers are to be used in the adsorption or immobilization of toxic heavy metals on an industrial scale, the associated reactions must be ecologically acceptable. However, this issue could be resolved by an appropriate screening of waste materials to be used as GP precursors. More research studies, both experimental and theoretical and encompassing adsorption kinetics and thermodynamics, regenerability and byproducts, and leaching and toxicity effects to ensure ecological acceptance, are needed to improve reliability and minimize costs for scale-up and long-term use.\(^\text{13}\)

GPs are more suitable for the removal of cationic substances from wastewater due to the negative charge of GPs from the charge efficiency of aluminum (Al). On the other hand, there are so many anionic-based pollutants in wastewater. Investigation on real wastewater should be done in the future to have a better understanding of the competition between different types of pollutants (cations such as heavy metals, organic compounds, and anions such as sulfate, ammonium, nitrogen, phosphorus) on the removal efficiency of the GP. Also, nitrate, sulfate, phosphate, fluoride, chloride, and oxalate also have hazardous effects. The presence of nutrients such as N and P in excessive amounts in the water system promotes eutrophication, which deteriorates water quality by depleting dissolved oxygen content and subsequently promoting the rapid growth of toxic cyanobacteria. Most adsorption studies to date have involved lab-scale experiments conducted to evaluate the removal of a single type of heavy metal ion from simulated wastewater solutions. However, the real challenges of mitigating the contamination of trace heavy metals in water bodies actually involve multicomplex systems, requiring multifaceted approaches. Therefore, the development of FA-based geopolymeric adsorbents that are simultaneously suitable for these multipollutants is needed and will be advantageous in addressing these challenges.

Since multicomponent waste streams are considered to be more realistic matrices to better mimic practical treatment scenarios, accelerated studies on the effects of water quality on the GP’s adsorption efficiency are needed to advance our scientific and technical understandings. Advanced modeling involving the coupling of GP synthesis physical—chemical parameters, sensitivity analysis of the various synthesis reaction pathways, pollutant adsorption kinetic—mass transfer process parameters, and efficiency is needed.\(^\text{59}\) Research efforts on the optimization procedures with a view to arrive at a set of conditions that yields optimal immobilization or adsorption effects and delineates the interaction between the synthesis and process parameters are also important. These should include process optimization of experimental approaches using methodologies such as Taguchi and response surface methods and artificial intelligence (machine learning or neural network) to ascertain new insights under realistic operating conditions and techno-economic analysis.\(^\text{30−45}\) Such studies should help in their cost—benefit evaluations and comparison to available/emerging technologies, aiding progress toward scale-up and industrial applications. These represent knowledge gaps and opportunities to be exploited moving forward. For large-scale applications and long-term use, addressing these aspects and demonstrating economic feasibility might prove to be the decisive issues.

6. CONCLUSION

The development of the advanced geopolymer technologies could make it possible to achieve the environmentally benign utilization of coal and improved productivity of new useful materials for construction and mitigation of toxic water and air pollution wastes, resulting in a significant reduction in adverse environmental impacts, therefore mitigating the pervasive solid waste management and associated disposal problems by converting these environmental liabilities sustainably and advantageously into assets. It goes without saying that the environment is essential in ensuring global stability, and energy is vital to human survival. The review of geopolymers and the environmental aspects of their applications, highlighting their use for the sequestration of aqueous and air contaminants, suggest that fly-ash-based geopolymeric adsorbents are generally more effective compared with raw fly ash and zeolite adsorbents for the sequestration of aqueous and air contaminants. However, the discussions above also indicate large gaps in the knowledge base, which require further experimental and theoretical investigations. This Mini-Review is expected to further provoke thinking beyond the cases presented and spur additional engineering-based research needed for the developments of novel and more cost-effective GP-based adsorbents and/or catalysts. It is also hoped that it will serve as a guide to advancing the commercialization of greener and sustainable technologies to mitigate polluted residential waters, industrial wastewaters, and flue gas systems and will promote further studies to address the emerging challenges of alternative and renewable energy production and storage.

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Notes
The author declares no competing financial interest.
Biography

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ACRONYMS

APD, average pore diameter; APS, average pore size; AVS, apparent specific volume; BET SA, Brunauer–Emmett–Teller—Teller surface area; BFA, biomass fly ash; CFA, coal fly ash; CFBEA, circulating fluidized bed fly ash; CO2-e, carbon dioxide equivalent; FA, fly ash; FAC, type C fly ash; FA-F, type F fly ash; FAG, fly-ash-based geopolymer; FBG, faujasite block geopolymer; GP, geopolymer; GP-ZCM, geopolymer zeolite composite membrane; HT, hydrothermal; IOT, iron ore tailing; MK, metakaolinite; MB, methylene blue; OCs, organic compounds; OPC, ordinary portland cement; PC, photocatalyst; PES-NMP, polyethersulfonic-N-methyl-2-pyrrolidone; PS, poly(sialate); PSS, poly(sialate-siloxy); PSDS, poly(sialate-disiloxy); PV, pore volume; RFA, raw fly ash; SSA, specific surface area; TS, tensile strength; TTHM, trace toxic heavy metal; TMP, transmembrane pressure; ZCM, zeolite composite membrane

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