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REVIEW PAPER

Green Synthesis of High-performance Graphene Reinforced Geopolymer Composites: A Review on Environment-Friendly Extraction of Nanomaterials

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Abstract: *The field of nanomaterials has greatly advanced in the last decade following a wide range of applications in the fields of electronics, automobiles, construction, and healthcare. Synthesis of the nanomaterials plays a crucial role in redefining the current engineering and science field. At the same time, procuring an environment-friendly end product through eco-friendly solutions and sustainable processes is the key to many global problems. Green synthesis of nanomaterials like graphene and its derivatives involves mild reaction conditions and nontoxic precursors because it is simple, cost-effective, relatively reproducible, and often results in more stable materials. This paper primarily focuses on the green synthesis of graphene and its derivatives (graphene oxide & reduced graphene oxide) and geopolymers; a green technology for preparing graphene reinforced geopolymer composites. Various methods used globally for green synthesis of graphene and geopolymer are briefly discussed and this paper tries to integrate these two areas for a green end product. Preparation techniques and possible applications of these green composites are also discussed to provide insights on the current growth and developments.*

Keywords: *environment, synthesis, composite, grapheme, geopolymer, nanomaterial.*

1. INTRODUCTION

Synthesis of nanomaterials or nanostructures plays a very vital role in the design and development of composites. These can be top-down or bottom-up approaches, depending upon various crucial factors such as cost-effectiveness, performance, large scale production, etc [1]. Fabrication of composites often involves ecologically unfriendly methods, which inevitably poses negative effect on the environment. Sustainable development should be the primary approach for the development of composites. Traditionally, physical and chemical methods are used in the synthesis of nanomaterials which include toxic stabilizing compounds, the formation of harmful by-products and various other environmental concerns [2]. Over the years, several studies have highlighted the beneficial usage of biological products such as plant extracts, microorganisms, organic acids, reducing sugars, amino acids, etc. as a potential precursor for synthesizing nanomaterials in a greener and non-hazardous way [3]. They offer an eco-friendly, cost-efficient and replicable approach by providing a swifter metallic nanoparticle production. The current work highlights the green synthesis methods or approaches by several researchers around the globe for producing graphene and geopolymer. According to several studies around the globe, graphene has been proved to be an excellent reinforcing and property enhancing nanomaterial. Geopolymer is an eco-friendly substitute of concrete or cement that uses waste materials rich in alumina-silicates such as fly ash, rice husk ash, ferrochrome ash, etc. and alkaline activators such as sodium hydroxide and sodium silicate. However, limited works have been carried out in the field of graphene reinforced geopolymer composites (GRGC). The current review study sheds light on the growth and development of research activities in the field of synthesizing graphene and geopolymer through environment-friendly measures. This study is focused on summarizing and highlighting the studies related to synthesizing graphene and geopolymer using environment-friendly methods to ensure a more sustainable future. Various approaches of introducing graphene into a geopolymer matrix have been elucidated in the paper along with its possible future application scenarios.

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2. GREEN SYNTHESIS OF GRAPHENE

The last decade has witnessed increased research on the two-dimensional (2D) form of carbon, graphene following its discovery by Andre Geim and Konstantin Novoselov in 2004 [4]. This interest in graphene has evolved due to its outstanding properties including a large surface area, high electrical and thermal conductivities, high optical transparency, high flexibility, great chemical stability, and excellent strength leading to its application in diverse areas including electronics, batteries, sensors, membranes, supercapacitors, composites, drug delivery, next-generation energy technologies such as solar cells, and so many others [5]. Diverse techniques have been used to synthesize graphene involving either the top-down approach or the bottom-up approach such as mechanical exfoliation, chemical synthesis, epitaxial growth, and chemical vapor deposition (CVD) [1]. Among all, the chemical synthesis of reduced graphene oxide (rGO) is believed to be the fastest and low-cost method for large-scale production. Reduced graphene oxide is obtained by the oxidation of graphite in a solution to yield graphene oxide (GO) followed by its reduction using reducing agents to remove the oxygen functionalities. Reduction strategies including thermal, photocatalytic, chemical, and electrochemical reduction have been reportedly used [6]. Amongst these, the chemical reduction approach using hydrazine has been mostly utilized and the preeminent technique as it produces reduced graphene oxide similar in properties to pristine graphene. However, hydrazine is a toxic and dangerous chemical reducing agent; thereby the use of hydrazine poses as a threat.

With rising environmental concerns, researchers have been encouraged to find alternative reducing agents that are non-toxic (termed “green reducers”) and other means of graphene synthesis from graphite. This has led to the use of green reducing agents that are environmentally friendly to both humans and nature while complying with the twelve principles of green chemistry [7]. This implied the development of eco-friendly and green synthesis approaches to obtaining graphene.

2.1. Green Synthesis of Reduced Graphene Oxide (rGO) from Graphene Oxide (GO) Precursor

In the search for a replacement for hydrazine as a reducing agent, many green reducers have been introduced including plant extracts; microorganisms, organic acids, amino acids, reducing sugars, etc. have been reported. Discussed below are some common green reducers used for deoxygenation of GO to produce graphene.

2.1.1. Plant Extracts

The chemical reduction of GO has been extensively accomplished using extracts from plants as reducing agents. Coconut water, Chinese wolfberry, Eucalyptus leaf, lemon juice, pomegranate juice, green tea, Salvadora persica, and nettle are just a few examples. The use of these plant extracts has successfully reduced the oxygen content of graphene oxide precursor (based on their antioxidant contents) while avoiding the use of toxic chemicals like hydrazine. Important parameters in the use of plant extracts for reducing GO include graphene oxide concentration, reduction temperature, and duration. The efficiency in the use of plant extracts for deoxygenation in GO is represented by the carbon to oxygen (C/O) ratio. In a typical reduction of GO to rGO, green tea rich in polyphenolic compounds were utilized by Wang et al. [8] for the deoxygenation of GO through the extracted tea polyphenol (TP) aromatic rings in the tea solution and used in the production of chitosan/graphene biocomposite. Hou et al. [9] first reported the use of chrysanthemum flower extract, a Chinese traditional herbal medicine for the reduction of 1 mg/mL GO at 95°C for 24 h. It was discovered that deoxygenation resulted in a color change of GO dispersion due to the transformation of the phytochemicals present in the extract (flavonoids like apigenin, diosmetin, glucoside, luteolin) to quinone as a result of existing oxygen-containing functional groups. The use of this reducing agent increased the C/O ratio from 1.36 to 4.96 as compared to 6.62 using hydrazine. Improvements in the deoxygenation efficiency were later obtained by Hou and his team when another herbal medicine, Lycium barbarum (Chinese wolfberry) extract was used for the reduction of GO using the same reduction parameters [10]. The presence of phytochemicals such as flavonoids, carotenoids, polyphenols, and polysaccharides increased the C/O ratio from 1.36 to 6.5, indicating that Lycium barbarum extract was more efficient in deoxygenation of GO to rGO and a better substitute for hydrazine.

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2.1.2. Microorganisms

Bacteria and fungi have been used as green reducers for the deoxygenation of GO to yield rGO. Bacteria including Shewanella [11], Escherichia coli (E. coli) [12], and Bacillus subtilis [13]; and fungi such as baker's yeast [14] and mushroom (Pleurotus flabellatus) [15] have been studied for their potential use in replacing hydrazine. Escherichia coli (E. coli) served as a green reducer for the reduction of GO in an anaerobic environment by Akhavan and Ghaderi Escherichia coli bacteria reduce graphene oxide to bactericidal graphene in a self-limiting manner [12]. GO solution of 5 mg/ mL was drop-casted on SiO_2/Si substrate and incubated in the presence of E. coli for 48 h. at 37°C. It was found that reduction of GO occurred due to metabolic activity of surviving bacteria with GO sheets acting as sites for adsorption and proliferation of surviving bacteria while bacterially-reduced GO sheets hindered the proliferation of surviving bacteria on their surface. The report indicated a 60% decrease in the oxygen functionalities of GO using E. coli [12]. In the work of Wang et al., Shewanella, a metal-reducing bacterium was used for the microbial reduction of 0.3 g/mL GO solution in a normal aerobic environment for 48 h. under ambient conditions (room temperature) as facilitated by the microbial respiration metabolism of the bacteria cells [11]. Their report indicated a continued increase in the C/O ratio (1.4 to 2.5 after 24 h. and 3.0 after 60 h.) as the reaction proceeded and outstanding electrochemical properties for the microbially-reduced GO. It was also established that the normal aerobic environment was sufficient for GO reduction and the anaerobic environment demonstrated by Salas et al. [16] was not required. Khanra et al. successfully performed simultaneous functionalization and reduction of GO through the enzymes of yeast, nicotinamide adenine dinucleotide phosphate (NADPH) [14]. Reaction of the epoxy functionalities in GO with the amine functional groups in NADPH resulted in stable dispersions of yeast-reduced GO with C/O ratio increasing from 2.2 to 5.9 and electrical conductivity of 43 S/m [14].

2.1.3. Organic Acids

Numerous reports have demonstrated the use of L-Ascorbic acid (also known as Vitamin C) for the reduction of graphene oxide as it produces stable dispersions of rGO [17]–[20]. Zhang et al. [17] prepared stabilized rGO dispersions in water under mild condition using L-Ascorbic acid (L-AA) at room temperature. The L-AA reduced GO showed the removal of significant quantity of oxygen functionalities from GO and a conductivity of 800 S/m for a 24h. reduction which was comparable to result obtained using hydrazine reducer [18]. Works by Fernandez-Merino et al. [19] and Xu et al. [20] compared the reduction efficiency of L-Ascorbic acid with other reducing agents to determine an ideal substitute for hydrazine. Both teams confirmed that L-AA was the best alternative to hydrazine as it yielded highly reduced GO suspensions. Results from Fernandez-Merino et al. indicated that an increase in concentration of vitamin C decreased the time for completing the reaction with an improvement in deoxygenation (C/O ratio of 12.5 and electrical conductivity of 7700 S/m). Also, L-AA-reduced GO were not only dispersible in water, but also in common organic solvents [19]. The vast use of ascorbic acid has been attributed to the minimization in the formation of heteroatoms during its use as a green reducer. Other organic acids demonstrated to show reduction of GO include caffeic acid [21], gallic acid [22], citric acid [23], and lemon juice [24].

2.1.4. Reducing Sugars

Reducing sugars including monosaccharides (simple sugar such as glucose and fructose), disaccharides, oligosaccharides, and polysaccharides have also been explored for use as green reducers for graphene oxide (GO). In the reduction of GO, the oxidized products of reducing sugars serves a dual role of deoxygenation of GO and stabilization of the aqueous dispersions of rGO, thereby serving as a capping agent. In a study, glucose, fructose, and sucrose were tested for their efficient reduction of GO by Zhu et al. [25] using a one-pot synthesis method. They discovered that reduction of GO in the presence of ammonia and at an elevated temperature of 95°C increased the reduction rate and concluded that an elevated temperature and ammonia solution was useful for improvement in the deoxygenation rate of GO. Glucose was found to have the best GO reducing capability than fructose and sucrose with strong and stable electrocatalytic activity towards catecholamines compounds (dopamine,

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epinephrine, and norepinephrine). However, the comparative study discussed earlier by Xu et al. [20] reported GO reduction by ascorbic acid was more effective than glucose even with the existence of ammonia. They reported ascorbic acid produced rGO with highest electrical conductivity of 980 S/m compared to 315 S/m for glucose and 136 S/m for tea polyphenol (TP) but glucose showed greatest improvement in deoxygenation of GO due to the oxidation of aldehyde group in the open-chained structure of glucose by GO. Likewise, Kim et al. reported the use of dextran, a polysaccharide for the reduction of GO to produce biocompatible rGO and rGO-based nanocomposite [26]. The dextran-reduced GO paper exhibited an electrical conductivity of 1.1 S/m which was dramatically increased to 10000 S/m upon 500 ˚C annealing treatment in an inert (argon) atmosphere.

2.1.5. Amino Acids

Amino acids are organic compounds containing thiol (-SH), amine (-NH_2), and carboxyl (-COOH) functional groups. Various amino acids including L-Cysteine [27], L-aspartic acid [28], L-lysine [29], glycine [30], and glutathione [31] have been investigated for their use in deoxygenation of GO. Using L-Cysteine, Chen et al. demonstrated the reduction of GO under mild conditions and discovered that the thiol functional group in L-Cysteine experiences redox reaction leading to its oxidized form, cystine [27]. They reported an improvement in the conductivity of rGO suspension by up to 106 times when compared with pristine GO. Similar work by Tran et al. [28] using thiol-free L-aspartic acid demonstrated an optimized GO reduction process with average conductivity of 700 S/m and good dispersion stability. Bose et al. reported on the dual role of glycine as a GO green reducer and a chemical functionalizer for rGO production under mild conditions [30]. They discovered that the amine group in glycine experiences covalent bonding with GO under refluxing conditions to produce rGO. Removal of oxygen functionalities was verified by an increase in C/O ratio (2.29 for GO to 11.24 for rGO).

Although several other alternative routes to reduction of GO exist, this paper strictly focuses its discussion on the extensively investigated solution-based reduction techniques. Apart from the above-mentioned green reducing agents used in reducing GO, other numerous green reducers for GO exist.

2.2. Green Synthesis of Graphene from Graphite Precursor

Graphene synthesis from graphene oxide requires initial oxidation of graphite as the precursor. Several techniques for oxidation of graphite such as Brodie, Staudenmaier and Hummer have been explored in the review by Adetayo and Runsewe [1]. With the need for eco-friendly processes that does not release toxic gases, the Tour method was proposed by Marcano et al. [32]. However, even with several modifications for improvement in the oxidation methods, graphene produced through this method suffers from significant structural damage in form of defects due to residual oxygen functionalities (even after reduction) that causes some disorder in the electronic structure of rGO. These defects reduce the properties of graphene and limit their application. Thus, researchers have developed protective green means to directly synthesize graphene from graphite. Considering this, the research group of Baek et al. demonstrated the green synthesis of graphene from graphite using the direct Friedel-Crafts acylation reaction [33, 34] and mechanochemical ball-milling technique [35, 36].

2.2.1. Direct Friedel-Crafts Acylation Reaction

Edge-selectively functionalized graphene (EFG) with high level of crystalline graphitic structure at the basal plane are produced using the direct Friedel-Crafts acylation reaction. This reaction proceeds by electrophilic aromatic substitution of graphitic aromatic rings with acyl compounds in a mildly acidic polyphosphoric acid (PPA) and phosphorous pentoxide (P_2O_5) medium. During the reaction, PPA aids in less destructive exfoliation of graphite, dispersion, and functionalization of graphene while P_2O_5 serves as a dehydrating agent. Using this technique, Choi et al. employed 4-aminobenzoic acid (ABA) as a reactive organic molecular wedge in combination with PPA/P_2O_5 medium to successfully synthesize highly crystalline EFG with stable polar solvent dispersions [34]. In their work, ABA organic wedge was selectively grafted to the edges of graphite i.e. the defect sites to produce EFG with an electrical

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conductivity of 20000 S/m after thermal annealing at 900 ˚C under argon atmosphere. Similar work by Bae et al. using 4-ethyl-benzoic acid (EBA) as organic wedge produced EFG similar to that obtained by Choi et al. [33].

2.2.2. Mechanochemical Ball-Milling

Through mechanochemical ball-milling of graphite, edge-selectively carboxylated graphene (ECG) have been synthesized just like the direct Friedel-Crafts acylation reaction technique. Jeon et al. demonstrated the high yield production of ECG by ball-milling graphite in the presence of a carboxylation reagent, dry ice (solid phase CO$_2$) [35]. They reported highly stable solvent dispersion of produced ECG for exfoliation into few layers of graphene nanosheets without the loss of the high crystalline graphitic structure at the basal plane. In comparison with GO, superior conductivity of 1214 S/m was obtained after thermal annealing (decarboxylation) of produced ECG at 900 ˚C under nitrogen atmosphere. In a later study by Jeon et al., [36], they developed edge-selectively halogenated (X) graphene nanoplatelets (XGnPs) by ball-milling with chlorine, bromine, and iodine as halogens (i.e. X=Cl, Br, I; XGnPs=ClGnP, BrGnP, IGnP). They discovered that XGnPs produced possessed good electrochemical performance and enhanced electrocatalytic performance towards oxygen reduction reaction due to the binding affinity of oxygen molecules to XGnPs.

These recently developed techniques towards environment friendly synthesis of graphene from graphite shows greater performance in comparison to methods involving the chemical reduction of GO. This is due to preserved high crystalline graphitic structure at the basal plane which sustains the inherent electronic structure and properties of graphene. With this, high-quality graphene with excellence performance can be produced for use in several applications. A comparative summary of a few green synthesis approaches used to obtain graphene from graphene oxide and graphite is presented in Table 1.

Table 1. Summary of green synthesis processes for graphene production (RT = room temperature)

Category	Reducing agent/method	Reduction/reaction conditions	C/O ratio	Conductivity (S/m)	Ref.
rGO from GO	Baker's yeast	Incubation, 72 h., 35-40ºC, 0.5 mg/mL GO	5.9	43	[14]
	Caffeic acid	Stirring, 2, 12, and 24 h., 95ºC, 0.1 mg/mL GO	7.15	-	[21]
	Caffeine	Sonication & stirring, 12 h., 80ºC, 0.1 mg/mL GO	6.5	-	[37]
	Carrot root	Stirring & refluxing, 72 h., RT, 0.5 mg/mL GO	8.5	-	[38]
	Chrysanthemum flower	Sonication, 24 h., 95ºC, 1 mg/mL GO	4.96	-	[9]
	Dextran	Sonication & stirring, 3 h., 95ºC, 1 mg/mL GO	-	10000	[26]
	E. coli	Incubation, 48 h., 37°C. 5 mg/ mL GO	-	-	[12]
	Eucalyptus leaf extract	Refluxing, 8 h. 80 ºC, 0.5 mg/mL GO	3.47	-	[39]
	Gallic acid	Sonication & stirring, 6 h., 95ºC, 4 mg/mL GO	5.28	36	[22]
	Grape extract	Refluxing, 1, 3 and 6 h., 95ºC, 0.6 mg/mL GO	-	-	[40]
	Green tea	Sonication & refluxing, 30 min, 90 ºC, 0.5 mg/mL GO	-	53	[8]
	Green tea extract	Refluxing, 8 h., 80ºC, 0.5 mg/mL GO	3.04	-	[41]
	Glucose	Sonication & stirring, 2 h., 95ºC, 0.1 mg/mL GO	2.89	315	[20]
	Glycine	Refluxing, 24 h., 95ºC, 0.25 mg/mL GO	11.24	-	[30]
	L-ascorbic acid	Sonication & stirring, 2 h., 95ºC, 0.1 mg/mL GO	5.15	980	[20]
	L-aspartic acid	Sonication & stirring, 3, 6 and 12 h., 90ºC, 0.1 mg/mL GO	-	700	[28]
	L-cysteine	Stirring, 12, 24, 48, and 72 h., RT, 0.5 mg/mL GO	-	0.124	[27]
	Lycium barbarum	Refluxing, 24 h., 95ºC, 1 mg/mL GO	6.5	-	[10]
	Pomegranate juice	Stirring & sonication, 12, 18, and 24 h, 60ºC, 2.5 mg/mL GO	-	-	[42]
	Shewanella	Incubation, 48 h., RT, 300 mg/mL GO	3.0	-	[11]
	Spinach leaves	Refluxing, 30 min, 100ºC, 1.6 mg/mL GO	-	-	[43]
	Sugarcane bagasse	Stirring, 12 h., 95°C, 0.5 mg/mL GO	4.27	-	[44]
	Tea polyphenols	Refluxing, 8 h., 80 ºC, 1 mg/mL GO	3.44	136	[20]
Graphene from graphite	Direct Friedel-Crafts acylation	Stirring, 4-aminobenzoic acid (ABA) in polyphosphoric acid and phosphorous pentoxide PPA/P$_2$O$_5$ medium, 72 h., 130ºC	-	20000	[34]
	Mechanochemical ball-milling	Edge-selectively carboxylated graphene using dry ice (CO$_2$)	-	1214	[35]

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3. GREEN SYNTHESIS OF GEOPOLYMERS

The geopolymers are new class inorganic binders that could be used as low carbon cements for concrete, resins for composite preparation and ceramics for thermal applications; from the early research in 1970s to today, this field has seen significant improvements in its application and synthesis. In early days of geopolymer synthesis the natural occurring aluminosilicate were used for its synthesis at an elevated temperature condition making this process unsustainable [45]; Metakaolin (MK) has been extensively experimented and used to prepare commercial grade geopolymers due to its mineralogical advantages [47-48], [54-83]; in order to prepare MK, kaolinite is thermally heated in a range of 650-750 ˚C to form a dehydroxylated amorphous product [46]. Since this process of dehydroxylation of kaolinite mineral is endothermic, large amount of energy is required to remove these chemically bonded hydroxyl groups from the main mineral structure; hence the process of obtaining the MK (source material) for geopolymers associates with carbon emissions. Furthermore, the elevated temperature curing of geopolymers had become another challenge for its in-situ-cast applications and also added further carbon emission to its production. However with new research findings and exploration, the substitution of MK with industrial wastes containing alumina and silica as a precursor in geopolymers has been widely established and instead of elevated temperature curing, atmospheric curing methods has been implemented with new modifications in process of synthesis [67]. Fly ash (FA), blast furnace slag (BFS), rice husk ash (RHA), calcine sludge (CS), ferrochrome slag (FS), red mud (RM) and such related wastes having silica/alumina or both has been experimented and used widely for making commercial grade geopolymers. The approach in this regards made geopolymers a viable tool for waste utilization with hazardous substance encapsulation promoting green synthesis of materials [45]. Recently, a new class of geopolymer based on iron-rich precursors is also gaining broad attention by the scientific community, Kaze et al. [49] reported the effect of iron-rich minerals in geopolymers and later J. Davidovits and R. Davidovits have clarified the exact role of "Fe" in the geopolymer chain structure [50]. They have described that in the polymeric chain, the Al atoms are substituted with Fe atoms and make poly (ferrosialates) type gel having chain structure like "-Fe-O-Si-O-Al-O-". Since the naturally occurring iron-rich source materials don't contain an adequate amount of silica, Kaze et al. [51] and Kamseu et al. [52] have incorporated additional RHA which is a great source of reactive silica as earlier established [53] and reported improvement in the overall performance of geopolymers. For geopolymeric synthesis of materials an activating agent is required to initiate the process of mineralization; mostly an alkali activating liquid is taken which is a combination of silicates and hydroxides of Na or K [55]. Nevertheless in case of phosphate geopolymers, preferably for ceramic application, a phosphate based acid is used for polymerization, the structures of this group of polymers are similar to that of silicates based minerals but the Si^+ of the polymer is partially or totally replaced by P^+. The major contrast between the silicate based geopolymers and phosphate geopolymers is their syntheses process. Poly(sialate) structured geopolymers and their derivatives are fabricated in alkaline environment, but phosphate geopolymers are by synthesized acid-base reactions [45]. Since the phosphate based geopolymers are synthesized at room temperature conditions, this process of geopolymerization evolved as an eco-friendly option.

3.1. Green Synthesis of Activating Alkali

The sodium based alkali activated geopolymers are most widely accepted for commercial implementations due to its better mechanical and durability properties (mostly in case of construction materials) [54, 55] due to formation of densified and stable gel structures. However the commercial production sodium silicate (Na_2SiO_3) is very energy intensive and also contributes to carbon emissions [56]; for the production, sodium carbonate is heated at a temperature range of 1400 to 1500 ˚C with silica (SiO_2) for calcination as depicted in the reaction below (eq-1).

$$Na_2CO_3 + SiO_2 + \Delta \rightarrow Na_2SiO_3 + CO_2\uparrow \qquad (1)$$

This process of production of Na-silicate also

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involves the burning of fossil fuel to obtain calcination temperature adding further carbons to its synthesis. This negative environmental effect of the production of sodium silicate has lead several researchers to develop alternative alkali activating precursors; essentially possessing similar reaction capability with less carbon footprint. Some of the methods of green synthesis of alkali activators are discussed below.

3.1.1. Silica Fume Modified Activator

Silica fume (SF) is a fine powder of silicon dioxide, which is mostly non-crystalline [57-58]; it is a polymorph of silica generated as a by-product in electric arc furnaces during the production of silicon-based alloys in ferrosilicon or related industries [58]. Due to high reactivity and surface area, this polymorph of silica can be used for the formation of aggressive silicate precursor for geopolymerization in the accumulation with alkali hydroxide (aqueous). Bajza et al. have derived a method of preparing high strength geopolymer composites similar to the Portland cement concrete type, with the help of a binder based on silica fume and sodium hydroxide [59]. Rowseková and Živica also conducted series of experiments regarding the viability of SF based alkaline activators (SF+ NaOH); they have stated that this SF modified activator could be used to synthesize high-performance geopolymer composites [59-62].

3.1.2. Nano Silica Modified Activator

Nano silica (NS) or nano sized silica is another polymorph of silicon dioxide similar to SF; however the particles of NS are in nano meters. Alkaline activators can be developed from NS in a similar way to the NS-type activators. Rodríguez et al. exhibited the suitability of using NS to synthesize alkaline activators for geopolymers and compared various properties of the resulted geopolymer composite (GC) with a conventional GC made with commercially available alkaline activators. NS-modified alkaline activators could be prepared by taking sodium (Na) or potassium (K) based hydroxide (aqueous) with desired molarity; it is suggested that the NS-Na based activator based GC displayed higher compressive strength with a refined pore structure however both the Na and K based NS alkali activator ensue less water demand and low permeability as compared to the GC prepared from the commercial alkaline activator [69].

3.1.3. RHA Modified Activator

Rice husk ash (RHA) is the by-product of rice mills or rice processing units; it's a siliceous material containing 85-95% of SiO_2. Earlier research findings have established RHA as a potential source of silica for both geopolymers and conventional cement based composite [68]. Since RHA is a rich source of amorphous silica [68]; alkali (Na/K) silicate synthesis from it has been well established [54] and commercial grade silicate solutions are also prepared from this. Eq-2 represents the reaction mechanism for the preparation of Na/K silicate from silica rich RHA.

$$2MOH + SiO_2 + \Delta \rightarrow M_2SiO_3 + H_2O \qquad (2)$$

Where M represents Na or K

However, alkali activators from rice husk ash (RHA) can be developed to activate the aluminosilicate precursor material for synthesis of geopolymers. Bernal et al. experimented taking RHA-Na based activating solution with MK-BFS based binder type GC; however the rate of strength gain in GC prepared with RHA based activator had a slow rate as compared to the SF/NS based activators [54]. The less reactivity of silica present in the RHA caused slow rate of silica dissolution causing in a mild rate of gel synthesis mechanism resulting in a slow rate of strength development. Furthermore, fig. 1, illustrates the procedure for obtaining alkali activator solution through environment friendly approaches.

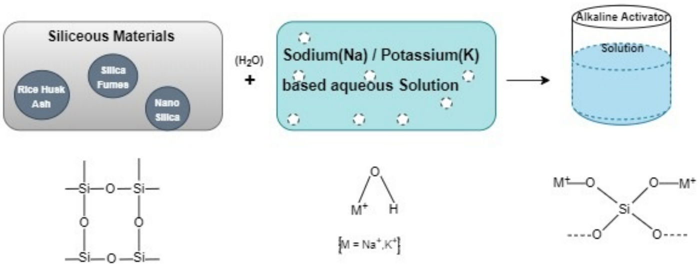

Fig. 1. Green synthesis of alkali activator solution.

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Table 2. Milestones in development and applications of geopolymers.

Decade	Year of invention	Inventors/ Researchers	Major Contributions/Applications/Significance	Ref.
1960	1969	Besson, Caillère and Hénin (French Museum of Natural History, Paris)	Low temperature synthesis of hydrosodalite from various phyllosilicates (kaolinite, montmorillonite, halloysite) in concentrated NaOH solution	[63]
1970	1970	Russian team Berg et al.,	The aluminosilicate kaolinite reacts with NaOH at 100°C-150°C and polycondenses into hydrated sodalite (atectoaluminosilicate), or hydrosodalite. Si2O5, Al2(OH)4 (kaolinite) + NaOH ⇨ Na(-Si-O-Al-O)n (hydrosodalite)	[63]
	1972	Joseph Davidovits (Cordi-Géopolymère, France)	Development of technology based on the geosynthesis by taking kaolinite and quartz (50/50 by wt.) in presence of NaOH solution (aqueous); initially the resulted granules were cold pressed then again hot pressed (thermosetting process) at a temperature 130°C-180°C to obtain a composite preferably having inorganic complexes resistant to fire.	[63]
	1973-1976		Development of Fire-resistant wood-chipboards for various applications.	[63]
	1974	Davidovits and Legrand	"SILIFACE Process" a US patent has been filed explaining the process of making kaolinite based inorganic polymers.	[63]
	1977-1978	Joseph Davidovits	Ceramic applications	[63]
1980	1979	Joseph Davidovits	Introduction of a new terminology "Geopolymers" to properly classify these mineral polymers.	[63]
	1977-1982		Low Temperature Geopolymeric Setting of ceramic (L.T.G.S).	[63]
	1979-1995	Joseph Davidovits	Geopolymeric Binders for composite preparation for several applications.	[63]
	1983		The Invention of Geopolymer High-Strength Cement.	[63]
	1985	Richard F. Heitzmann, Mark Fitzgerald, James L. Sawyer	A hybrid Portland-geopolymer cement was developed. The binder composition described above is blended with Portland cement, or Portland cement modified in ways presently known to the art to provide the high early strength, high ultimate strength compositions. Among the materials which can be included with the Portland cement are fly ash, various admixtures or retarders. The curing temperature was 150° F. to 195° F.	[70]
	1986		Geopolymer composites was used in French aeronautic company Dassault Aviation to make Rafale fighter plane.	[63]
	1987	Nick G. Costopoulos, H. Kent Newhouse	Introduction of fly ash (FA) as a source material to synthesize building materials such as concrete, brick or foamed concrete; the foamed concrete could be broken to small pieces which can be used as light weight aggregates in concrete. Sodium silicate (Na2SiO3) was used along with water as the binding agent; both OPC and FA were used for the composite preparation process whereas the curing condition was atmospheric.	[71]
	1987		A new method for solidifying and disposing of waste in geopolymer complex was developed. The waste was combined and mixed with an alkali-activated silico-aluminate geopolymer complex.	[72]
1990	1991	Joseph Davidovits, Michel Davidovits, Nicolas Davidovits (Institut Géopolymère, France)	A process for obtaining a geopolymer of the alkaline poly(sialate-disiloxo) family has been developed for high thermal applications; alkali silicate was taken as the binding media for the aluminosilicate materials.	[73]
	1992	Bill E. Laney, F. Truman Williams, Ronald L. Rutherford, David T. Bailey	Mostly, this invention proposed to synthesize ambient cured, controlled density, advanced geopolymer composites whose macroscopic physical properties can be shaped for specific applications, over substantial temperature arrays, by careful specifications of dispersed phase components and selective chemical alterations to produce pre-gelled geopolymer resins.	[74]
	1994-2000		Aviation applications; Geopolymeric materials have been chosen for several application in aviation sectors; cargo linings, ceiling, floor plates, dividers and sidewalls, stowage bins, wire insulation, Aircraft cabin materials also have been made with GC due to its fire resistance properties.	[63]
	1994 and 1995		Automotive applications; Geoplymer composites essentially posseses good thermal and shock resistance properties. The Formula-1 team (Benetton) designed a car with geopolymer composites and the performance of the body was excellent due to such unique properties of GC.	[63]

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Table 2. Milestones in development and applications of geopolymers.

Decade	Year of invention	Inventors/ Researchers	Major Contributions/Applications/Significance	Ref.
	1997	Rousekova, I., Bajza, A., Živica, V (Institute of Construction and Architecture of the Slovak Academy of Sciences and Slovak Technical University, Slovak Republic)	Develpoment of geopolymer composites based on SF-blast furnace slag with SF based alkaline activators.	[62]
2000	2004	Hardjito, Steenie E. Wallah, Dody M. J. Sumajouw, and B.Vijaya Rangan (Curtin University, Australia)	Development of Fly Ash-Based Geopolymer Concrete	[75]
	2004	Živica, V, Bajza, A., Rouseková, I. (Institute of Construction and Architecture of the Slovak Academy of Sciences and Slovak Technical University, Slovak Republic)	Green synthesis of alkaline activators from silica fume (SF) for making geopolymers.	[60-62]
2010	2011	Susan A. Bernal, Erich D. Rodríguez, Ruby Mejia de Gutiérrez, John L. Provis & Silvio Delvasto (University of Melbourne, Australia)	Green synthesis of alkaline activators from SF and RHA.	[54]
	2015	P. Nath, P. K. Sarker, V. B. Rangan (Curtin University, Australia)	Development of high strength geopolymer concrete at ambient temperature conditions	[67]
	2017-20	R.C Kaze et al., E. Kamsue et al. and J Davidovits and R. Davidovits (Geopolymer Institute, France)	Synthesis of a new class geopolymer having poly (ferrosialates) type gel and structure like "-Fe-O-Si-O-Al-O-".	[49-52]
	2019	Ahmet Özcan and Mehmet Burhan Karakoç (Inonu University, Turkey)	Utilization of ferrochrome waste such as ferrochrome slag (FCS) and ferrochrome ash (FCA) in geopolymers as a tool for encapsulation of hazardous matter. Özcan et al. used FCS (ground) as a source material for geopolymerization.	[64]
		S. Jena and R. Panigrahi (VSSUT, India)	Jena et al. used FCA (raw) in the place of natural coarse aggregates.	[65]
	2020	J. Mishra, S. K. Das, R. S. Krishna, B. Nanda, S. K. Patro, S. M. Mustakim (CSIR-IMMT and VSSUT, India)	Mishra et al. used FCA as a major part in binder phase of the prepared geopolymers along with BFS at atmospheric conditions.	[66]

4. PREPARATION TECHNIQUES

Researchers across the globe have approached various methods for the fabrication of graphene reinforced geopolymer composites (GRGC). Preparation of such composites would promote the use of green raw materials while reducing the dependency on the conventional raw materials. Saafi et al. established that the incorporation of in-situ reduced rGO sheets (0.35-wt. %) into the geopolymer matrix while utilizing fly-ash (class F) as binders, yielded a rise in flexural strength (134%), young's modulus (376%) & toughness (56%) [76]. GO has been sporadically utilized in the development of GRGCs, as the oxygen bonding molecules of GO tend to cause a combination of structural defects, poor dispersion and restacking in composites [77]. Furthermore,

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Ranjbar et al. introduced GNP’s (1-wt.%) homogenously into the matrix of geopolymer composite which resulted in increased compressive strength (144%), flexural strength(216%) and decreased wettability, whereas samples having more concentration of GNP exhibited gel formation which constrained its usability [78]. Curing conditions and time period play vital roles in determining the final outcome of the composite. According to Yan et al. partial onsite reduction of GO could be achieved through geopolymeric solution composed of KOH at room temperature in a short period of time and the geopolymeric composite with rGO (0.5-wt.%) addition, exhibited a rise in fracture toughness (61.5%) [79]. Likewise, Zhang et al. employed metakaolin as the geopolymer binder and reported gradual improvement in compressive strength of the geopolymer composite with the addition of increased amounts of graphene; allowable to a certain limit [80]. Molecular dynamics simulations designed by Zhang et al. divulged that Si-doping of graphene enhances hydrophilicity of surface while promoting better dispersibility in aqueous media. Moreover, the simulations revealed a chemically bonded interface that is formed by typical condensation reactions resulting in an increase of strength and assists to arrest the formation of voids and cracks in geopolymer matrices [81]. Fig. 2 epitomizes the development of GRGCs; for a wide range of geopolymer binders as well as graphene addititves.

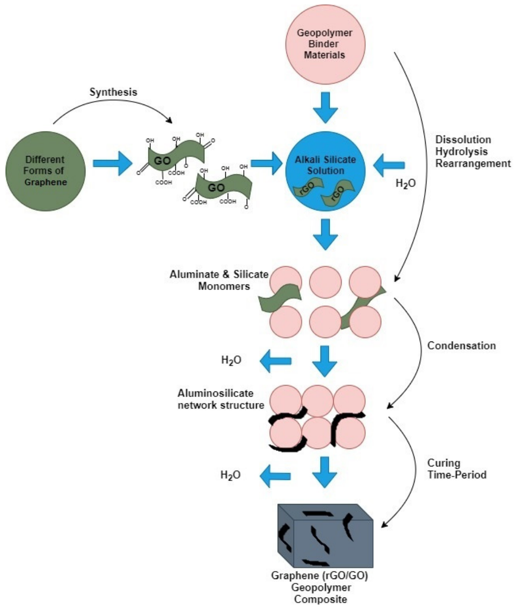

Fig. 2. Progression of GRGC.

5. APPLICATIONS

Graphene based geopolymer composites showcases a breadth of engineering applications. Nevertheless, in this paper, applications related to civil engineering have been discussed more elaborately. Several researchers worldwide have been able to successfully integrate new age graphene and geopolymers, thus providing sustainable alternatives while replacing conventional cement-based composites in the construction sector [76,78,79,82]. Saafi *et al.* demonstrated the improved mechanical characteristics of graphene/fly ash based geopolymeric composite. They incorporated rGO into the geopolymers which acted as void fillers thus exhibiting excellent microstructural properties too [76]. In another paper by the same authors [82], addition of rGO sheets into the fly ash based geopolymeric system was investigated and they reported that the rGO-geopolymer composites exhibited enhanced electro-mechanical properties which is best suited for applications related to civil engineering i.e. buildings, roads etc. Based on the evaluated strain pattern, the composites exhibited self-sensing properties and could be utilized in structural materials. Zhang *et al.* developed a new graphene reinforced geopolymer nanocomposite for degradation of dye wastewater applications. The authors synthesized the nanocomposite by mixing graphene and alkali activated granulated blast furnace slag-based geopolymer (ASG) which was used as photocatalyst for degradation of methyl violet from the wastewater and it’s relatively a new area to be explored [83]. The high degradation of methyl violet attribute to the dense microstructure and pore parameters which is due to incorporation of graphene into geopolymers thus beneficial for degradation. Applications of GRGC are vast expanding and in near future, it might motivate several researchers and industries worldwide. Till date, the civil engineering applications of these green composites are many but still computational and several theoretical studies are required to step forward for real-time applications in larger scale. However, fig. 3 illustrates several other applications of the composite.

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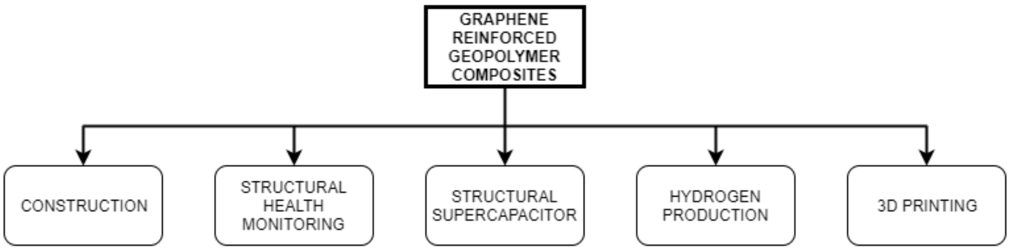

Fig. 3. Various applications of GRGC.

6. DISCUSSION

The study has highlighted the beneficial reinforcement of graphene in the plain geopolymer network. According to the studies, the enhanced properties of GRGC were attained due to the distinctive physical structure and multifarious properties of graphene. The improvement in the mechanical properties (i.e. flexural, compressive, fracture) of the composite is mostly due to the decrease of the overall porosity owing to the interaction between GO and the alkaline solution of geopolymer to produce highly reduced and cross-linked GO flakes [76, 78, 79]. Certain investigations revealed that rGO binds more favourably in the geopolymer matrix, resulting in the increase of the degree of densification of the composite. Longer curing regimes of the composite have also been found to enhance the mechanical properties while decreasing the amorphousness of the material. rGOs wrinkled physical structure in addition with the pull-out, wrapping, and anchoring effects within the geopolymer matrix plays a significantly role in strengthening of the composite. The interlinked surface between rGO and the substrate is evenly mixed, and under the influence of external stress, it will impede the propagation of cracks and enhance the fracture toughness and bending strength of the material [76, 78, 79]. Microstructure evaluation from a number of investigations evidenced that no new compounds are formed through the reaction of graphene in geopolymeric solution. Graphene considerably improves the microstructure of the geopolymer composite, resulting from the pore filling potentiality of graphene additives. Moreover, green extraction of graphene and geopolymer would further lead a step in the development of environment friendly construction materials.

7. CONCLUSION

This review study revealed numerous green methods for synthesizing graphene and geopolymers and facilitate in the development of GRGC. Considering the detrimental effects of conventional synthesizing methods, the study epitomizes several beneficial impacts of adapting eco-friendly synthesizing methods. Preparation of composites from graphene and geopolymer nano materials has been substantially elaborated to provide a brief synopsis over the subject matter. Application of the composite will greatly influence its credibility and assist in perceiving the composite deeply.

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