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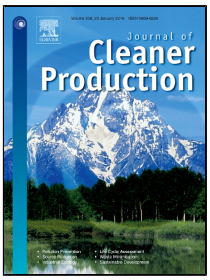

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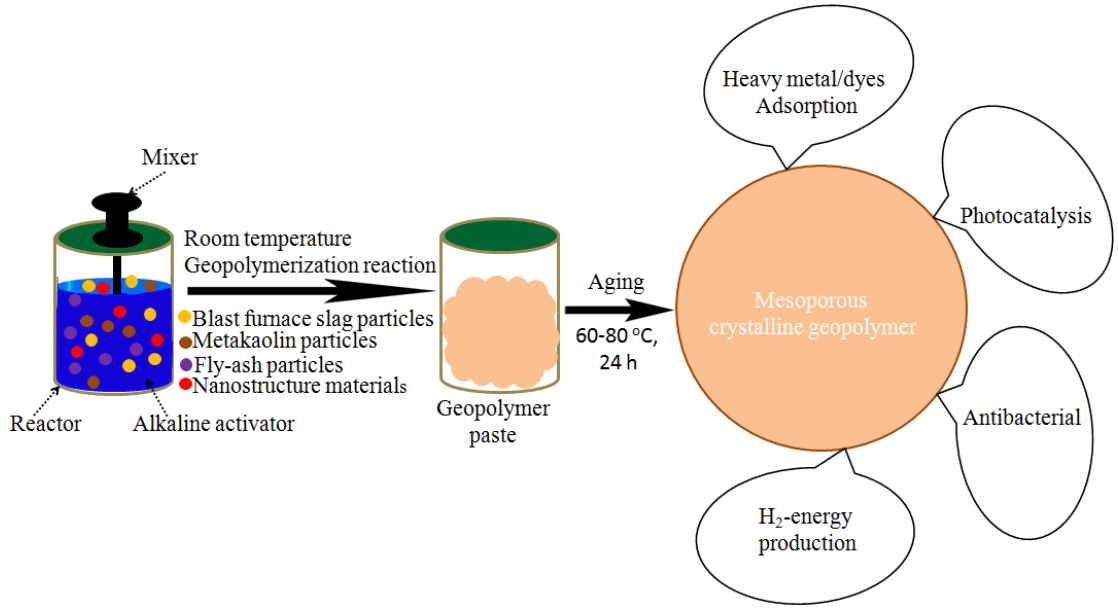

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Geopolymer for use in heavy metals adsorption, and advanced oxidative processes: a critical review

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Abstract

Geopolymer is a ceramic material, most often amorphous; finds applications in fire- and heat-resistant coatings and adhesives, medicines, refractory ceramics and binders, and manufacturing of radioactive waste container. Over the last decade, new cement based on geopolymers has been developed. Most relevant to this review is the fact that its porous nature and chemical similarity to zeolites is being employed for applications pertaining to wastewater treatment. Most of the work has been on the adsorptive treatment of water. However, using chemical reasoning and literature available we show that geopolymers have relevance for further activity on additional areas of relevance to waste water treatment such as photocatalysis, disinfection, and H_2-energy production from waste water etc. These applications would depend strongly on the properties of geopolymers, which in turn would rely on the precursors employed and the synthetic methods used. The relevance of geopolymers for cleaner production is also highlighted. The use of fly ashes and metakaolin composites for the fabrication and surface tailoring of geopolymers (perhaps using relevant surfactants) is suggested as a plausible step in the right direction. Given the critical analysis of the state of the art, and the plausible directions identified, this article will benefit environmental scientists, engineers and chemists interested in deploying geopolymers for environmental remediation purposes. However moving forward, barriers are

to be anticipated for the large scale implementation of geopolymers. Several barriers (e.g. legal, economical, technocrats and synthetic challenges) that are likely to hinder future research and translation are highlighted.

Keywords: Metakaolin-geopolymer; Fly ash; adsorbent; photocatalytic support; antibacterial activity

1. Introduction

Heavy metal removal and organic molecule degradation from wastewater have become a major topic of the public interest, due to their relevance to health and environment. Heavy metal and hazardous organic molecules are known to be toxic and a precursor to ill-health of the populace (Jaishankar et al., 2014). They are primarily released into the environment through human/industrial activities (Azimi et al., 2017). Hence research on multifunctional materials which relates to simultaneous environmental remediation and energy production are relevant to contemporary technologies connected with cleaner production.

Geopolymers are a promising category of materials, for the removal of toxic substances from industrial and household effluents. It is usually prepared from a rather simple and eco-friendly reaction between an alkali such as $NaOH/Na_2SiO_3$ or KOH; and Al and Si source (s), making it a material amenable to clean production. Geopolymers obtained thus are often applied for the removal of metal ions such as Cs^+, Pb^{2+}, Cd^{2+} etc. from wastewater. Geopolymers have come a long way, since their first discovery four decades ago (Davidovits, 1976). It has gained attention primarily because of the ease with which it can be synthesized with little or zero emission of green house gases (CO_2. SO_2, NO_x etc.) (Noor ul et al., 2016). This coupled with its properties which include toughness, fire and heat resistance (i.e. its refractory nature), radiation hardness (making it relevant for radioactive waste containment) and pozzolanic action (Carsten, 2013), make geopolymers truly multifunctional.

In fact, plenty of industrially relevant materials have been derived through geopolymers. For instance, geopolymer-fiber composites are characterized with fire resistant properties. Several

geopolymer composites are deployed in metal tool coatings, and construction of airplane cabinets and buildings, in order to reduce the intensity of inferno accidents (Salwa et al., 2013). Also due to its polymeric chain-like structure that gives rise to high chemical resistance, low shrinkage, high resistance to abrasion and early mechanical strength (Aizat et al., 2015; Singh et al., 2015), geopolymers have become an emergent class of materials for the sustainable revamp of dilapidated infrastructures, sustainable reinforcement of structural amenities and reclamation of swamp environments. Geopolymers can be tailored to have highly workable properties as a result of its water retention ability, while having a shear stress of ~80 Pa at a shear rate of 110 s^{-1} and compressive strengths of ~40 MPa at 7 days curing ages (Geddes et al., 2018). These are also the properties that make geopolymers an important category of emerging materials for the capping and containment of nuclear wastes threats (Perera et al., 2011).

Geopolymers can be made from (i) fly ash (ii) clay (iii) slag, (iv) raw kaolin, and (v) metakaolin, (CĂTĂNESCU et al., 2012; Villaquirán-Caicedo and Gutiérrez, 2015). Furthermore, in recent times, its' applications in disinfection have gained ground (Timakul et al., 2016). All these are making the system (i.e. geopolymer) of substantial interest to researchers focusing on cleaner production.

From the standpoint of technological applications; the major attraction of geopolymers comes from the fact that its production is readily scalable. In addition, considering the fact that it employs minerals of geological origin, the process is rendered rather green and eco-friendly. Also, geopolymer manufacturing enables beneficiation of industrial and agricultural waste (e.g. fly ash, slag, and rice husks) (Sturm et al., 2016). This has been an add-on for researchers focusing on geopolymer fabrication for infrastructure design and reclamation (Prachasaree et al., 2014). In fact, it brings about a huge reduction of both industrial and agricultural wastes, which in turn enables cleaner production systems in the manufacturing industries.

From a fundamental standpoint too, these compounds raise rather interesting questions. For instance, the near-complete elimination of diffusion of sequestered metal ions and avoidance of leaching related

problems associated with geopolymer adsorbents, raise interesting questions about their surface and structure (Cioffi et al., 2003). Structurally, geopolymers are known to involve inter-crossed linked bonds with cationic ends on the surface. It is these that allow entrapment of the radioactive and toxic metals through charge-balancing (Vu and Tran, 2018). However, the precise roles of the (a) anionic substitution into the its structure and (b) surface chemistries due to the surface cationic species(e.g. Fe^{3+}, Ti^{4+}, Ca^{2+}, Al^{3+} or Si^{4+}) is not fully understood. Nonetheless, its microstructure in the nanometric scale (5-10 nm) often consists of several pores within a highly porous -Al-O-Si- repeated unit; these pores are likely to give room for ionic incorporation, substitution and balances (Duxson et al., 2007a). It may be noted here that geopolymers have been reported to show a substantial removal of heavy metals such as Cd(II), Ni(II), Pb(II) and Cu (II) (Cheng et al., 2012), and anions such as phosphate, fluoride, and radionuclide of ^{137}Cs and ^{90}Sr, and dyes (Ahmaruzzaman, 2010; López et al., 2013). However, it is important to note that surface redox reactions in general and origins of photoactivity remain largely open questions in the context of geopolymers. This certainly merits further investigation considering the fact that it has a relation to its disinfecting properties. In short, while geopolymers have already made it to several commercial applications; their fundamental surface chemistry and electronic structure continue to offer opportunities for further exploration. Here, we critically survey available literature to offer specific details relevant to geopolymers' physicochemical properties; especially those related to their electronic structures which are expected to enable their applications useful for water remediation (i.e. photodegradation of hazardous organic compounds, energy evolution/storage, heavy metals adsorption and antibacterial).

2. Chemistry of geopolymers

2.1 Geopolymerization of Aluminosilicate

Geopolymers are skeleton structures that emerge from the polycondensation of aluminosilicate materials. The reaction mechanism involved is responsible for the formation of this rigid structure; the

reaction involves a complete dissolution of the aluminosilicate phase in alkali solution, which in turn produces two distinct tetrahedral ends {i.e. silicates (SiO_4) and aluminates (AlO_4)}, connected through oxygen atoms (Khale and Chaudhary, 2007). The typical stages for aluminosilicate framework transformation to geopolymer solid structure are shown in Table. 1.

Table 1: Chemistry of geopolymerization for the transformation of aluminosilicate materials to solid state geopolymers.

Reaction stage	Geopolymer phase	Reaction mechanism
(1) Aluminosilicate dissolution and separation into alumina and silicate ends	(1) poly(sialate)	$n(Si_2O_5, Al_2O_2) + nH_2O + NaOH/KOH \rightarrow n(OH)_3\text{-}Si\text{-}O\text{-}Al(OH)_3 + Na^+/K^+$
	(2) Poly(sialate-siloxo)	$n(Si_2O_5, Al_2O_2) + nSiO_2 + nH_2O + NaOH/KOH \rightarrow n(OH)_3\text{-}Si\text{-}O\text{-}Al^-\text{-}O\text{-}Si\text{-}(OH)_3 + Na^+/K^+$
(2) Polycondensation/polymerization	(1) Poly(sialate)	$n(OH)_3\text{-}Si\text{-}O\text{-}Al(OH)_3 + NaOH/KOH \rightarrow (Na+/K+)\text{-}(Si^-\text{-}O\text{-}Al^-\text{-}O\text{-})n + nH_2O$
	(2) Poly(sialate-siloxo)	$n(OH)_3\text{-}Si\text{-}O\text{-}Al^-\text{-}O\text{-}Si\text{-}(OH)_3 + NaOH/KOH \rightarrow (Na^+/K^+)\text{-}(Si^-\text{-}O\text{-}Al^-\text{-}O\text{-}Si^-\text{-}O\text{-})n + nH_2O$

*Note;*Al⁻: -Al-O- and *Si⁻:-Si-O-*

As shown in Table 1, two primary phases are likely to be derived depending on the ratio of SiO_2 to Al_2O_3 in the raw material used. For instance, the use of additional source of SiO_2 {e.g. sodium silicate (Na_2SiO_3)} together with NaOH/KOH produces poly(sialate-siloxo) framework, while pure NaOH/KOH produces poly(sialate) framework (Srinivasan and Sivakumar, 2013). Stage 1 of the reaction involves leaching of powder-like aluminosilicate materials inside alkaline solutions which leads to the formation of aluminum and silicon hydroxide structure-like ends in an open chain system. The two ends can undergo polycondensation reaction as a result of a condensation reaction between two hydroxyl groups to release water molecules, thereby forming a long chain reaction which produces a gel-like material. The diffusion of ionic species (Na^+/K^+) balances ionic reaction, thereby causing polymerization reaction as shown in reaction stage 2. At this stage, a vigorous mixing is required to ensure complete diffusion of the alkali species, in order to prevent the formation of non-polymerized alumina and silicate ends within the final geopolymer matrix. Exposure of the polymerized material to temperatures slightly above that of

ambient atmosphere will result into solid and stable geopolymer structures (Srinivasan and Sivakumar, 2013). Considering the speciation of the aluminosilicate structure in alkali solution, the Si^{4+}, or Al^{3+} often coordinated with four oxygen atoms to give $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ respectively, which are referred to as aluminosilicate units. The ratio of the $[SiO_4]^{4-}$ to $[AlO_4]^{5-}$ is one of useful parameters for the determination of geopolymerization process and structural properties of the final geopolymer (Yao et al., 2009).

2.2 Distinct features

From the physicochemical standpoint, the chemical composition of geopolymer is relatively similar to zeolites. However, unlike zeolites, geopolymers have no crystalline order. In fact, they are considered amorphous (Bakharev, 2005; Duxson et al., 2007b; Khale and Chaudhary, 2007). The largely amorphous nature of geopolymers stems from the mixture of unrefined minerals (e.g. quartz, kaolin, hematite, and illite) present in it, most of which are largely non-crystalline. The phase that is dominant is that which consists of Al_2O_3 and SiO_2 (often present even as aluminosilicates) (Djobo et al., 2014). In fact most of the geological minerals and industrial waste containing these components (e.g. Al_2O_3 and SiO_2) are usually suitable for geopolymer synthesis (Djobo et al., 2014). Thermal annealing of these precursors (especially from geological sources) and fillers introduction (e.g. mesoporous silica) oftentimes result in a phase separation between the Al_2O_3 and SiO_2, thereby yielding better crystallinity in the final product (Zahid et al., 2018). This process can in fact impact reactivity towards alkaline activators, and also result in reasonable porosity. However, it is evident that much more needs to be done for ensuring applications in catalysis, and allied areas. Simultaneous engineering of geopolymers to achieve the right combination of crystallinity, porosity, particles sizes and electrons conductivity will continue to be a relevant activity.

Another major point to be noted from an applied chemistry perspective is that the pozzolanic action of geopolymers is very different from that of well-known cements. In particular, calcium-silicate-hydrate (CSH) matrices do not occur in geopolymers. Regardless of this; its mechanical strength is comparable to

or better than that of Ordinary Portland cement (OPC), i.e. 64 MPa of geopolymer (Živica et al., 2011; Xu and Deventer, 2003), against 52.96 MPa of OPC (Živica et al., 2011; Husem, 2006). This attribute results from significant amount of SiO_2 (i.e. ~ 93.7%) in the geopolymer matrix (Okoye et al., 2016). In fact, considering its high adsorption capacity towards hazardous materials, high SiO_2 content in geopolymer often enhances its ability to separate and stabilize hazardous materials from environmental medium, respectively (López et al., 2014). Furthermore, the geopolymers offer stable support making it relevant for co-catalyst applications as well. Of particular value here are geopolymers that are derived from fly ash, metakaolin and blast furnace slag. Such geopolymers are reasonable co-catalyst or catalyst supports since they offer good intimate contact between the targeted molecules and catalyst phases owing to their properties (i.e. small particle sizes, high surface area, nanostructure surfaces, large proportion of metal oxides consisting of exposed oxygen atoms, and high SiO_2 content). All these are strongly related to electronic structures in the system, which oftentimes offer effective electron transfers (Fallah et al., 2015). However, further investigation into electronic properties of geopolymer is likely to be helpful in this field. In addition, these geopolymers tend to have relatively robust active sites. This stems from the fact that materials with large proportion of SiO_2 (such as geopolymers) oftentimes consists of high density of outer-, meso- and inner-pores (Panda et al., 2017; Wang et al., 2018) to facilitate: (I) good penetration of the targeted molecules into the catalyst system, and (II) large area for the mass transfer of both ions and electrons in the inner surface of the catalyst. Thus, the higher the SiO_2 content in the geopolymer matrix the better will its effective activity be, as either a co-catalyst or as a catalyst-support.

3. Method and analysis section

Given the state of the art in geopolymers research, and considering the relevance of compositional, structural and morphological modifications for achieving relevant functional properties along with poison resistance; in this review, we will focus on synthesis-properties (of relevance to water treatment) correlations of geopolymers. The following sections contain details and a critical analysis of (a) synthesis of geopolymers and the mechanisms, (b) properties of various raw materials, (c) interaction of

geopolymer products with water (with specifics to do with the water chemistries involved), (d) adsorption, photocatalysis, antibacterial, and H_2-evolution applications of advanced geopolymers, (e) the likely ways forward. (a-e) is written by carefully sifting through literatures using content analysis approaches, and by employing careful searches performed using standard journal data bases and search engines (Science Direct and Google scholar). For catalytic applications, factors involved in electron generation and transfer from surface of geopolymers are essential. These factors can be modified in an application-specific manner using surface tailoring. The significance of powder X-ray diffractometer (PXRD) and Fourier transform infra red spectroscopy (FTIR) for the investigation of the crystallinity and existence of relevant bonds in the raw material phases prior to their use for geopolymer synthesis is highlighted based on current literature. Correlations between the Brunauer–Emmett–Teller (BET) surface area and pore volume to the synthesis methods are systematically examined based on recent results. The practices essential for deployment of geopolymer for water remediation are consistently highlighted. Post-treatment and disposal of the spent geopolymers' adsorbent/photocatalyst are usually straightforward since these systems do not leach readily.

4. Synthesis of geopolymers and mechanisms involved

The mechanism that is currently accepted for the synthesis of geopolymers involves a polycondensation reaction between silica and alumina precursors, where a partial substitution of Si^{4+} with Al^{3+} takes place, followed by a complete ionic-balance with the Na^+/K^+ of the alkaline activator (Zhuang et al., 2016). This results in an extended Al-O-Si network, which has high bond strength of ~3.02 KJ/mol. Such high values are due to the mixed and somewhat covalent bonds associated with the following pairs present in geopolymers: Al-O, Si-O and highly ionic Na-O (Hu et al., 2008; Jaarsveld et al., 2002). The relatively high ionicity associated with geopolymers has to do with the electronegativity differences that exist between the cations (Al and Si) and the anion (O) (Hu et al., 2008). The resultant network has a substantial structural strength (i.e. 30 MPa) at room temperature after ~24 h of synthesis, which is one of the hallmarks of geopolymers (Rovnaník, 2010). Nearly all kinds of geopolymers'

synthesis are carried out at room temperature making the process a cleaner production when compared to other similar ceramics.

During the synthesis, the choice of the alkaline activator plays a significant role since cation (Na^+ or K^+) from alkaline solution is responsible for achieving the charge-balance of the $Al(OH)^{4-}$ in the pores of the geopolymer paste (Duxson et al., 2005). As such, species with a higher ionic radius (i.e. K^+=1.33pm) has lesser chances of penetration into the pores thereby resulting in a lot of unreacted phase (Samantasinghar and Singh, 2018). Of course, this is likely to result in a fast solidification of the final geopolymer since the reaction is taking place at the surface of the material. However, severe internal cracking, lower porosity and low compressive strength may occur when compared to system with Na^+ ions (i.e. from $NaOH/Na_2SiO_3$), which has a smaller ionic radius of 0.98pm. In fact, Na^+ has better chances of deep penetration into the geopolymer pores for a complete reaction (Abdul Rahim et al., 2014). Alkaline solutions used for the synthesis offer means to determine the emergent structural, chemical and physical properties of the geopolymer as illustrated in Fig. 1 (Samantasinghar and Singh, 2018). In fact, one reasonable approach here would be to use a mixture of metal hydroxide and silicate solution, (as alkaline activator) (Ma et al., 2013), in order to increase silica content for improving the viability from the standpoint of environmental remediation and catalytic applications. For instance, when a mixture of potassium hydroxide and calcium silicate is used; poly(sialate-disiloxo) sanidine is obtained, (Zhang et al., 2008). On the other hand, sodium silicate/hydroxide yields poly(sialate) sodalite and calcium silicate yields poly(disialate) anorthite (ref: Fig. 1) (Davidovits, 1994). Likewise, potassium silicate/hydroxide yields poly(sialate-siloxo) leucite and potassium hydroxide will eventually yield poly(sialate) kalsilite frameworks (ref: Fig. 1), (Davidovits, 1994). All these show important of structural transformation based on NaOH or KOH/silicate mixing strategies. Such transformations are useful for the determination of mechanical properties and microstructure of the expected final geopolymer in accordance with the orthogonal design principle (material design and structural proposition prior the synthesis practices). Among the frameworks described above; poly(sialate) sodalites have a rigid molecular structure, which

is desirable for structural applications (e.g. pavement, road and building construction), due to its high compressive (Bakri et al., 2011; Hoy et al., 2016). Other structures however provide opportunities for the mechanical entrapment of toxic and hazardous substances. In summary, fundamental investigations correlating surface chemical features, initial precursors, and process parameters are essential to developing 'functional geopolymers' related particularly to applications of relevance to environmental applications.

4.1 Metakaolin precursor-derived from kaolin clay and their role in the degree of crystallinity

Metakaolin, a precursor for the synthesis of geopolymers is obtained through dehydroxylation of kaolinite (also referred to as kaolin) over a temperature range of 520-650°C (Ke et al., 2018; Ogundiran and Enakerakpo, 2018; Samal et al., 2017). Metakaolin rather than kaolinite as a starting material offers unique advantages in terms of high reactivity and purity (Cheng et al., 2012; Yip et al., 2004), this oftentimes results in a geopolymer with better compressive strength, high surface area, and voluminous porous surfaces. In addition, geopolymers made using this precursor has several metal oxides including Al_2O_3 37.6%, Fe_2O_3 0.94%, TiO_2 0.8%, MgO 0.24%, K_2O 0.22%, CaO 0.2%, and Na_2O 0.13% (Strini et al., 2016; Temuujin et al., 2009). This makes this system (i.e. metakaolin based geopolymer) relevant for semiconductor catalysis applications. These materials can interact with light of relevant wavelengths, resulting in the creation of photogenerated carriers (electrons and holes). Hence, these materials can have reasonable photocatalytic activities (Strini et al., 2016; Zhang et al., 2012). Of particular note for further activity is the fact that metakaolin-based geopolymers can be tailored to exhibit crystalline phases (zeolite-like nanocrystalline) (López et al., 2014; Luukkonen et al., 2017). This is in fact achievable even through room temperature synthesis routes make it relevant for cleaner production step. Such crystallinity will increase the surface area, and the exposure of its metal oxides (Hoy et al., 2016), thereby enabling catalytic activity under visible light irradiation (i.e. wavelength 400-800 nm). With this, low cost and cleaner production of water treatment reactors/reservoirs are likely to be achieved. The properties (i.e. purity, crystallinity high surface areas, and metal oxides) make metakaolin-based geopolymers a rather interesting category (Bernal et al., 2011; Tang et al., 2016; Trivunac et al., 2016).

Furthermore, it offers an additional handle on the properties of the materials like making it readily relevant, through rather green chemical approaches, for applications involving nanocrystallities (Strini et al., 2016). In all cases, the selection and characterization of clays play a vital role in benchmarking synthetic procedures. Clay with large degrees of crystalline kaolinite (ref: Fig. 2) offer opportunities to obtain reasonable quantities of metakaolin in the product, after the dehydroxylation process (Alshaaer et al., 2017; Faqir et al., 2018; Murray, 2006). In such process ,significant loss of O-H and Si-O-Al bonds is often observable (Gasparini et al., 2013). In fact, good dehydroxylation and a large amount of metakaolin are often obtained in a clay containing a high proportion of kaolinite unit structures (Fig. 3a), with a silica end consists of pseudo-hexagonal, and alumina phase consists of octahedral shape in a uniform array as shown in Fig. 3b and c respectively (Murray, 2006).

Thermal dehydroxylation of kaolinite oftentimes leads to a structural transformation from pseudo-hexagonal/octahedral to a tetrahedral shape of highly reactive metakaolin (Černý et al., 2009; Murray, 2006). Besides this, the endothermic process involved here (i.e. kaolinite dehydroxylation) implies that a large amount of energy is required to remove the chemically bonded hydroxyl group. This operation results in: (I) separation of the stacked layers of kaolinite (ref: Fig. 4a), and (II) formation of metakaolin with high crystallinity, and subsequent modification of bonding behaviors (ref: Fig. 4b and c respectively) (Seynou et al., 2016).

For the researchers working with kaolin based geopolymers, it is worth noting that kaolinite dehydroxylates at ~600°C resulting in a large proportion of quartz minerals (i.e. a major constituent of metakaolin) and gives reasonable stability to the final geopolymer product (Kljajević et al., 2017; Seynou et al., 2016). In Fig. 4c, Fourier transform infra red spectroscopy analysis (FTIR) shows that dehydroxylation of -Si-O-Al- with band between 3600 and 1000 cm^{-1} often takes place at 600°C (Černý et al., 2009; Masliana et al.; Seynou et al., 2016). This process often gives substantial amount of -Si-O-Al- framework structure which is a major phase of quartz (Černý et al., 2009; Masliana et al.; Seynou et al., 2016). Specifically, the presence and large amount of quartz in the metakaolin plays significant roles for

the formation of geopolymer with high compressive strength, for effective encapsulation of hazardous materials (i.e. larger the amount of quartz, better is the geopolymer strength).

Table 2: Summary of various clay, kaolinite, and metakaolin-derived geopolymers with their physicochemical properties relevant for environmental applications.

Precursor	Alkaline activator	Setting parameter	Geopolymer properties	Drawbacks	Ref.
Clay and sand	NaOH (10M)	Room temperature	Compressive strength=14.92MPa	NaOH>10% results in compressive strength decrease	(Rahman et al., 2016)
Kaolinite, and zeolitic tuff	NaOH (8.7M)	80°C, 24 h	Surface area=47.9m^2 g^{-1}	Incomplete zeolitic dissolution	(Yousef et al., 2012)
Kaolinite	NaOH	At room temperature with secondary treatment in NaOH, temperature=80°C, 1 h	Compressive strength=60MPa	High content of residual water-soluble salt results in compressive strength reduction	(Alshaaer, 2013)
Kaolinite	Na_2SiO_3/NaOH (12M)	80°C, 1-3 days	-	High Na^+ dissolution causes low compressive strength	(Heah et al., 2013)
Kaolinite	NaOH (8M)	Room temperature, post treatment by steam curing increases compressive strength	-	-	(Hamaideh et al., 2014)
Metakaolin and sand	Na_2SiO_3/NaOH (8M)	Room temperature	Compressive strength=64MPa, Flexural strength=17.6MPa	Increase in curing temperature reduces strength	(Pelisser et al., 2013)
Metakaolin	NaOH (8M)	-	-	High curing temperature (>80°C) causes $NaAlO_2$	(López et al., 2014)

			dissolution, and low compressive strength

Appropriate choice of precursors, experimental parameters and its correlation with observed properties in the final product are likely to result in fresh avenues (ref: Table 2). This is especially true since in the context of approaches towards modifications of geopolymer properties of relevance to water remediation, there is hitherto very little known. Here, it would be of interest to note that raw clay- and kaolinite-based geopolymer use inexpensive synthetic approaches (including those with no pre-thermal treatment involved). However, such materials have less reactivity, porosity, crystallinity, and stability (Bignozzi et al., 2013; Fabbri et al., 2013; Khale and Chaudhary, 2007), making it of low interest especially in the field of heavy metal adsorption, photocatalysis and even newly emerging disinfectant applications. Hence, there is an emerging emphasis on metakaolin based geopolymers that are mesoporous, and highly crystalline (Ofer-Rozovsky et al., 2016). Nevertheless, considerable attention needs to be placed towards its alkaline activator post-dissolution which often hinders the stabilization. Here, it is believed that considerable advancements can be achieved by using industrial waste which will serve as filler to increases the stability of the final geopolymer (Lee et al., 2016; Lee et al., 2017). Coupling this with steam curing methods is likely to increase the workability of the geopolymer, which may then be pulverized for use in heavy metals' adsorption and catalysis purposes (i.e. applications involving water remediation). This is also likely to make geopolymer useful for sewage slug containment which in turn would be relevant for cleaner approaches to water dispensary sectors. In summary, considerable attention needs to be given to metakaolin-based geopolymer for water remediation, due to its purity, high surface area, in-built crystallinity and various kinds of metal oxides within its matrix

5. Use of industrial waste as filler for the fabrication of crystalline metakaolin-based geopolymer.

5.1 Fly ash

Fly ashes are fine and glassy powders that are recovered as a byproduct of coal combustion (used for production of electricity etc.). It consists of substantial amounts of silicon dioxide (SiO_2), calcium oxide (CaO), aluminum oxide (Al_2O_3) and iron oxide (Fe_2O_3) in Fig. 5 (Pacheco-Torgal et al.,

2008). Glassy particles (e.g. quartz, and mullite) are the major portions of the material (KIM, 2012). These make fly ash a good composite for the fabrication of geopolymer. Two classes (namely F and C) of this fly ash are particularly useful for geopolymer synthesis.

Class-F is produced mainly by burning harder, older anthracite and bituminous coal. Compositionally, this fly ash is pozzolanic in nature, and contains less than 7 % lime (CaO). Class-C fly ash is produced from the burning of younger lignite or sub-bituminous coal. In addition to pozzolanic properties; Class-C also has some self-cementing properties due to its CaO (i.e. lime) content (~20 %) (Ahmaruzzaman, 2010; KIM, 2012; Pacheco-Torgal et al., 2008). In fact, a Class-C fly ash requires lesser amount of alkaline activator when compared to class-F, for the geopolymer fabrication. In general, the use of fly-ash as a filler in geopolymers increases its compressive strength, surface area and catalytic sites. This in fact would be a viable means to use the fly ash derived from coal-powered stations. This offers a rather clean production of geopolymers in several countries (including China) that are strongly depended on coal-based electricity. This will be so, due to the fact that a high magnitude of fly-ash will be removed from environment, and of course, threat of heavy metals leaching from the fly-ashes (i.e. in the dumping sites) to water bodies is likely to be allayed. For instance, Motorwala et al. (2008) reported low-calcium fly ash (i.e. Class-F fly ash) for geopolymer synthesis. In their report, the following raw materials; coarse aggregate and fine aggregate sand, fly-ash, sodium silicate and different concentration of NaOH solution (i.e. 8M, 10M, and 12M) are used for the geopolymer production. Therein, all the constituents are thoroughly mixed together and cast into a cube to form concrete and left for 30 min under ambient condition before curing aging for 24 h at various temperature. The highest curing temperature gives the highest compressive strength with no further improvement after 80°C. Their work shows that the compressive strength of the geopolymer increases with an increase in the fly ash content; reverse is the case with an increase in extra water content. In addition to this, fly ash-based geopolymers do have the following physical properties: (i) the higher the alkaline concentration the better the compressive strength of geopolymer, (ii) the higher the ratio of sodium silicate solution-to-sodium hydroxide solution by mass, the higher is the compressive strength of geopolymer concrete.

All these show the significance of fly ash when it is being selected as component or filler for metakaolin-based geopolymers. This will eventually have direct advantages when such geopolymer composites are used for adsorption and stabilization of both heavy metals and hazardous organic molecules (Zhuang et al., 2016). Furthermore, considering the high contents of Fe_2O_3 in fly ash (Yu et al., 2012), it is likely that using it either as a composite or single phase geopolymer material that will meet the requirements for real-world practical applications of photocatalysis.

In summary, nanoparticle impregnation in geopolymer matrices and in some cases elimination of the need for nanoparticle embedment is plausible for achieving desired catalytic activity enhancement. With this, low cost and eco-friendly geopolymer-based catalysts can be produced. Considering this, cleaner production is likely to be achieved in the field of complete water remediation, since excessive use of nanoparticle containing materials in water systems also has negative side-effects if not properly handled (Agarwal et al., 2013). Of course whether or not this will happen will depend upon the synthetic approaches that will be employed.

5.2 Slag based geopolymer

Slag is another interesting geopolymer filler for stability enhancement, and is commonly produced from industrial manufacturing processes like iron ore purification, and combustion of coke residue, limestone, and serpentine (Fhwa, 1998; Saheb, 2012). This material is sub-categorized into three types depending on the process of its formation as illustrated in Fig.6. For instance, blast furnace slag (BFS) is formed from iron, while both basic oxygen furnace slag (BOFS) and electric arc furnace slag (EAFS) are formed from steel (Proctor et al., 2000). Lime is the common chemical composition of all the three types of slag (Proctor et al., 2000). BFS is primarily made up of silica and alumina with various amounts of lime depending on the quantity of fluxing agent used in the iron or steel processing (McGannon, 1971). However, all three types of the slag are similar in composition except iron and manganese contents which are higher in BOFS and EAFS when compared to BFS (McGannon, 1971). Use of slag as an additive in the geopolymer fabrication may be of advantages (i.e. especially for the applications that involve catalysis and cleaned water reclamation). This is for the fact that the high content of SiO_2 (~

30%) in BFS will increase workability and stability of the final geopolymer (Deb et al., 2014) which in turn will enable high pulverization of the materials into small particle sizes with uniform radius prior its use as catalysts or adsorbents. In fact, a substantial catalytic performance is likely to be achieved since a material with uniform surface or/and spherical shape enables ease with which water flow through it thereby bringing molecules into direct contact with the active sites. Furthermore, other advantages are likely to be achieved: (i) minimization of waste produced by iron and steel companies, (ii) reduction of the cost of production wherein BFS will serve as additional silica source thereby reducing the demand of the alkaline solution, (iii) high mechanical strength of geopolymer, offering lower maintenance and operation costs of metakaolin derived geopolymers, (iv) increase in the available land for the other uses (since slag storage requirements would reduce), and (v) minimization of the toxicity concerns around slag storage and management (since this is a known source of metal-containing leachates). It is evident that geopolymer production has several advantages from a cleaner production standpoint.

It worth here to say that all kinds of BFS serves pre-cleaner processes during the iron-smelting stages by trapping-out SO_2 gas before being cooled and discharged into the environment. Nevertheless, BFS can be distinctly further sub-divided into different categories (i.e. foamed blast furnace slag, pelletized blast furnace slag, granulated blast furnace slag); depending on the method employed in the cooling of the final BFS. Although all forms of BFS are relevant; due to the presence of significant amounts of silica, aluminosilicates, and calcium-alumina-silicates in them, however granulated BFS seems more promising. This is because granulated BFS is made-up of small particles with high specific surface area, therefore making it an excellent candidate for the geopolymer fabrication (Robayo et al., 2016; Xu et al., 2014). Considering this fact, BFS-based geopolymer is likely thus to have high regeneration or recyclability after their initial deployment for water reclamation or photocatalysis. Table 3 shows the chemical composition of granulated BFS, where a high content of calcium and silicon oxide are observable. The silicon in BFS often used to supplement the alkaline solution, making the geopolymerization process rapid and effective.

Nevertheless, prior to the deployment of these materials (i.e. both fly ash and BFS-based geopolymer) for water reclamation and catalysis, a pre-analytical examination is considered paramount in order to assess the heavy metal leaching rate of the systems. However, oftentimes these materials are regarded as good binders with high density of binding sites for heavy metals within their matrices. The mechanism involved in this process (i.e. entrapment of heavy metals within geopolymer matrix) is related to the fact that the metal-ions often participate in the charge-balancing of $[AlO_4]^{5-}$ in the geopolymer network (Vu and Tran, 2018), thereby undergoing mechanical entrapment within the geopolymer after solidification. For instance, Izquierdo et al. (2009) reported fly ash-slag based geopolymer with microstructure surfaces; leaching rate of heavy metals from the synthesized geopolymer is recorded. In their report, the fly ash-slag based geopolymer is synthesized without prior thermal activation of starting materials.

Table 3: Chemical composition of BFS.(Emery, 1992)

Constituent	Percent
Calcium Oxide (CaO)	31-48
Silicon Dioxide (SiO_2)	27-45
Aluminum Oxide (Al_2O_3)	7-18
Magnesium Oxide (MgO)	2-19
Iron (FeO or Fe_2O_3)	0.1-1.6
Manganese Oxide (MnO)	0.1-2.3
Sulfur (S)	1.0-2.3

The fly ash is mixed with the blast furnace slag, water and an activator solution (SiO_2/K_2O = 1.25). The geopolymeric paste obtained is then cast into cylindrical containers (diameter 29 and 39 mm height) and cured in a closed container at room temperature for 28 days. The process generates geopolymer with a desirable microstructure, and even with this, the batch leaching test performed on the sample shows that fly ash-BFS based geopolymer inhibits metals mobility. Results prove that a number of trace pollutants such as Ba, Be, Bi, Cd, Co, Cr, Cu, Nb, Ni, Pb, Rb, Sr, Sn, Th, U, Y, and Zr are retained within the geopolymer matrix. Thus, this can be regarded as a cleaned product from a production process. In fact, such remarkable result is attributed to mechanical strength resulting from good compactness contributed

by BFS. In another interesting report shown by Cheng and Chiu, (2003); metakaolin-BFS based geopolymer with high fire-resistance are obtained. In their report, granulated BFS is used as filler to increase mechanical strength and ability to withstand fire. The fire resistance property is conducted by subjecting the 10 mm thickness of the as-synthesized geopolymer into 1100°C flame; with the reverse-side temperature measurement reaches less than 240-283°C after 35 min. In summary, it is will be reasonable to say that slag can be used as reinforcement for crystalline metakaolin-, fly ash-based geopolymer to attain environmental stability after thermo- or photo-mechanical entrapment or conversion of either organic or inorganic hazardous substances. Other such novel controls and modifications on the mesoporous/crystalline geopolymers, are likely and will open avenues in near future for further adoption of this ceramic material in heavy metal adsorption, organic molecule photodegradation, radioactive encapsulation and micro-organisms disinfectants.

5.3 BET surface area and pore structure correlation with synthesis applications.

In catalytic applications and heavy metal adsorption, the performance of photocatalysts and adsorbents often progresses with certain structural properties (e.g. pore volume and surface area). Geopolymers are well known materials which often consist of high pore volume and large surface area. These have been found to substantially contribute to heavy metal adsorption. Synthesis methods play a significant role in fine-tuning these properties. For instance, Tang et al., (2015) reported a metakaolin based geopolymer with a BET surface area of 53.95 m^2/g and porosity of about 60.30%. The high surface area and porosity are derived through the use of suspension and solidification method, where foaming agent SLS (i.e. K_{12} sodium lauryl sulphate) is used to increase the mesoporous nature of the geopolymer. This geopolymer shows high adsorption capacity for Pb^{2+}, Cu^{2+} and Ca^{2+} with removal capacity of 45.6, 35.5 and 24.0 mg/g respectively. Spherically shaped geopolymer/alginate hybrid with high BET surface area (16.2 m^2/g), pore size (11.5 nm) and pore volume of 0.05 mL/g is also reported by Ge et al., (2017) via one-pot impregnation method. In fact, this specific surface area (i.e. 16.2 m^2/g) is about 1.7 times higher than of pure metakaolin-based geopolymer (i.e. with BET surface area of ~9.6 m^2/g) (Ge et al., 2017). The use of sodium alginate to coat the metakaolin based geopolymer in an $CaCl_2$ aqueous solution

is known to be an efficient method to create mesoporous surface and abundant inner pores which contribute immensely to the high adsorption capacity towards Cu(II) (Ge et al., 2017). Similarly, Lee et al. (2016) have recently shown that post-hydrothermal treatment method can be used to obtain fly-ash based geopolymer with high surface area and pore volume of 114.16 m^2/g and 0.2677 cm^3/g respectively. These obviously give advantages such as high adsorption capacity relevant for the removal of Cs^+ from aqueous solution (Lee et al., 2017). Hence synthesis methods continue to be relevant for improving the surface area and pore volume of the geopolymers for water remediation and related applications.

6. Result and Discussion on applications driven by the surface chemistry of geopolymers in water

Geopolymer surfaces tend to have photoactive sites, due to the presence of metal oxide moieties. This makes it directly relevant for disinfection. Also given its porosity, the phases that are not photoactive could find application as adsorbents. In particular, heavy metal ion adsorption has been most widely explored (Siyal et al., 2018).

Despite all of the above; geopolymers, do not compete favorably with nanoparticles with respect to catalytic and adsorptive applications (Falah, 2015). However, efforts to improve the catalytic and adsorptive functionalities would be valuable since geopolymers offer obvious advantages (primarily scalable, and cleaner production from fly ash and metakaolin composites is obviously favorable for photocatalysis, and the presence of crystalline metakaolin favors heavy metal adsorption) (Xu and Deventer, 2000; Zhang and Liu, 2013).

6.1 Heavy metal adsorption by geopolymer

Adsorption involves removal of metal ions using solid surfaces. Adhesion forces are created between the metal ions and mesopores (reference to geopolymer is shown Fig.7) which is the reason for the observed adsorption. Mesoporous surfaces are also essential for desorption processes relevant for the regeneration/reusability of the adsorbents. This oftentimes is carried out through simple washing, chemical treatment, steam washing or thermal treatment. The adsorption process is either chemisorption

or physisorption depending on whether or not the adsorption results in the formation of a chemical bond. Oftentimes, physisorption adsorption process gives favorable adsorption and offers easy regeneration due to the weak Van der Waal interactions involved (ref: Fig. 7). In fact, this mechanism (i.e. physisoprtion adsorption process) gives high regeneration ability to the adsorbent with about ≤1-10% reduction in the adsorption capacity for about 6-10 consecutive times of usage (Lata et al., 2015). Considering all the above pointers and its porosity, metakaolin-based geopolymer is likely to fulfill all the promising properties for adsorption operation. For instance, Cheng et al. (2012) have investigated the adsorption of four different heavy metals by using metakaolin-based geopolymers. The geopolymer is made by condensing the mixture of metakaolin and (NaOH) alkaline solution at room temperature, and the geopolymer is pre-crushed to a fixed-radius size through the use of sieving devices. The geopolymer exhibits excellent adsorption capacity towards (i.e. Pb^{2+}, Cu^{2+}, Cr^{3+}, and Cd^{2+}) due to its high porosity and surface area. This outstanding performance of ~ 90 % removal capacity towards all the metal ions is related to the mesoporous surface created by Al-Si-O network. In another interesting report given by López et al. (2014), metakaolin-based geopolymer is used as a selective adsorbent; it is prepared from a mixture of silica and metakaolin, and applied for the selective removal of Cs^{+} and Pb^{2+} from heavy metal ions mixture. The heavy metal adsorption behavior is described well using the Langmuir model, which proves that the metakaolin-based geopolymer has multiple and different types of binding active sites; this is attributed to the formation of more than one adsorptive layer (i.e. for Cs^{+} and Pb^{2+}). Similarly, Al-Zboon et al. (2016) reported natural volcanic tuff based geopolymer for the removal of Zn^{2+} with the efficient uptake of 97.7 % against 78.5 % of ordinary/natural volcanic tuff (porous rock formed by volcanic ash consolidation) as it is previously reported. In their research work, batch adsorption technique is used to study the adsorption isotherms of Zn^{2+} onto the geopolymer surface. Different concentrations of Zn^{2+} are added to a constant dose of geopolymer (0.4 g) at different temperatures (25, 35, 45 °C) and at different pH values (5, 6, and 7). The removal efficiency increases as the geopolymer dosage, contact time and temperature increases. This implies that the adsorption active sites of the geopolymer do not get saturated instantly, and a gradual increase in the metal-ion transfer onto the

surface of the geopolymer is observed up to the point where the equilibrium position is established. This is due to the high density of adsorptive sites present in the geopolymers, which are not gotten saturated instantaneously. Thus, this shows that metakaolin-based geopolymers can serve as wastewater purifier in a bed filter systems (i.e. heavy metal getters) for a real world applications. In addition to this, use of metakaolin-based geopolymer for the fabrication and design of water pipe-lines is likely to bring low-cost water circulation in both urban and rural areas for the fact that the materials are from the geological origins, and the threats of trace and heavy metals can be well prevented with this system. Naghsh and Shams, (2017) recently used kaolin based geopolymer for efficient removal of Ca^{2+} and Mg^{2+} from aqueous solution. It is however shown that the high charge density and easy hydration of the Mg^{2+} (Siyal et al., 2018) usually results in ready precipitation, which in turn causes lower removal rates when compared to Ca^{2+}. In case of Ca^{2+}, the larger ionic size radius (i.e. ionic size radius of Ca^{2+}=0.99Å and Mg^{2+}=0.66Å) makes it rather readily removable using geopolymer adsorbents. In fact, Ca^{2+} is likely to have higher transfer rates toward the pores and adsorptive sites of the geopolymer (Tognonvi et al., 2012). Due to the ability to remove Ca^{2+}, geopolymers are promising softeners for elimination of water hardness making it a promising material for the cleaner production of laundry houses and alike.

Not only metakaolin-based geopolymers; but also fly-ash-based geopolymer has been proven to be a good adsorbents for heavy metals, (Al-Harahsheh et al., 2015). In fact, the presence of several metal oxides phases (e.g. Fe_2O_3, SiO_2 and Al_2O_3) (Al-Zboon et al., 2011), in this system plays an important role since it contributes to the enhancement of specific surface area (with a contribution of as high as ~74.6% pore volume) (Duan et al., 2016). In fact, in order to form fine particles and to achieve enough mesoporous surface on crystalline metakaolin-based geopolymer; surface modification with fly ash is likely to be a way out. Further advantage can be obtained by employing high density anionic ends (O^{2-}) in such a composite system which will ensure rapid gettering of metal ions through ionic exchange processes. Furthermore, the well exposed oxygen atoms in the geopolymer matrix will facilitate formation of heavy metals-O_2 complexes, and hence will result in precipitates from the water solution.

This will lead to substantial removal of the toxic metal-ions from water. Table 4 shows various geopolymeric adsorbents used for the removal of heavy metal-ions from aqueous solution. Therein, most of the results fitted well into Langmuir isotherm, this indicates chemisorptive adsorption process (Batool et al., 2018), as a result of bond interaction between the anionic ends (i.e. adsorbent sites) and the metal ions.

Table 4: Various work done on the adsorption of heavy metals onto geopolymer adsorbent.

Adsorbent	medium	Removal capacity	Model	Heavy metal	Ref.
FA based G	WW	152mg/g	L, Ho	Cu^{2+}	(Al-Harahsheh et al., 2015)
ZT based G	AS	7.8mg/g	-	Cu^{2+}	(Alshaaer et al., 2015)
FA based G	AS	97.7%	L	Pb^{2+}	(Al-Zboon et al., 2011)
NVT based G	AS	100%	L	Zn^{2+}	(Al-Zboon et al., 2016)
MK based G	AS	100%	L	Zn^{2+}, Cu^{2+},Cd^{2+}	(Andrejkovičová et al., 2016)
MK based G	AS	-	L	Sr^{2+}, Co^{2+}, Cs^{+}	(Chen et al., 2013)
MK based G	As	-	L, Ho	Pb^{2+}, Cu^{2+}, Cr^{3+},	(Cheng et al., 2012)
FA based G	WW	113.41mg/g	F, L	Cu^{2+}	(Duan et al., 2016)
MK based G	WW	-	-	Ni^{2+}	(Ge et al., 2015b)
MK based G	AS	-	L, Ho	Cu^{2+}	(Ge et al., 2015a)
PA based G	AS	99±3.4%	L, Ho	Cu^{2+}	(Ge et al., 2017)
Z based G	AS	-	L, Ho	Cu^{2+}	(Javadian et al., 2015)
MK based G	AS	-	L, Ho	Zn^{2+}, Ni^{2+}	(Kara et al., 2017)
FA based G	AS	118.6mg/g	Ho	Pb^{2+}	(Liu et al., 2016)
MK based G	AS	-	-	Cs^{+}	(Luukkonen et al., 2016)
BFS based G	SME	90-100%	L,F,	Ni^{2+}, AS^{2+}, Sb^{2+}	(Luukkonen et al., 2016)
FA based G	WW	-	Ho	Cu^{2+}	(Mužek et al., 2014)
FA based G	AS	6.34mg/g	-	Pb^{2+}	(Novais et al., 2016)
BFS based G	WW	85.29mg/g	L, Ho	Ni^{2+}	(Sarkar et al., 2017)

*Note; *L: Langmuir isotherm, *F: Freundlich isotherm, *BFS: blast furnace slag, *FA: fly Ash, *MK: metakaolin, *Z: zeolite, *ZT: zeolitic tuff, *NVT: natural volcanic tuff, *PA: polymer-alginate, *G: geopolymer, H_o: pseudo-second-order, WW: wastewater, AS: aqueous solution, *SME: spike mine effluent.*

Pseudo-first and pseudo-second-order, and intra-particle diffusion models consist of kinetic parameters often used to investigate thermo-chemical adsorption process fully detailed elsewhere (El-Geundi, 1991; Itodo et al., 2010). Fly-ash/metakaolin-based geopolymers often show remarkable adsorption capacity towards divalent metal ions (e.g. Pb^{2+}, Cu^{2+}, Sr^{2+}, Co^{2+}, Cs^{+}, Cu^{2+} Cd^{2+}, Zn^{2+}, Ni^{2+}),

as demonstrated (Cheng et al., 2012; Ge et al., 2015a; Kara et al., 2017), with pseudo-second-order adsorption process, which in turn indicates that the heterogeneous surface of the geopolymers are favorable for the removal of the metal ions.

In summary, fly-ash/metakaolin-based geopolymers which have metal oxide inclusions and which are composites with large surface areas offer advantages that can be further leveraged for the development of cheap adsorbents for heavy metal removal from contaminated water.

6.2 Catalyst derived geopolymer.

Due to the resistance of most organic molecules (e.g. dyes, Cl^- and NO_X containing molecules) to the mineralization, a catalyst is often employed for hastening their degradation. In fact, since photodegradation rather than traditional adsorption process is considered as the efficient way to completely remove hazardous organic molecules from water, it is reasonable to dwell on this theme. Recently geopolymers have been explored as co-catalyst or/and as supports for photocatalytic degradation of these organic compounds. Owing to its high surface area, porosity, and photoactivity, these nano-metal oxides (e.g. Fe_2O_3) (ref: Fig.8) offer rapid initial adsorption of the target organic molecules (Rui et al., 2018; Zhang et al., 2015). This is followed by subsequent oxidative/hydrolytic reaction (Kovářík et al., 2017; Novais et al., 2018). Particularly, fly-ash based geopolymer has been used to achieve ~92.7% photodegradation of methylene blue (MB) under UV irradiation (Zhang and Liu, 2013). The observed desirable performance is attributed to presence of several pores (mostly in the range ~17− 700 nm) and semiconductor metal oxides present in the geopolymers. The simple photocatalytic mechanism is carried out by metal oxides in these geopolymers. The process is enabled by the ionization of MB dye molecules to a cation (reaction 1), which is followed by the adsorption of the cation onto negatively charged tetrahedron $[AlO_4]^{5-}$ (reaction 2). Thereafter, the photo-excitation of the semiconductor Fe_2O_3 in the geopolymer leads to the formation of an electron (e^-) - hole (h^+) pair (reaction 3). Consequently, the reduction of Fe^{3+} to Fe^{2+} in the fly ash-based geopolymer ensures rapid hydrolytic reaction between the hole (h^+) and H_2O molecule to produce hydroxyl radical (reaction 5). This subsequently results in the mineralization of the cationic methylene blue (reaction 6) (Zhang and Liu, 2013).

$$\text{Dye} \xrightarrow{H_2O} \text{dye}^+ + A^- \quad \text{A=anion} \tag{1}$$

$$\text{Dye}^+ + \text{-Si-O-Al-O-Si-} \rightarrow \text{dye}^+\text{-O-Si-O-Al-O-Si-} \tag{2}$$

$$Fe_2O_3 \xrightarrow{h\nu} Fe_2O_3(h^+) + e^- \tag{3}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{4}$$

$$h^+ + H_2O \rightarrow H^+ + OH^* \tag{5}$$

$$\text{Dye}^+ + OH^* \rightarrow CO_2 + H_2O + SO_4^{2-} + NO_3^- + Cl^- \tag{6}$$

The interesting fact about this ceramic-photocatalyst is that various kinds of metal oxides (e.g. Fe_2O_3, TiO_2, Al_2O_3, and MgO) are formed in the Al-O-Si-O- framework during geopolymerization. These are photocatalysts useful for degradation of organic molecules. In fact such catalytic reaction is likely to be achieved under visible light irradiation provided surface functionalization and tailoring are employed (Falah et al., 2016; Falah, 2015).

From literature conducted so far, the high pore volume of metakaolin-based geopolymer is utilized to incorporate TiO_2, so as to obtain TiO_2-nanoparticles-geopolymer composites (Ancora et al., 2012). The geopolymer matrix exhibits excellent catalytic activities not only at the surface, as is often reported; but also in the bulk of the composite (due to sufficient porosity). Similarly, thin film titanium oxide (TiO_2) nanoparticle is coated on the surface of geopolymer for photocatalytic degradation of methylene blue (Chen et al., 2017). Such systems exhibit high activity which can be attributed to the combination of high porosity and overall pore volume (i.e. surface area of 216 $m^2\ g^{-1}$ and pore volume of 0.22 $cm^2\ g^{-1}$) (Singhal et al., 2017). Considering the high toxicity of these dyes coupled with the threats they cause to water bodies; complete mineralization can indeed be considered as a cleaner-approach rather than mere adsorption (which is so often reported). In another interesting report, both TiO_2 and Cu_2O nanoparticles are used to modify catalytic properties of metakaolin-based geopolymer (Falah et al., 2016). The two metal oxides are used to increase the density of cations in the system (ref: Fig. 9) as the

catalytic active sites.

A recent report by Falah et al. (2016) is notable in the above context; here precipitation of metal oxides beneath fly ash-based geopolymer (FAG) during photocatalytic activity is investigated by varying pH of reaction medium (i.e. aqueous solution). Therein, it is highlighted that pH fluctuation affects the photocatalytic activities owing to in situ metal oxides precipitation. This in turn results in the formation of hydroxides on the surface and pores of the geopolymer. Interestingly, this is rather effectively solved by Falah et al. (2016) using cetyltrimethylammonium bromide (CTAB) which hinders the precipitation process. In fact used of CTAB increases the pH tolerance of the modified geopolymer as well as its photocatalytic performances. Thus, the use of surfactant or reductants (such as poly(vinyl alcohol), citric, tartaric acid, gluconic acid, hydroxamate, dimercaptosuccinic acid, or phosphoryl choline) to control the size and shape of the prominent metal oxides (e.g. Fe_2O_3) is likely to make the system suitable for advanced catalysis. In fact, nanostructure properties can be achieved through this approach since use of surfactant is considered as a way of tailoring material surfaces, particles sizes, morphologies, surface areas and intra-particle ionic strengths. This can also be done through pH-adjustment (Stojanovic et al., 2018).

Furthermore, graphene is used to dramatically improve the conductivity of fly-ash/graphene-based geopolymer (FAG) (Zhang et al., 2018), where graphene serves as electron acceptor to improve electronic conductivity of geopolymer (i.e. ~348.8times increase in electronic conductivity, as shown in Fig. 10a), this consequently gives rise to a significant photodegradation of indigo carmine dye through the photogenerated hydroxyl radical under UV irradiation (Fig 10b-c). In fact, the system exhibits appreciable regeneration ability with activity retention of ~90 % over 5times of recyclability (Fig. 10d). Therefore, at present, it is reasonable to believe that surface modification of these materials (i.e. geopolymers) is helpful for catalytic applications. Nevertheless, there is certainly further scope for exploring experimental control in synthetic reactions; especially those that may lead to phase modification or/and incorporate crystal/nanostructures entities into geopolymer for better catalytic activity. For instance, a notable results

is one wherein alkali-activated granulated blast furnace slag-based geopolymer (BFSG) with a particle size in the range of ~50 nm (ref: Fig 11a) is synthesized via geopolymerization, and Fe_2O_3 is incorporated into the system using impregnation methods (Yao et al., 2013). Significant photocatalytic degradation of Congo Red (CR) dye is observed (ref: Fig. 11b-c), for reasons mainly attributed to the prohibition of recombination of photogenerated hole-electron (Fig. 11d). In fact, here it is important to note that BFS-based geopolymer enables substitution of Fe^{3+} (i.e. of Fe_2O_3 nanoparticles) with Na^+, Al^{3+} and Ca^{2+} (Sazama et al., 2011; Zhang et al., 2012); this is known to increase the photo-activity substantially.

Ionic exchange mechanism like the ones depicted in Fig. 12 has been used by Zhang et al. (2012) for the fabrication of nickel-alkali-activated steel slag-based geopolymer, where Ni^{2+} is used to replace almost all the Na^+ ions in the matrix of (Na, Ca)-cementitious geopolymer. The ionic replacement ensures reduction of electronic conductivity resistance (i.e. a UV–vis and near infrared ray spectrum undergoes blue shift), due to the strong interaction between Ni^{2+} and negative charge of $[AlO_4]^{5-}$ tetrahedron in the framework of the geopolymer material. The host ($[AlO_4]^{5-}$) and guest (Ni^{2+}) undergo interaction, that often involves Van der Waal forces (ref: Fig. 12) (Li et al., 2016), which eventually favors fast electron excitation to conduction bands.

Considering the reasonable compatibility of metal oxides/metallic nanoparticles or graphene with geopolymers for photocatalytic activity; the aggregate forms of the Mn^{2+}, CuO and graphene has been used recently to functionalize alkali-activated geopolymer for both catalytic hydrogen evolution and direct sky blue 5B dye degradation (Zhang et al., 2017). In fact, due to uniform distribution of all the guests in the mesoporous structure of the geopolymer (with small crystallite sizes and good electronic couplings) (ref: Fig. 13a, inset shows the composition distribution), about 2853.7 mmol g^{-1} of hydrogen is successfully generated (ref: Fig. 13b), making the system relevant for catalytic purposes in energy production. Likewise with this system ~100% photodegradation of direct sky blue 5B dye (Fig. 13c) is achieved under visible light irradiation. Hence a plausible cleaner production approach (e.g. involving water splitting-oxygen evolution and hydrogen evolution reaction) can be envisaged if good electron

conductors like metal nitrides and carbides are used for surface functionalization of the geopolymer. However, further investigation is recommended to examine the exact mechanism involved in the process of surface functionalization. This will enable reasonable identification and quantification of the catalytic active sites in these materials.

In summary, given the above discussion, it is clear that geopolymer composites are promising catalyst supports. However if the pure phase of the geopolymer is to be employed for photocatalysis or electrocatalysis in future, surface tailoring and experimental controls (i.e. use of surfactant to improve pH tolerances and specific surface areas) is likely to be a way forward. Furthermore, nanostructuring of geopolymers could also offer a means to enhance its photoactivity an eventual utility.

6.3 Antibacterial derived geopolymer

Geopolymer is being considered as functional-surface-coating materials for inhibiting the growth of bacteria (Bortnovsky et al., 2010; Moya et al., 2013). This system is often used to change the surface properties of the substrate in order to make it tolerant to the wetter and coastal organisms (e.g. planktons). For instances, in 2017, Pratama, (2017) synthesized nano-silver (Ag)-geopolymer composite as a functional surface coating material for bacteria growth inhibition. The Ag-nanoparticles is successfully incorporated onto the surface of geopolymer matrix via bioreduction mechanism. This process results in the need for a rather prolonged curing period; however after reaching a stable state, the function of each of the constituents is rather distinct. Nano-Ag and geopolymer matrix are considered as antibacterial and supportive refractory agents respectively. Before then, solution treatment method is applied for printing of copper chloride onto the surface metakaolin-based geopolymer (Hashimoto et al., 2015). Here, geopolymer matrix prepared from a mixture of metakaolin and potassium hydroxide (KOH) after 7days of curing (at temperature=60°C), is completely immersed in a solution of 0.1 mol/L $CuCl_2$ for 24 h. This solid-state geopolymer changes from yellow to green due to ionic exchange. The system is then applied as antibacterial material; the desirable performance here is attributed to the mesoporous surface of the geopolymer which in turn enables fast and quick ionic exchange between the Cu^{2+} of $CuCl_2$ and K^{+} of

geopolymer matrix. In fact, this approach can be used to solve the problem of prolonged curing time (akin to the bioreduction of $AgNO_3$). This in fact allows easy scalability of the geopolymers as antibacterial materials/surfaces for the treatment of water containing micro-organisms. With this, different treatment measures for industrial wastewater (i.e. microbial, heavy metals and organic compounds removal) are likely to be achieved within a single geopolymer treatment plant. It will eventually reduce industrial production cost and enable industries to comply with environmental law and regulation.

In addition, geopolymers composites based on metakaolin and nano-ZnO for antibacterial applications are reported by Nur et al. (2017). Therein, a solid solution of metakaolin and ZnO-nanoparticles is made; this is then mixed with an alkaline solution (NaOH) to produce the geopolymer matrix. This system exhibits high mechanical strength, and is used to inhibit bacterial growth. Although, the nanoparticles can stand alone be a reasonable antibacterial; better performances are observed with ZnO-geopolymer composites (indicating co-activity from the matrix as well). Such activity can be attributed to the presence of a significant amount of metal oxides and Al-O-Si network in the geopolymer which plausibly offers synergistic anti-bacterial activity.

Likewise Triclosan-geopolymer composites have been reported as antibacterial agents against Escherichia Coli (Gram-negative bacteria) (Fig. 14a) and Staphylococcus Aureus (Gram-positive bacteria) (Fig, 14b) using the Halo method (Rubio-Avalos, 2018). The reproduction rate of these bacteria is effectively controlled through a substantial distribution of Triclosan in the geopolymer substrate that serves as reinforcement and disperser. However, use of nanoparticles in composite forms to functionalize the surface of geopolymer for inhibiting the growth of sulphuroxidizing microbes and other alkaline-tolerant microbes, (i.e. colony at the surface of concrete) is considered as one of best systems (Diercks et al., 1991; Islander et al., 1991; Wei et al., 2010). For instance, ZnO-SiO_2 composite coated fly ash-based geopolymer ($GM_{ZnO\text{-}Si}$) (Sarkar et al., 2018), is used as an anti-microbial (i.e. against E. coli, S. aureus, A. niger) as shown in Fig. 15a-c, while maintaining the mechanical properties of the $GM_{ZnO\text{-}Si}$ composite, therein the presence of the two nanoparticles phases (i.e. ZnO and SiO_2) on the geopolymer make it

exhibits substantial antibacterial performances far better than the single nanoparticles (SiO_2). Such performance indicates that high charge transfer from ZnO-SiO_2 hybrid within the geopolymer results in faster rupture of bacterial DNA when compared to the use of single phase SiO_2 or ZnO (Sarkar et al., 2018).

In summary, antibacterial geopolymers are promising devices for the fabrication of water treatment plant, and water filter bed. In fact, they have potential to offer cleaner production routes for industrial, health and governmental sectors. However, overcoming challenges associated with incorporation of metal/metal oxides molecules onto the earthly abundant metakaolin is needed. This will have a bearing on tackling issues concerning scalability and stability. Furthermore, fly-ash/metakaolin-based geopolymer is likely to fill the space of metal oxides-nanoparticles/geopolymer composites as antibiotics in the near future. These possibilities are currently hindered by challenges highlighted below making geopolymer production in a scalable manner difficult, in practice.

7. Barriers to utilization

Currently, a number of technical and legal barriers are restricting the use of most waste materials (e.g. fly ash, and blast furnace slag) for any further application without prior treatment (Ahmaruzzaman, 2010). This makes access to the industrial waste materials rather difficult, which in turn causes limited research work on them. The major constraints are the lack of data related to their specifications, in-process standardization, and characterization data from the production centers. However, proper institutional documentation and specification is likely to remove most of these barriers.

Likewise logistic barriers exist due to the bulky nature of the precursors (i.e. BFS, kaolin, fly ash) which makes their transportation difficult. Allocation of reasonable funds from both institutes, non- and governmental sectors are likely to further increase the interest of research communities in the design and fabrication of advanced geopolymer-based catalysts for cleaner production (especially for applications related to water remediation).

Another obvious barrier is the legal restriction placed on the exploitation of natural minerals like kaolin in many countries and regions (e.g. ref: Minnesota's Mining Laws in states) making the raw materials expensive, which in turn limits their applications. Application of geopolymer for the removal of hazardous heavy metals and organic compounds is an efficient and effective approach. However, regeneration of the spent geopolymeric-photocatalyst and/or adsorbent by backwashing with water is still a challenge and never reported so far. Although for other materials like nanoparticles and activated charcoal, just to mention few; different regeneration methods (e.g. chemical treatment, backwashing, thermal treatment, and steam treatment) have been reported for the treatment of the spent adsorbent/photocatalysts (Burakov et al., 2017; Lata et al., 2015; Rasaki et al., 2018). Among these methods, thermal treatment, back- and steam-washing seem effective. Chemical treatment too appear to be a promising method for geopolymer (Naghsh and Shams, 2017). Furthermore safe disposal of the materials after using them into a geotextile landfill is crucial (Richardson and Zhao, 2010; Rowe, 2007). Reduction in the compressive strength and stability after incorporating metal oxides/nanoparticles into the geopolymer matrix often hinders the crushing and pulverization of the solid geopolymers; this is another great challenge.

8. Future research and prospects

Geopolymers offer substantial prospective value in environmental remediation technologies. Its high flexural strength, low carbon footprint, fast curing time and solidification, high fire and poison resistance, offer fresh possibilities for researchers. When engineered, it has the potential to perform even better than activated carbon or zeolites for the adsorption of hazardous materials both in the air or water polluted environment. This is due to its high porosity. Adsorption performance of geopolymer depends on raw materials used for its synthesis. With appropriate use of precursors and synthetic strategies, waste water can be easily converted to cleaned water through use of geopolymer as a purifier.

Furthermore, geopolymers can be viable photocatalyst supports, due to its characteristic composition which yield various metal oxides. However, further research is required in provision of scalable technologies involving geopolymers adsorbent and photocatalyst supports. Surface

nanostructuring, coating and composites generation are likely to be major activities to this end, in near future. Synthesis and process controls will be relevant to optimize in all these cases.

9. Conclusion

Geopolymeric materials can offer valuable solutions to environmental remediation challenges. These solutions are likely to be low on infrastructure maintenance, and of relevance to the scalability needs of current industrial waste water treatment plants. The possibility of (i) synthesizing from accessible and rather abundantly available raw materials and (ii) fabrication using room temperature approaches with low or zero green house gases emission have made geopolymer a material relevant for cleaner production and for green technologies. This also offers windows of 'green technology' opportunities in allied industries - including construction, surface engineering, and healthcare. Advanced uses of this material for catalysis applications and energy production will particularly benefit industries which focus on waste treatment and water remediation. We believe that this review will offer insights into the use of geopolymers as a plausibly green and sustainable material that offers viable solutions to global environmental challenges associated with waste water treatment, energy production and slag management. Furthermore the barriers to technology outlined in this work are expected to be of direct relevance to stakeholders of the various clean and green production sectors, and for policy makers in the government.

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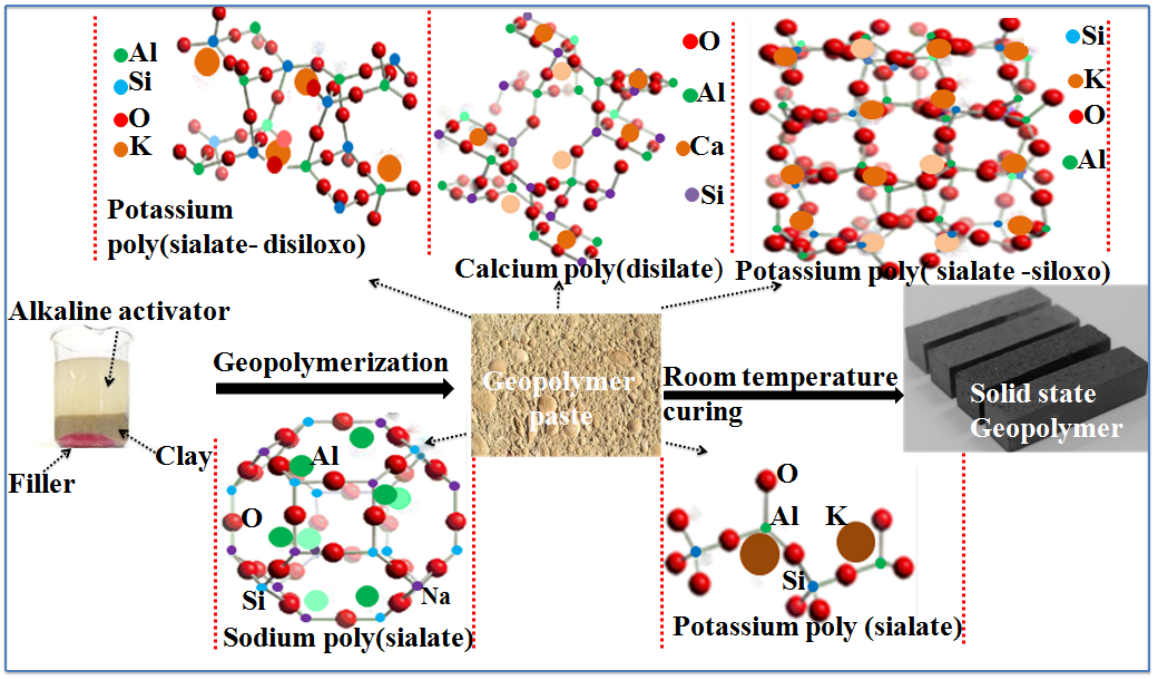

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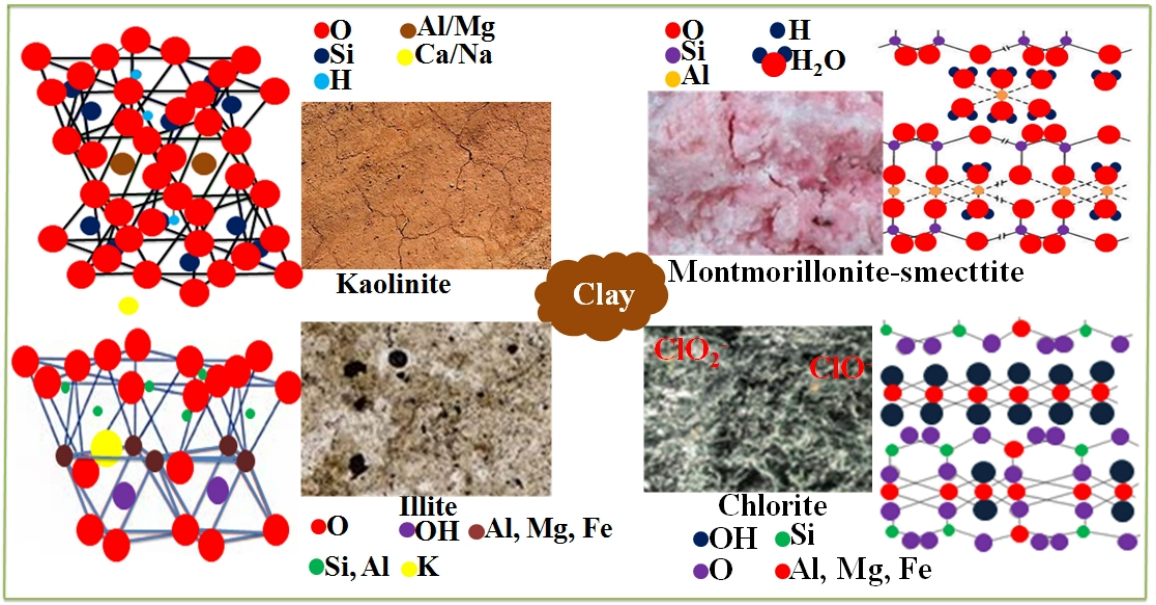

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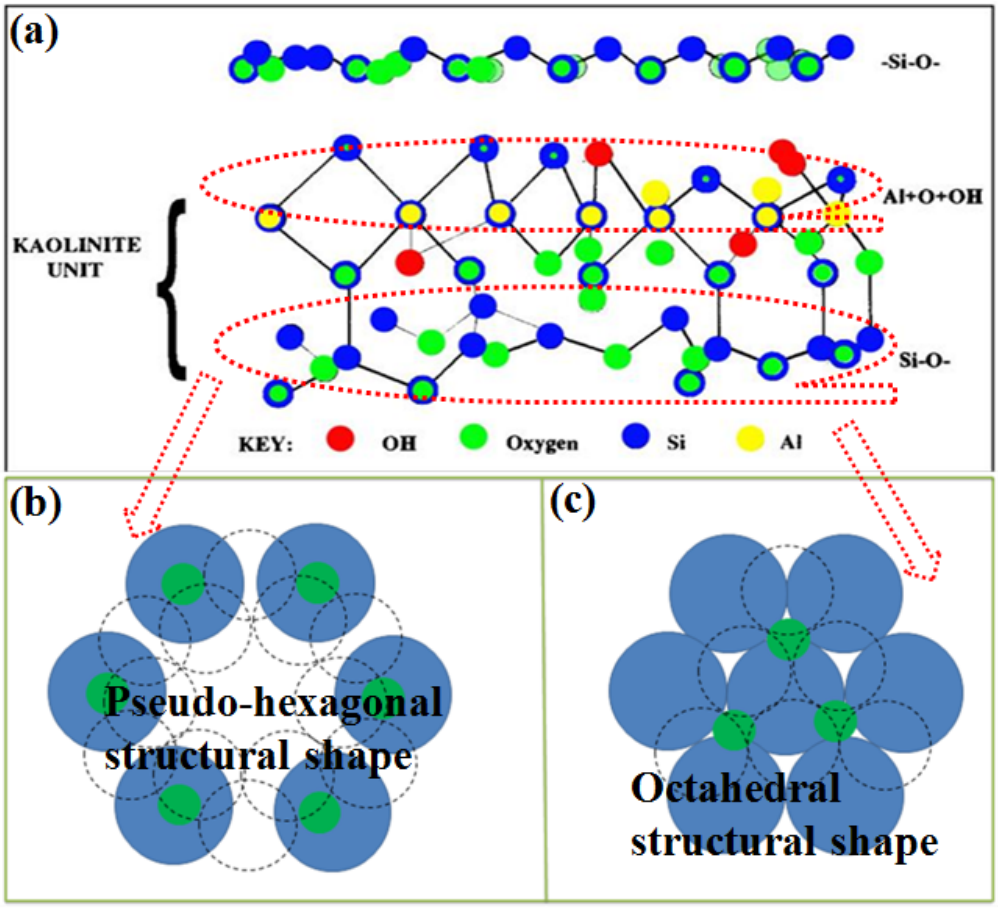

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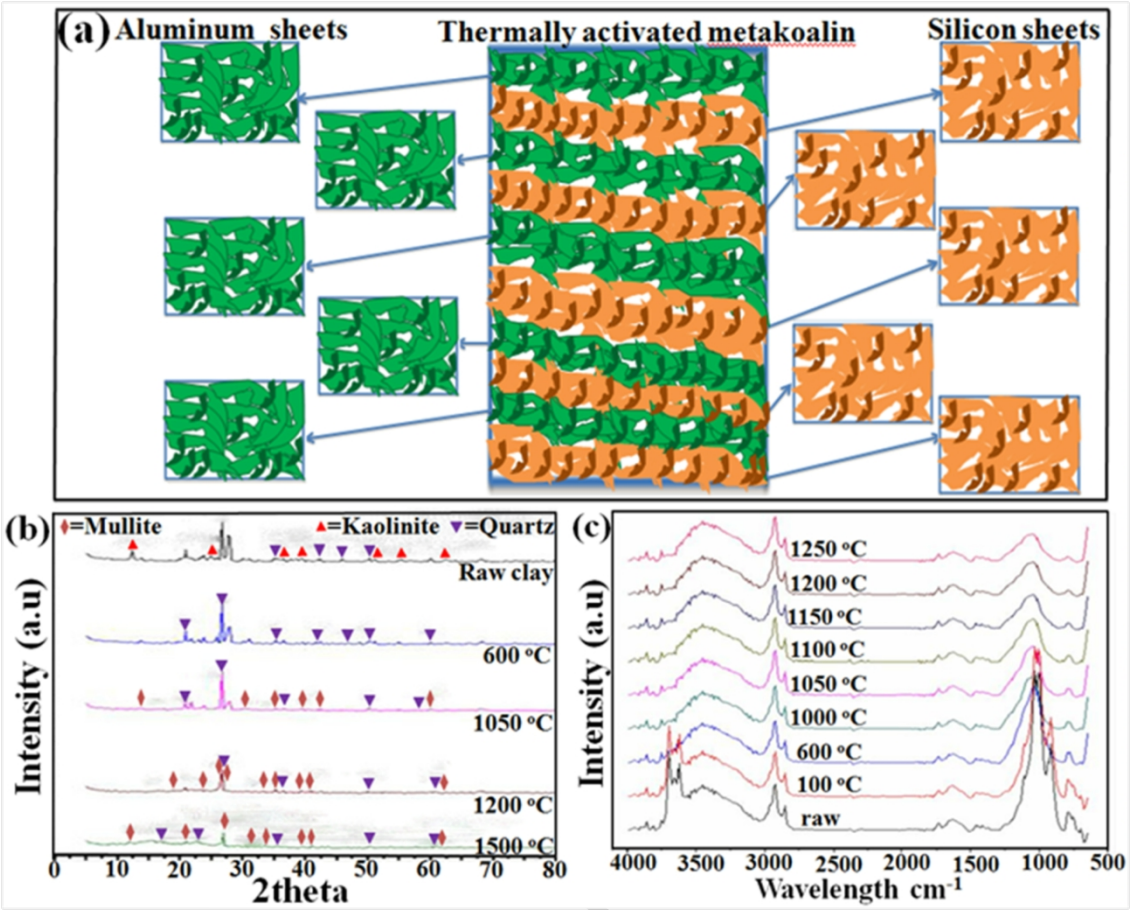

(a) Aluminum sheets
Thermally activated metakoalin
Silicon sheets
(b)
♦=Mullite
▲=Kaolinite
▼=Quartz
Raw clay
600 °C
1050 °C
1200 °C
1500 °C
Intensity (a.u)
0 10 20 30 40 50 60 70 80
2theta
(c)
1250 °C
1200 °C
1150 °C
1100 °C
1050 °C
1000 °C
600 °C
100 °C
raw
Intensity (a.u)
4000 3500 3000 2500 2000 1500 1000 500
Wavelength cm-1

Fig. 4

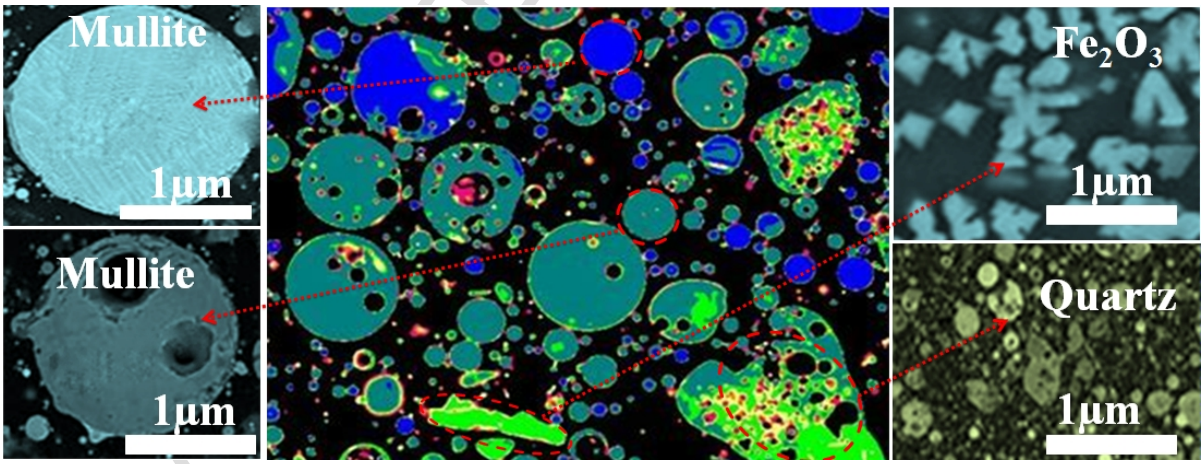

Mullite
1μm
Mullite
1μm
Fe2O3
1μm
Quartz
1μm

Fig. 5

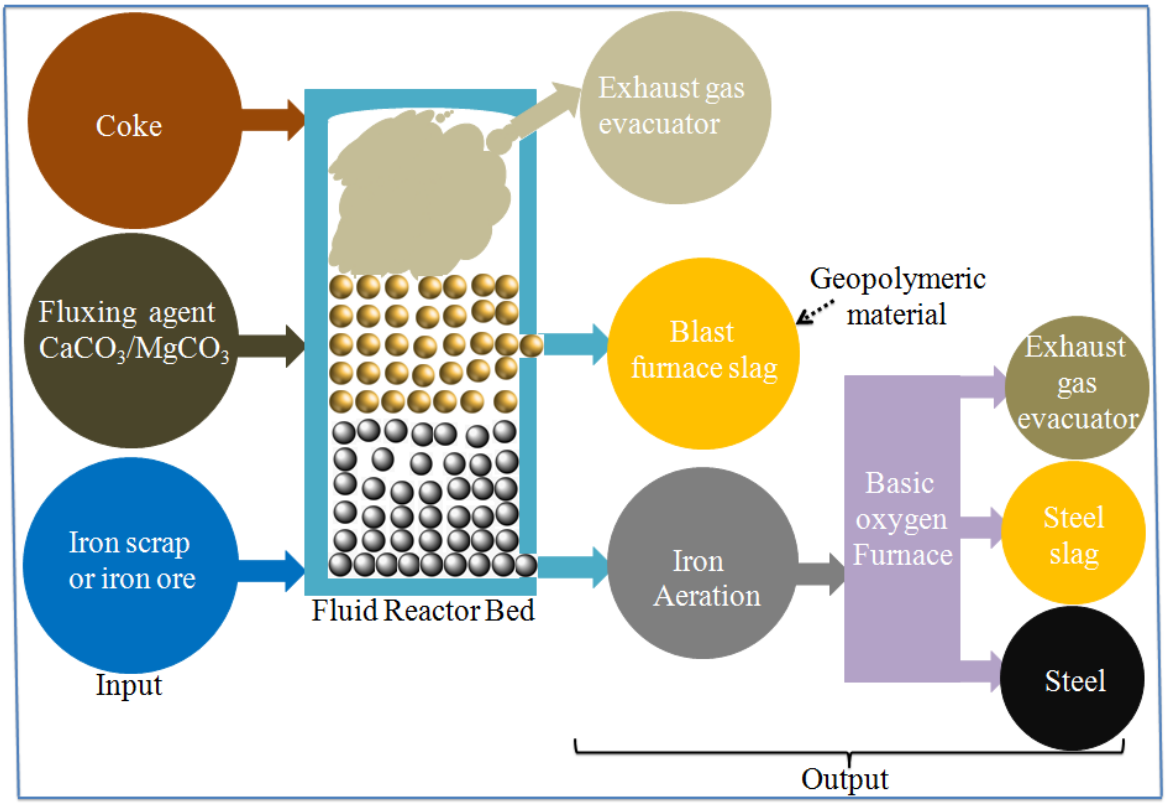


Fig. 6

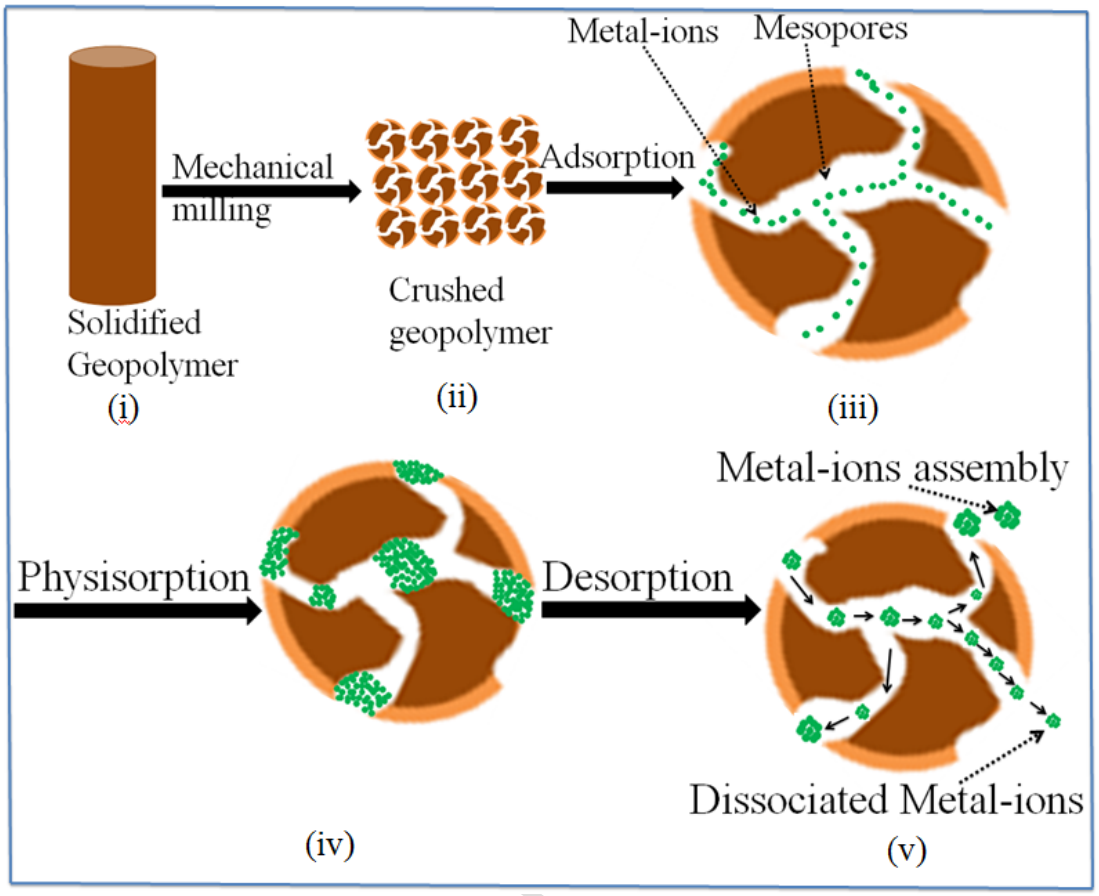

Metal-ions
Mesopores
Mechanical milling
Adsorption
Solidified Geopolymer
(i)
Crushed geopolymer
(ii)
(iii)
Metal-ions assembly
Physisorption
Desorption
Dissociated Metal-ions
(iv)
(v)

Fig.7

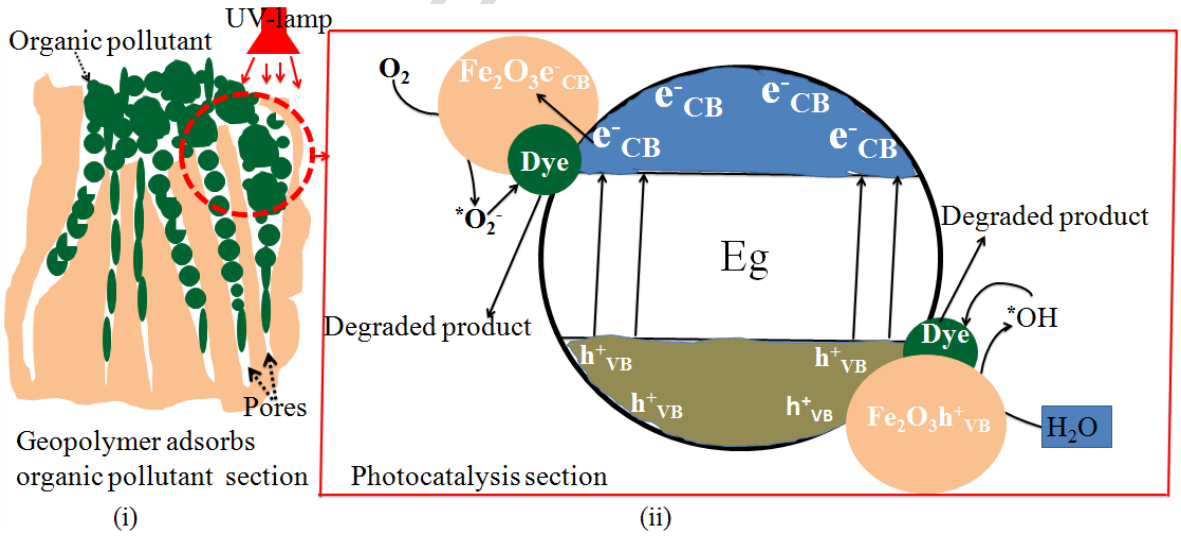

Organic pollutant
UV-lamp
Pores
Geopolymer adsorbs organic pollutant section
(i)
O2
Fe2O3e-CB
e-CB
Dye
*O2-
Degraded product
Eg
Degraded product
*OH
h+VB
Fe2O3h+VB
H2O
Photocatalysis section
(ii)

Fig. 8

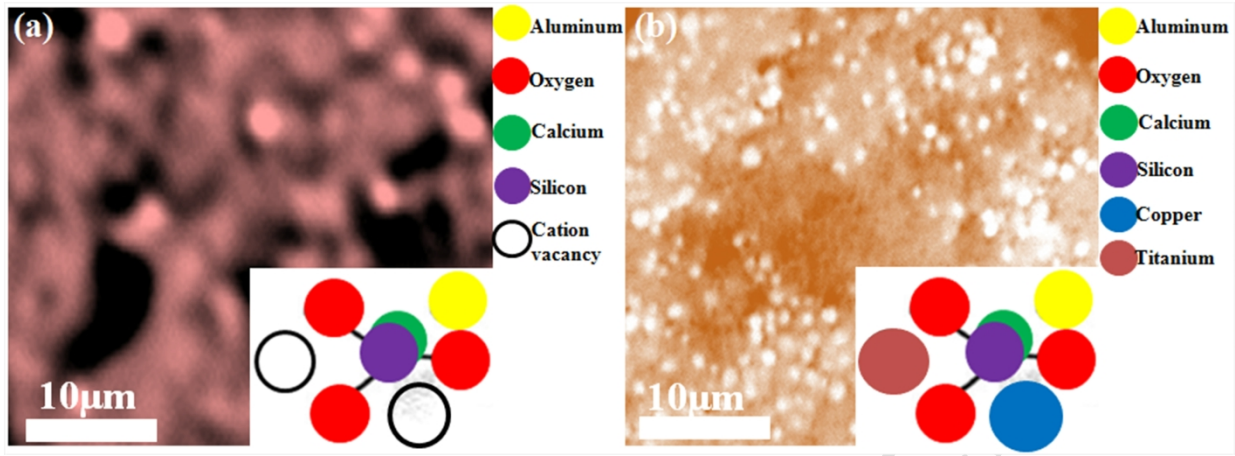

(a)
Aluminum
Oxygen
Calcium
Silicon
Cation vacancy
10μm
(b)
Aluminum
Oxygen
Calcium
Silicon
Copper
Titanium
10μm

Fig.9

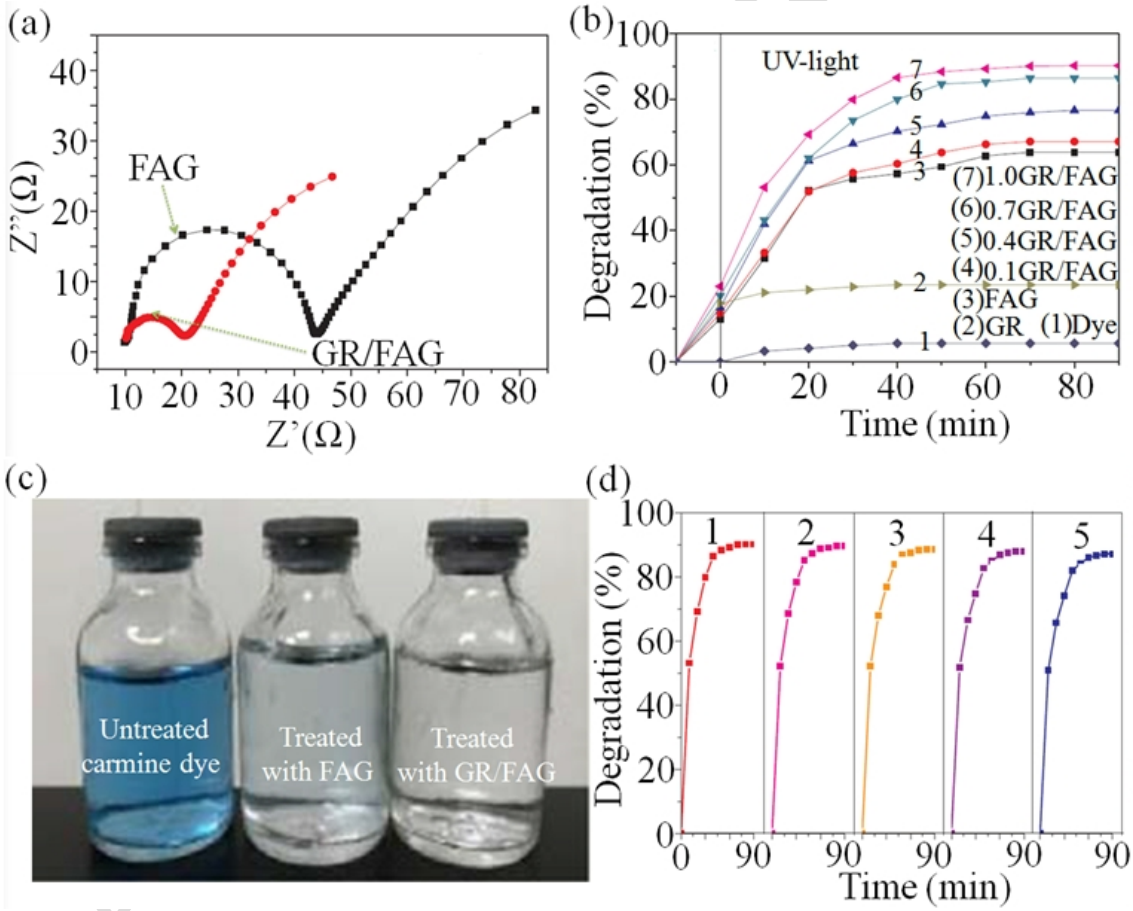

(a)
FAG
GR/FAG
Z''(Ω)
Z'(Ω)
(b)
UV-light
Degradation (%)
Time (min)
(7)1.0GR/FAG
(6)0.7GR/FAG
(5)0.4GR/FAG
(4)0.1GR/FAG
(3)FAG
(2)GR
(1)Dye
(c)
Untreated carmine dye
Treated with FAG
Treated with GR/FAG
(d)
Degradation (%)
Time (min)

Fig. 10

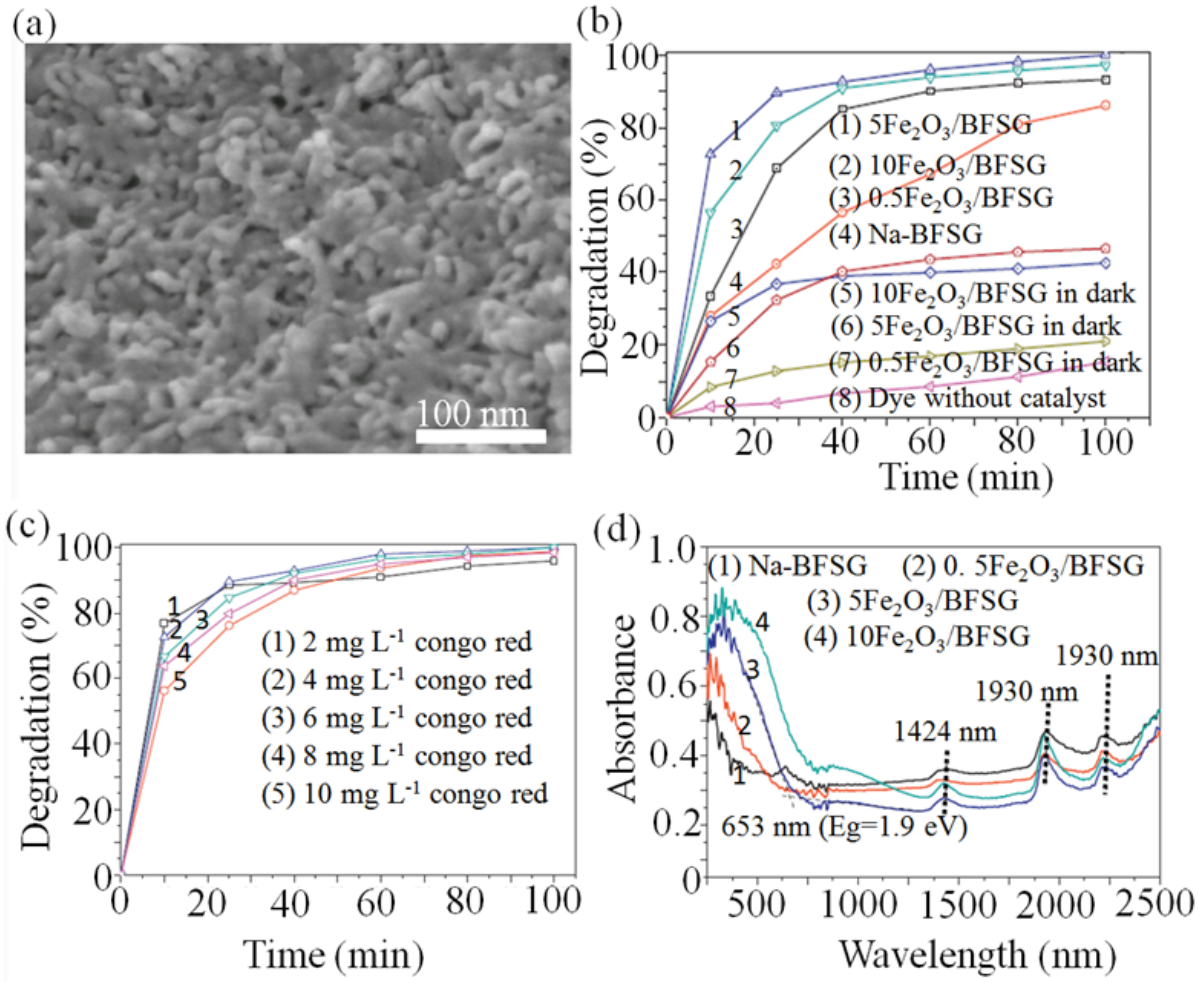
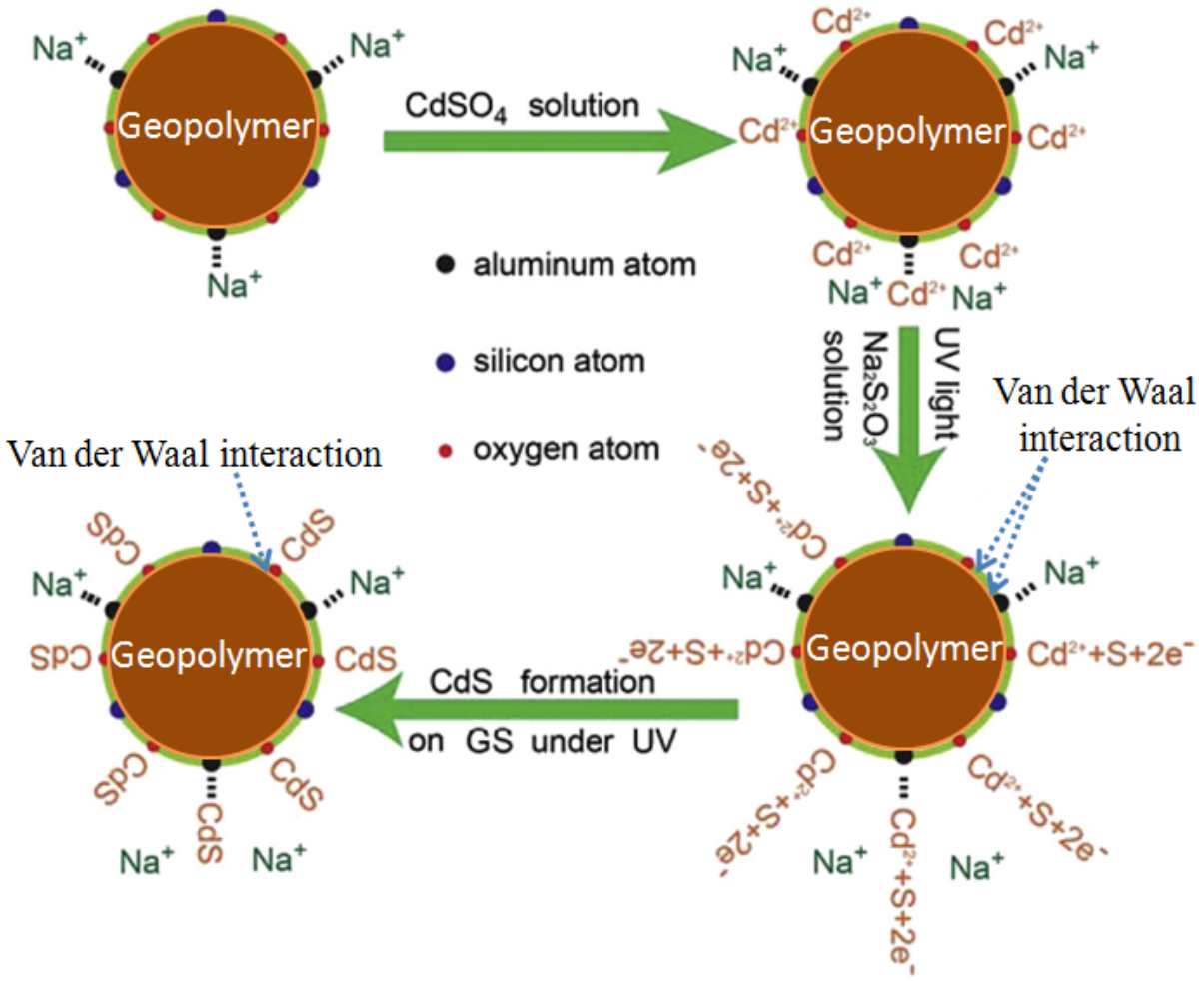


Fig. 11



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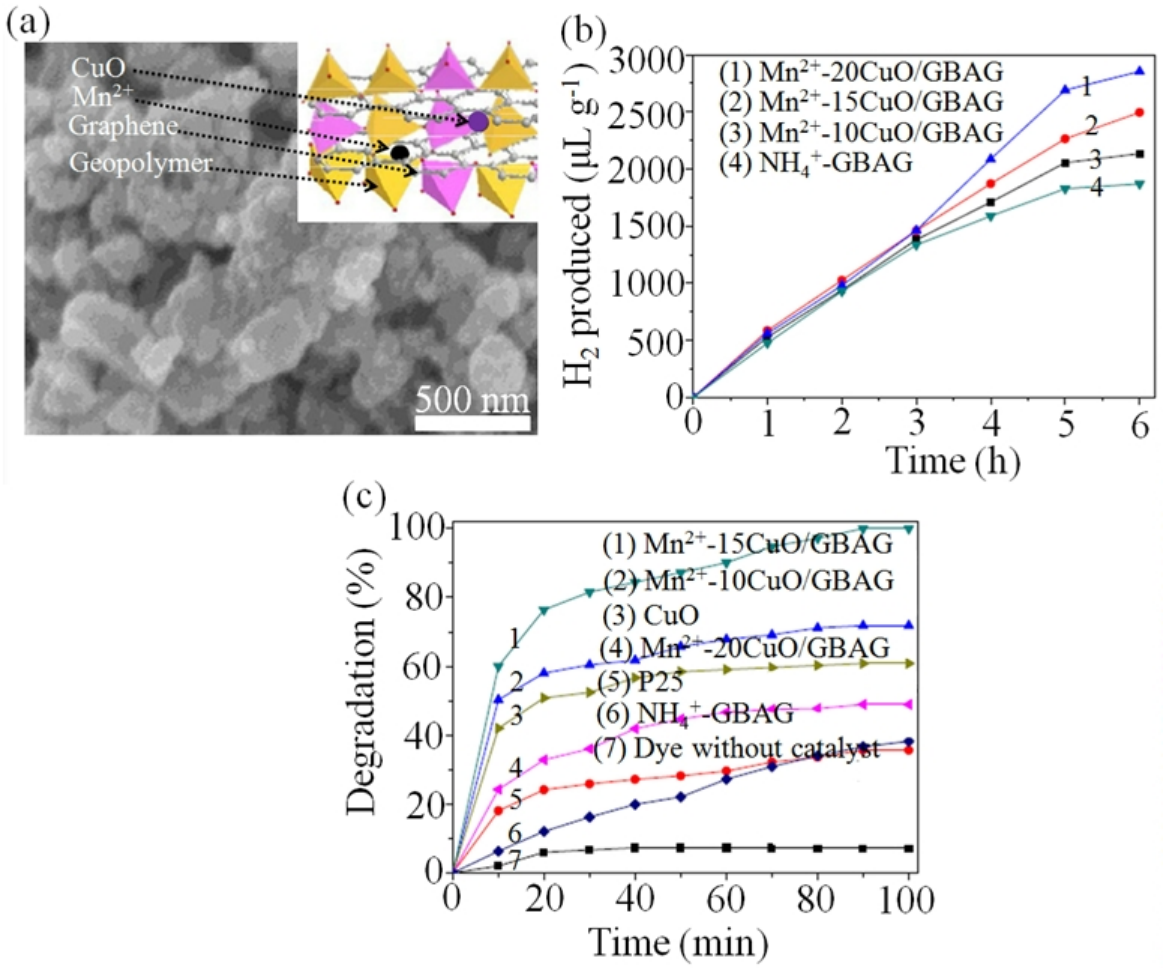

Fig. 13

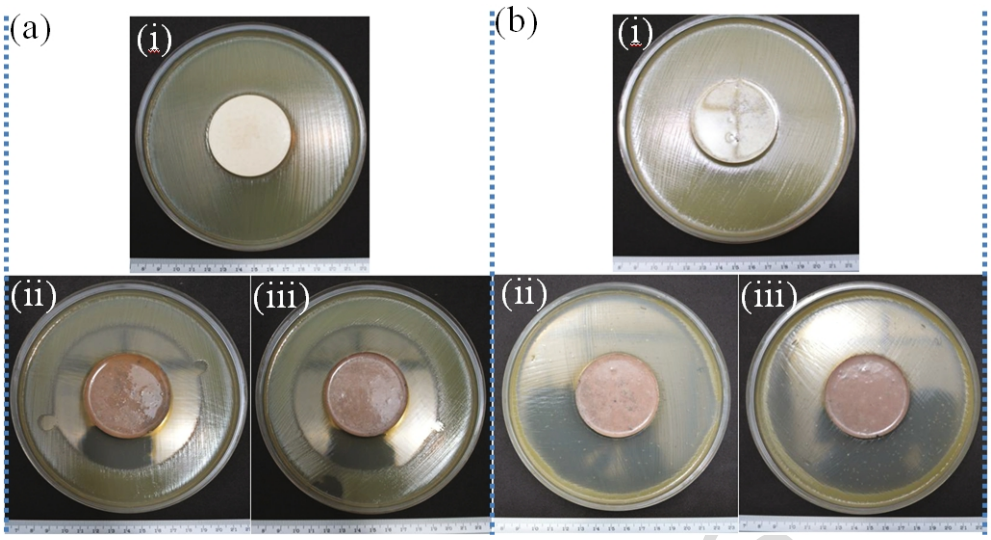
(a)
(i)
(ii)
(iii)
(b)
(i)
(ii)
(iii)

Fig. 14

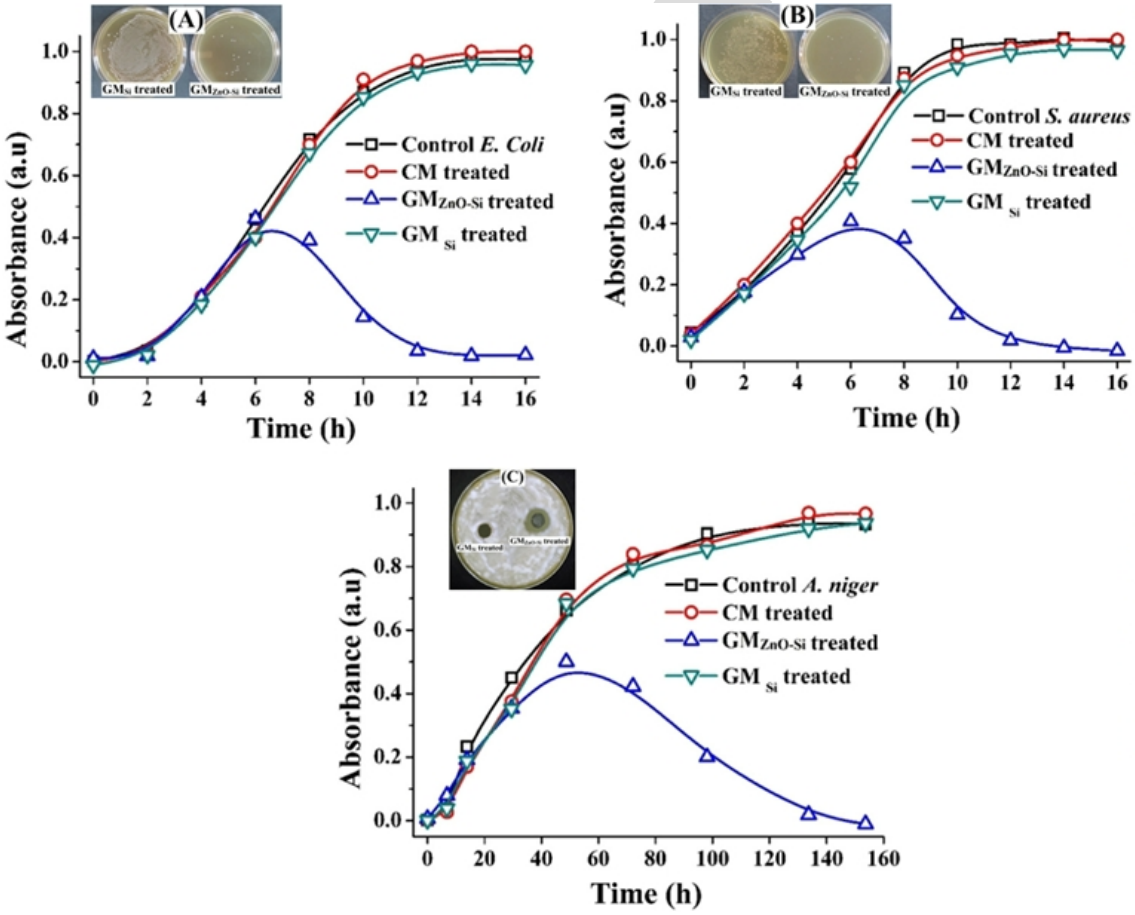
(A)
GMSi treated
GMZnO-Si treated
Control E. Coli
CM treated
GMZnO-Si treated
GM Si treated
Absorbance (a.u)
Time (h)
(B)
Control S. aureus
CM treated
GMZnO-Si treated
GM Si treated
Absorbance (a.u)
Time (h)
(C)
Control A. niger
CM treated
GMZnO-Si treated
GM Si treated
Absorbance (a.u)
Time (h)

Fig. 15

Figure captions

Fig. 1:
Illustration of geopolymer synthesis and emergent structural framework based on alkaline activator used, and the eventual phase of the final geopolymer.

Fig. 2:
Physicochemical comparison of kaolinite, illite, chlorite and montmorillonite as the clay constituents,(Murray 2006) (kaolinite has the most uniform surface and substantial amount of Na/Ca atoms making it a best clay constituent for aiding geopolymerization process). *Adapted from: Muray book.*

Fig. 3:
(a) Structural condensation of the kaolinite unit phases. (b) Pseudo-hexagonal sheet of silica (c) octahedral sheet of alumina(Murray 2006). (The pseudo structural phases of both alumina and silica units enable easy dehydroxylation and structural transformation into metakaolin with tetrahedral shape). *Adapted from: Muray book.*

Fig. 4:
(a) Stack layer of thermally activated metakaolin. (b) XRD patterns of thermally activated metakaolin at different temperature. (c) FTIR spectra of thermal activated metakaolin at different temperature (Kljajević et al., 2017; Seynou et al., 2016). *Courtesy: (Kljajević et al. and Seynou et al.)*

Fig. 5:
Phase mapping of SEM image of fly ash (arrows indicate the distribution of mesoporous metal oxides, quartz which consists of SiO_2; Al_2O_3; and CaO, and other constituents) (Kutchko and Kim 2006). *Adapted from: Kutchko and Kim*

Fig. 6:
Schematic diagram of blast furnace operation and blast furnace slag production (Chesner, Collins et al. 1998, Saheb 2012). *Courtesy: Saheb et al*.

Fig.7:
Diagrammatical illustration of adsorption and desorption process of metal ions on the surface of geopolymer. {(i) uncrushed geopolymer (ii) geopolymer crushed into nanosphere shapes with small and approximately equal radius size, (iii) transfer of metal-ions through mesopores of the nanosphere geopolymer, (iv) accumulation of the metal-ions onto the adsorption active sites, and (v) desorption of the metal-ions from the surface of geopolymer via simple washing process}.

Fig. 8:
Schematic illustration of organic compound photodegradation using geopolymer photocatalysts. (i) Initial adsorption stages of organic molecules, and (ii) photodegradation of adsorbed organic molecules.

Fig.9:
SEM image of (a) undoped geopolymer (inset: geopolymer structural unit with cation vacancy) where the mesoporous surface serves as nanoparticle or cations venues/vacancies, and (b) doped

geopolymer (inset: geopolymer structural unit with the cation substitution), here the porous surface is occupied by CuO and TiO_2 for the cationic exchange and incorporation (Falah, MacKenzie et al. 2016). *Adapted from Falah et al.*

Fig. 10:
(a) Electroconductivity of fly-ash based geopolymer and graphene decorated fly-ash-based geopolymer. (b) Photodegradation of indigo carmine dye using various graphene decorated fly ash-based geopolymer, fly ash-based geopolymer, and graphene catalysts, and without catalyst under UV-lamp. (c) Quantitative comparison of indigo carmine dye photodegradation using graphene decorated fly-ash based geopolymer, fly ash-based geopolymer, and without catalyst under UV-light. (d) Regeneration of graphene decorated fly ash based geopolymer as a indigo carmine dye photocatalyst (Zhang, He et al. 2018). (A substantial regeneration is attained due to the synergetic effect between the graphene and geopolymer). *Courtesy: Zhang et. al.*

Fig. 11:
(a) SEM images of Fe_2O_3/blast furnace slag based geopolymer. (b) Photodegradation of congo red using various Fe_2O_3/blast furnace slag based geopolymer, Na-blast furnace slag based geopolymer catalyst, and without using catalyst under UV. (c) Use of 20%Fe_2O_3/blast furnace slag based geopolymer photocatalyst as a function of Congo Red concentration. (d) Photoluminescence absorbance of Fe_2O_3/blast furnace slag based geopolymer, Na-blast furnace slag based geopolymer (Yao, Li et al. 2013). (A dissolution limit to initiate good electron transfer is established at 5%Fe2O3@BFSG which shows that the BFSG also has photocatalytic properties) *Courtesy: Yao et. al.*

Fig. 12:
Illustration of ionic exchange of Na^+, K^+, Ca^{2+} of alkaline activator used for geopolymer fabrication with transitional metal-ion for enhancing photocatalytic properties (Li, He et al. 2016). (The presence of weak Van der Waal forces enable easy replacement of alkaline/alkali metal-ions with the photoactive transition metal-ions) *Courtesy: Li et. al.*

Fig. 13:
SEM images of Mn^{2+}-CuO/graphene decorated geopolymer (inset corresponds to composite distribution). (b) Amount of hydrogen generated against each catalyst. (c) Use of Mn^{2+}-CuO/graphene decorated geopolymer, NH^{4+}-geopolymer as a photocatalyst and with catalyst for the degradation of direct sky blue 5B dye under UV light (Zhang, He et al. 2017). *Courtesy: Zhang et. al.*

Fig. 14:
(a) (i) Activity evaluation against E. Coli using a standard metakaolin based geopolymer cement without E. Coli inhibition. (ii) A geopolymer cement disk with 0.5% (w/w) of Triclosan against E. Coli and a 90 mm Halo was developed on it. (iii) A geopolymer cement disk with 1.5% (w/w) of Triclosan against E. Coli. A 90 mm Halo was developed on it. B (i) S. aureus activity evaluation of a standard metakaolin based Geopolymer cement disk without bacteria inhibition. (ii) Activity evaluation against S. aureus of a geopolymer cement disk with 0.5% (w/w) of Triclosán. A 116 mm Halo was developed on it. (iii) Activity evaluation against S. aureus of a geopolymer cement disk with 1.5% (w/w) of Triclosán. A 116 mm Halo was also developed on it

(Rubio-Avalos 2018). (Although pure geopolymer shows little or zero inhibition against both gram positive and negative bacteria growth, but it is a good support for the Triclosan for antibacterial activity) *Courtesy: Nur. et al.*

Fig. 15:
Mortality studies of the (a) E. Coli (b) S. aureus, and (c) A. niger (inset show the Agar plate/SDA images of microbial strain corresponding to each bacteria)(Sarkar, Maiti et al. 2018). (Use of ZnO-SiO_2 composites to functionalize geopolymer have enhanced activity when compared to single ZnO or SiO_2) *Courtesy: Sarkar et. al.*

Highlights

- (i) Raw materials, and (ii) synthetic/process parameters influence geopolymer properties.
- Properties relevant for H_2-production and photodegradation are elaborated.
- Filler-materials from wastes relevant for catalytic-enhancement are identified.
- Heavy-metal removal using geopolymers: methods and mechanisms are elucidated.
- Technology barriers of relevance to all stake holders are projected.