

Fly Ash Based Self-Cleaning Geopolymer Concrete Using Nanotechnology - A Review

S.K. Maniarasan, V. Santhosh Kumar, P.Chandrasekaran

Abstract: The materials which widely used in construction for building technology is concrete. Anyway, the production of cement releases high amounts of greenhouse gases (CO_2) to the atmosphere that leads to increased global warming. Accordingly, an alternative, sustainable construction material, geopolymer concrete, has been established. Geopolymer concrete seeks a greener alternative binder, which is an innovative construction material that alternates the Portland cement. Introduction of nano-particles in the cement paste to enhance the mechanical properties of geopolymer concrete. The content of concrete has been undertaken to be performed as a self-cleaning material in construction. The self-cleaning concrete properties are encouraging by introducing photocatalytic material of Titania (TiO_2). These photocatalysts in Self-cleaning concrete will be motivated by ultraviolet radiation from the source such as the sun and promote the disintegration of organic particles. Hence, the stainlessness. Of the TiO_2 surfaces can be sustained, and environmental pollution can be reduced. In this review paper, the mechanism, properties, application of both geopolymer and Titania, and health risk hazards are discussed from different author results. In summary, this review paper offers guidance for researchers in the future regarding self-cleaning nanotechnology in geopolymer concrete.

Index Terms : Application of Titania in geopolymer concrete, Nanotechnology in geopolymer, Photocatalytic Geopolymer concrete, Self-cleaning technology.

1 INTRODUCTION

Among the world, India is in the second position to the manufacturing of cement. Portland cement is a primary binder that is commonly used to form a concrete matrix and concrete structure durability[1]. It is essential to introduce the alternative binding material instead of Ordinary Portland Cement. By manufacturing cement, it causes pollution such as emission of CO_2 , for 1 ton of cement production, nearly 1 ton of greenhouse gas causes global warming[2]. In early 1970, a French academician Davidovits introduced the term "Geopolymer." The thermally activated materials such as Industrial byproducts or Meta kaolinite. In Geopolymers, there are three types of polysilates present, which were distinguished by Davidovits, namely polysialates (-Si-O-Al-O), polysiloxosialates (-Si-O-Al-O-Si-O) and poly-disiloxosialates (-Si-O-Al-O-Si-O), as represented in Fig-1[3]. A source of Silicon and aluminum are alkaline activators to form a gel known as aluminosilicates, which are obtained from fly ash and slags as industrial byproducts. A geopolymer becomes binder when an alkaline activating solution is dissolved with silicon and aluminum source material. It forms a molecular chain from polymerizes at a low elevated temperature of about $60\text{-}80^\circ\text{C}$ [4]. Fly ash is readily available worldwide from residual coal combustion, which leads to a proposal of waste management[5]. Geopolymer concrete is superior in mechanical properties, acid resistance in both Sulfuric and Nitric acid, thermal stability, low density, low creep, low shrinkage[6], [7], [8], [9]. It can encapsulate hazardous waste into sustainable building material.

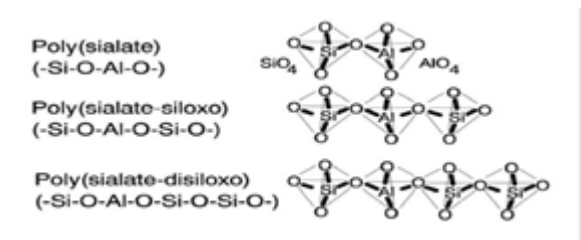
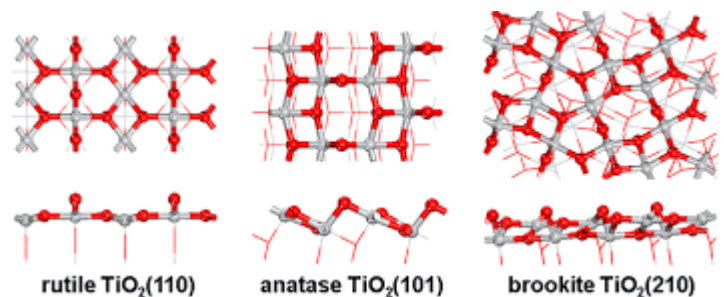


Fig-1. Three types of polysilates[3]

From past decades, the development of Nanotechnology has numerous novels, and the application of Titania is developed. Titanium dioxide (TiO_2) is a safe and inert material that has been used for decades. It is the naturally occurring oxides of titanium. TiO_2 usually has a range of particle sizes between 200-300 nm[10]. Titanium minerals exist in three crystalline forms, such as rutile, which is the stable form, anatase, and brookite[11], [12]. These minerals are available on the earth's crust as rocks and soils. Titania act as a semiconducting material, self-cleansing and de-polluting capabilities, chemical stability, high refractive index, and non-toxic[13]. The UV light on the surface of the content, it activates the photocatalyst reaction, and it will decompose organic materials like dirt, airborne pollutants (VOC, NO_x , and SO_x), chemicals that cause odors and biological organisms (allergens, algae, and bacteria)[14], [15], [16], [17], [18]. To reducing attentiveness of toxic and irritating ozone, a key element of smog that forms on hot, sunny days on the potential of Photocatalytic air cleaning for removing pollutants in urban air, consequently[19], [20].



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Fig-2. Crystalline form of TiO₂ (a) Rutile, (b)Anatase, (c)Brookite[11], [21]



(a) The Dives in Misericordia Church in Rome[29]

In 1973, Wilhelm Barthlott discovered the self-cleaning principle. The Self-cleaning geopolymer concrete has a behavior of green alternatives to our environment[22]. It has a benefit of reducing greenhouse gas emission, economical, eco-friendly, and durable. It has a unique property to withstand high temperatures and capable of resisting acid attack. In concrete material, the addition of Titania can contribute to air purification due to the Photocatalytic process. It keeps the surface clean from pollutants shown in Fig-3. As concluding, the air quality can improve by the degradation of airborne pollutants and also maintain the aesthetic appearance of the building[23].

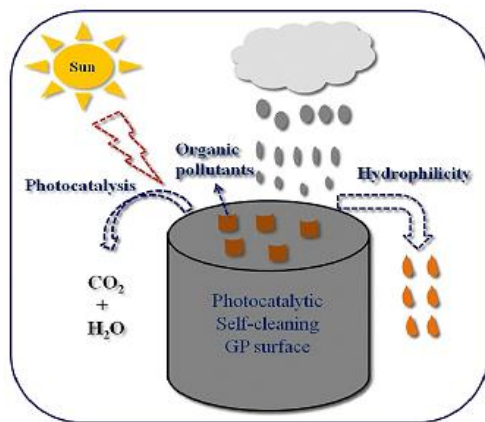


Fig-3. Self-cleaning Geopolymer concrete [24]

2 NANOTECHNOLOGY IN CONSTRUCTION

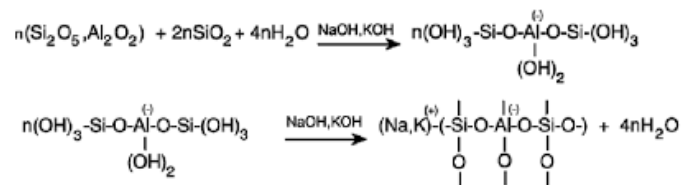
Nanotechnology is the erection and use of functional structures designed with at least one permanent dimension measured in nanometers. To put it from a reasonable position, the typical width of the hair of humans is 50 micrometers. One micrometer is the same length as 1000 nanometers. In explanation, one nanometer is 50,000 times smaller than the width of a human hair[25]. A common misunderstand belief is that nanotechnology is the science imagination, which is called fiction. This proportion, however, could not be falser. Working with technology at such a microscopic scale allows scientists to importantly improve various properties such as physical, chemical, and biological properties[26]. Activity at the nano-scale may not be as foreseeable as those of a larger one. Nanotechnology can furnish the objects that can give a positive footprint in many fields[27]. Nanotechnology is especially applicable in the field of construction, with the strengthened techniques. Coatings and paints can be given insulation. Being used in construction is through the development of materials such as glass, steel, and presently, concrete. There are various ways to subsume nanotechnology into concrete that will significantly improve its basic course of action of properties, such as durability, strength, ductility, and cleanliness. The implementation of the self-cleaning abilities to alter cement blends for the construction of the church "Dives in Misericordia" in Rome for the first time in 1998 [28], [29].



(b)The Milan Expo 2015 - a pavilion with an air-cleaning facade [30]

3 POLYMERIZATION MECHANISM OF GEOPOLYMER

The Fly ash reaction with an aqueous solution containing sodium hydroxide and sodium silicate in their stoichiometric ratio, ensuring in a material with 3-D polymeric chain and ring structure consisting of Si-O-Al-O bonds, has been narrated by Davidovits[3], [4].



The illustrative of geopolymer material formation is normally described by equations (1) and (2). An important different feature in geopolymer concrete emergence is that water is expelled during curing and continuous drying, which is a dissimilarity to the case of Portland cement concrete where the water is absorbed owing to the hydration of calcium silicate calcium oxide. This variation has a major influence on the geopolymer concrete of mechanical and chemical properties of resulting, and heat resistance, water approach, the reactivity of alkali-aggregate, and another form of an attack of chemical as indicated by Kunal Kupwade et al., Brett Tempest et al., and Bondar et al.[3], [31], [32]. The source material, fly ash is mixed with an activating solution that furnishes the alkalinity (sodium hydroxide or potassium hydroxide are often used) needed to release the Si and Al and possibly with an additional source of silica (sodium silicate is most commonly used). During curing, the temperature is a dominant factor,

and based on the source materials and activating solution, heat frequently must be sought to promote polymerization.

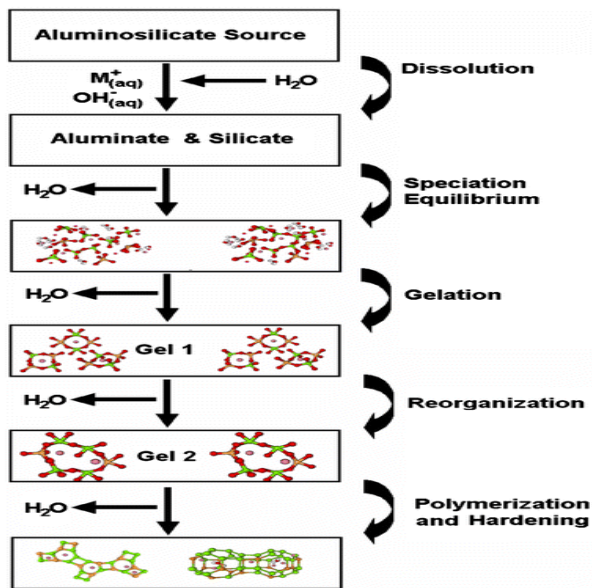


Fig-5. Conceptual model of Geopolymerization [33]

4 PHOTOCATALYTIC MECHANISM OF TiO₂

Photocatalytic activity is the material ability to create an electron-hole pair as a consequence of submission to UV radiation. Photo-Catalysis is acceleration by the attendance of a catalyst. A catalyst does not change in itself or being consumed in the chemical reaction[34]. The photocatalytic oxidation mechanism of NO_x can be represented by Equations (1-9).



Equation (1) dispends the absorption of photons ($h\nu$) of UV light. Radiation by TiO₂ semiconductor, resulting in an electron transfer (e^-) from the valence band to the conduction band with the valence band to initiation of a hole (h^+). The equations (2-4) show the adsorption of the reagent's H₂O, O₂, and NO by TiO₂. The surface of the semiconductor generates adsorbed hydroxyl radicals (OH[•]) from water molecules, as denoted in the equations (5 and 6). Eventually, these radicals are involved in the oxidation of NO and NO₂ to NO₃ (Equations (7-9)). Thus, the nitrates ions are the degradation products of NO_x [34]. Bonato et al. result that the elevated rate of NO_x degradation is observed when there is a 30-50% content of photoactive material. It is not suitable for the environment and feasible to use more volumes of material in financially. A method to estimate the efficiency of photocatalytic of TiO₂ for the oxidation of NO_x gas is evolving. The presence of 30-50% of TiO₂ in mortar is irradiated under a UV light, and there can

be a reduction of 40% of NO. Besides, the integration of photocatalytic agents in the mortar for the construction of various concrete remains is an up-and-coming technique for minimizing pollutants, which can be used on different objects, such as in electric poles for distribution of power[35].

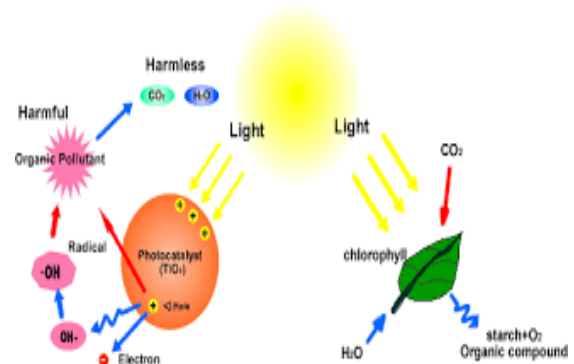


Fig-6. Photocatalytic process triggered by TiO₂ in concrete[36]

5 PROPERTIES OF GEOPOLYMER CONCRETE

5.1 Workability:

In geopolymer concrete, the role of water is essential to workability as much as nominal concrete. The workability of mortar and more superplastic is increased by extra water is added to it. The workability is improved by increases in water contents; at the same time, the porosity of concrete will increase at the elevated temperature of about 60-80°C on the water curing process[7]. The value of slump in geopolymer concrete is in-between 115-135 mm, which determined by the ratio of Na₂SiO₃ to NaOH and the concentration level of sodium oxide. Alkaline soluble calcium level is low, GPC slump loss in case of fly ash with low calcium is resulting equal or less than that of nominal concrete as ordinary Portland cement. Bleeding geopolymer concrete gives less workability than that of nominal concrete. The liquid mass ratio of geopolymer solids is more than 0.22 gives theoretical results, while low water absorption aggregates are used [37]. The use of a naphthalene-based superplasticizer improves the workability property of geopolymer concrete. Around 2-4% of the fly ash mass is the suggested quantity of liquid naphthalene (44% reliable solution) [38], [39]. To increase the amount of fly ash /sand, which leads to improves workability flow. Increases of Na₂O/SiO₂ ratio in the sodium silicate solution, which resultant increases in geopolymer concrete workability [7]. The fly ash ratio and fineness of fly ash, Na₂SiO₃ ratio solution ratio to NaOH and fly ash ratio directly affects the workability [38]. The alkaline activator without the use of sodium hydroxide can reduce the slump value of geopolymer concrete, which may be assigned to Na₂SiO₃ of high viscosity [40].

5.2 Setting time:

There is no effect on the fly ash ratio/Alkaline activator and NaOH ratio [41]. The concentration of NaOH governs the setting time of geopolymer concrete because of the molarity of NaOH effectively delay of setting time [7], which shows that setting time is inversely proportional to molarity of NaOH. Initial setting time happens quickly

by numerous degrees setting on the acid resolution and ash material. The setting time of initial and final varies from 129 to 270 minutes. Higher the curing temperature, the lesser will be the setting time is needed[42], [43].

5.3 Compressive strength:

In geopolymer concrete curing time and curing temperature resulting in the geopolymer concrete compressive strength. The strength of geopolymer concrete depends on the source material fineness, which is smaller than $43\mu\text{m}$. The finest of fly ash increases then the compressive strength also increases. The curing time of 24 to 72 hours and temperature of $60\text{-}90^\circ\text{C}$, which gives the compressive strength of $400\text{-}500\text{ kg/cm}^2$ [44]. By use of activator such as sodium silicate solution ($n=1.5$; $10\% \text{Na}_2\text{O}$), gains more compressive strength [45]. The presence of dissolved and partially polymerized silicon in sodium silicates, which reacts easily and improves the strength of mortar characterizes[46]. Geopolymer concrete of Heat cured LCFA gains full strength after one day cured at $80\text{-}90^\circ\text{C}$, where almost 90% of strength is developed within a few hours [47]. As resulting, ambient environment curing gains high strength and takes a short duration of time while compare with nominal concrete. The increases of binder/sand ratio from 0.25 to 0.5 gains the high compressive strength of geopolymer concrete[48]. Geopolymer concrete contains a higher concentration of sodium hydroxide solution that will produce a higher compressive strength due to NaOH will make good bonding between and concrete paste[49]. Geopolymer concrete compressive strength is about 1.5 times more than that of Ordinary portland cement compressive strength[49], [50]. The compressive strength of geopolymer concrete deprecates on the age factor of concrete[51].

5.4 Durability:

The material durability affects the design period, safety, and mechanical behavior of the materials. Geopolymer concrete is heat resistant, water ingress, sulfate attack resistant, and alkali-aggregate reaction. Geopolymer concrete causes a flash setting when geopolymer concrete consists of calcium fly ash [52]. Due to the better resistant against the aggressive environment, it can be used in the construct of marine structures[50]. The type of chemical solution increases over time, regardless of which the samples were submerged as resultant, increases the durability of geopolymer concrete[53]. On the production of geopolymer concrete, both Na_2O dosage and activator modulus are the essential parameters. The durability of fly ash-based geopolymer concrete is better in terms of carbonization and resistance of chloride, which exhibits strength comparable to ordinary portland cement concrete[54]. Geopolymer concrete is useful in thermal resistant where it resists the heat up to 1200°C with no sign of spalling. The geopolymer concrete, heat resistance decreases with increases of water amount and sodium silicate when exposed to fire and also found that the ' potassium silicate' geopolymer has 1400°C thermal stability, which is comparatively very high[55].

6 PROPERTIES OF TITANIUM DIOXIDE (TiO_2)

To reducing the air pollutants in the environment, the self-cleaning materials are a potential approach to make the polluted air cleaner. The ultra-smooth surface is fabricated

with Portland cement and addition of Titania i.e. Calcium Silicate Hydrates products (C-S-H). Since its ultra-smooth surface Due to the photocatalytic activity of TiO_2 will reduce CO_2 emission in the atmosphere[56]. It cleans itself. It filters pollutants out of the air around has been popping up on new infrastructure and photocatalytic properties. Its residue of contaminants will be washed away by the rain. Titania has the stability to purify the air, water, soil proof such as anti-fogging function, sterilization, and deodorization. The addition of photocatalysts in concrete there will be the creation of environmentally compatible materials which reduces the pollutants and act as self-cleaning surface and reduction in maintenance cost of the buildings. By use of nano titanium dioxide can shows the difference in workability, compressive strength, and setting time of concrete. Due to the presence of Titania to concrete, it will decrease the workability by delays in setting time of blended cement. In compressive strength, there is no extended strength on vital accomplishment in water porosity of concrete and flexural strength with nanoparticles in the lime water [57]. To protect the metal from chloride attack on protection and corrosion under insulation. On coating with Titania on steel structure provides excellent fire resistance [58]. The self-cleaning coating is of two types (i) superhydrophobic and (ii) super hydrophilic [59]. Increase of photocatalytic activity due to the rise in surface area and porosity of concrete [60]. By the use of more amount of TiO_2 in specific, there will slightly decrease in strength and increase of water absorption [24]. The reason for TiO_2 added with cementitious materials to enhance the photocatalytic reaction only due to the requirement of water, O_2 , and UV rays present in sunlight. With the presence of the sun, the organic compound breaks down the particles. If any dirt particles present on the surface, the water will penetrate the solution of rhodamine B in the concrete surface to evaluate self-cleaning activity [22].

7 APPLICATION OF GEOPOLYMER CONCRETE

To sum up, there is large possibly for concrete of geopolymer usage for bridges, by its nature structural elements of precast and decks, as well as retrofits of structure using geopolymer-fiber composites. The technology of Geopolymer is most promote in the implementation of precast due to the relative ease in materials of holding sensitive, for example, high-alkali activating solutions and the need for a restrict curing of high-temperature environment required for many present geopolymers. Other applications similarly, precast pavers and slabs for paving, bricks and precast pipes, etc., [52], [57], [61]. Nowadays, the industries of precast can be used in Geopolymer concrete to enhance production and reduce production in a short period. Also, it reduced the breakage during transportation. In the reinforced concrete structure, which is effectively used in beam and column joints. By use of fly ash occupying geopolymer concrete, which results in no depot to dump the industrial waste like fly ash[62].

TABLE 1

Physicalmechanical properties and environmental impact Portland cement vs GP[24]

Properties		Portland Cement	Geo-polymer	Remarks
Physical & mechanical properties	Setting time	30–300 min	10–60 min	Usually quicker than Portland cement, but depends on source material.
	Compressive Strength	33–53 MPa after 28 days	30–120 MPa after seven days □	Of reactivity and alkali concentration. Strength can be customized by raw material reactivity and alkali concentration. □
	Durability	Moderate	More durable	GP systems, resistant to acid attack is aluminosilicate
Environmental impact	CO ₂ emission	800–900 kg/ton	150–200 kg/ton	The discharge of CO ₂ in GP is during the production of alkali hydroxide and silicate from carbonates.
	Embodied Energy	4000–4400 MJ/ton	2200–2400 MJ/ton	As it uses waste and by-products with no realization of energy.
	Water requirement	600 Liters /ton	450 Liters /ton	Geopolymer doesn't require curing with water as opposed to Portland cement.

Due to the use of a geopolymer, concrete can easily attain high strength, high compressive strength. Mainly this type of concrete is used in rehabilitation and repair works to achieve strength in an earlier stage. Fly ash in geopolymers can be used in the manufacturing of bricks, which gives 90 % of strength within 24 to 48 hours at an elevated temperature of 60-90°C[63].

8. APPLICATION OF TITANIUM DIOXIDE (TiO₂)

The Parameters of photocatalysis, such as mass, the light intensity, wavelength, pH, and temperature, the nature of a photocatalyst, Surface area, Particle Size, surface adsorption, and substrate concentration[64]. TiO₂ nanoparticles applications have used in various fields based on properties involved purification of air, purification of water, decontamination, antibacterial, toothpaste, protection from UV rays, sensing and paint manufacturing, some proceed towards

have been accomplishing, surpassing the surface of TiO₂ by hydrophilic polymer virtual as polyethylene glycol with paint. Better appearance of a surface, the resistance of perfect chemical, reduce in permeability environment[65]. It has superior properties of corrosion, thermally stable, transparency in optical, and simple to the clean surface, anti-skid, anti-fogging, anti-fouling and anti-graffiti characteristics, perfect thermal. The conductivity of electrical, ideal retention of gloss, and other attributes of mechanical virtual as resistance from scratches, anti-reflective in nature, chromate and lead-free, good adherence on numerous materials[66]. The photo convinces hydrophilic conversion of the TiO₂ surface has been exploited commercialized to develop anti-fogging, self-cleaning surfaces for various uses such as fabrics, paints, glass, tile, and cement. Using transparent TiO₂ photocatalysts of moderation of glass and tiles, thin windows films have been used to construct building materials with photocatalytic self-cleaning properties [67], [68], [69], [70], [71]. Active represents the victorious self-cleaning products and is currently used in various private enterprise building in world-wide. A short time ago, the anatase phase was stable up to 900°C when visible-light-active, oxygen-rich TiO₂ has been developed[72]. High stability of thermal of anatase TiO₂ can useful to come about self-cleaning materials. Anatase TiO₂ nanoparticles are coated to produce a tint (paint) that can be an overlay on both rigid and pulpy materials to create a self-cleaning surface. These coatings of superhydrophobic can seek to attire (cloths), notepaper, glass, and steel rebars for numerous self-cleaning applications[73]. The huge prospective of TiO₂ based photocatalytic and self-cleaning materials, as discussed above, can be realized through the rational designing of a photocatalyst to utilize solar and indoor irradiation.

Self-cleaning	Material for residential and office buildings	Elevation tiles, components of kitchen and bathroom, interior furnishings, surfaces of plastic, building stones
	Indoor and outdoor lamps and related systems	Indoor lamp covers of translucent paper, fluorescent lamps coating
	Materials for roads	Soundproofed wall, traffic signs, and reflectors, Tunnel wall
	Others	The material of tent, hospital garments clothes and uniforms and car spray coating
	Indoor air cleaners	Air cleaner in rooms, photocatalyst-equipped air conditioners, and factories interior air cleaner. □
Air-cleaning	Outdoor air purifiers	Highways Concrete, footpaths, and roadways walls in a tunnel, soundproofed walls, and building
Water disinfection	Drinking water	Purification river water, under groundwater, lakes and storage tanks of water
Antitumor activity	Cancer therapy	Endoscopic as like instruments
Self-sterilizing	Hospital Tiles	To envelop the floor and walls of operating rooms, medical catheters by silicone rubber and hospital garments and uniforms

9 HEALTH AND ENVIRONMENTAL RISKS

Humans have been visible to Nanoparticles, which always been existing in the surroundings, and use them. Human health can be constituted by ashes together with other solids dispersed in the air (i.e., aerosols). Since human endocrinology is capable of protecting itself against no longer desired substances in most cases of humans showing to naturally present aerosols. The reticuloendothelial system which usually completely remove viruses and nonbiological particles from the body[74]. For several decades, the nanoparticles of anthropogenic have been produced, mainly because of more industrial growth and the use of combustion-based engines the released number of nanoparticles has increased astronomically in recent years. 40% of particles below 10 nm unexpectedly are faced with at the roadside as high technological advancement has not only increased the things of nanoparticles but also enlarged the nanoparticle's diversity present in the environment[75], [76]. In contrast with the past, there are by now many by-products that contain nanomaterials in them a way of ensuring, such as sunscreen with TiO_2 of nano size and silica fume in concrete (containing micro- and nano-silica particles). There is no harmonized legislation in some countries that already products in the market containing nanoparticles. The submission of living organisms to nanoparticles can be harmful to health. There are two of the main reasons for the danger of nanoparticles are (i) that infiltrate the structure of some cells which disturbing their functions due to their small size of the particles and (ii) nanoparticles can be transformed to several tissues, organs, and inclusive of the brain [74]. After subjection to nanoparticles, some of the following diseases can be observed: (i) oxidative stress[77], (ii) inflammation of tissues and pulmonary diseases[78], (iii) cytotoxicity[79], [80], (iv) DNA damage[81], [82], (v) carcinogenic effects[83], (vi) neurological diseases[84], and (vii) heart diseases[81], [85]. Hazard studies exhibit that ultrafine or nanoparticles operate to the lung produce more dynamic adverse effects in the form of swelling and later tumors compared with large-sized particles of similar composition of chemical at equivalent mass concentrations doses. Properties of surface, such as the chemistry of surface and area, may play an important role in nanoparticle toxicity of particle [86], [87]. The extremely high size-particular overturning of nanoparticles when in-breath as singlet ultrafine particles preferably than aggregated ones also contributes to their effect. Some statement suggests that inhaled nanoparticles, following deposition in the alveolar regions of the lung, mostly get away lung defense (alveolar macrophage) observation and migration from airspace to the lung of artificial additive regions, considered to be a risk for anatomical parts in the respiratory system [88], [89]. Due to a scarcity of health, welfare, and environs facts on nanomaterials, hazard studies need to be executed with a variety of nanoparticle types before any inflexible ending can be extracted about their budding risks. Additionally, as with other particle and fiber types, it is likely that there will be different toxicity results with varying kinds of a nanoparticle. However, all nanoparticle types will not be either benign or toxic [89], [90], [91].

10 CONCLUSION

This review aims to give an overview of the self-cleaning of geopolymer concrete. User-friendly Geopolymer is superior to

Ordinary Portland Cement in terms of economy, ecology, and durability at high temperatures. Geopolymer is additional corrosion resistant and fire resistant and has high strength in compressive and tensile, due to fast curing, which is second hand in the precast industry. Geopolymer concrete possesses all desirable mechanical and structural properties that make it an ideal choice for the erection, and it can be used in repair and rehabilitation works. The practice of industrial waste of fly ash source material can reduce the need for landfills. This application is encouraging to make use of self-cleaning building material. With these developments of application of science to industry, pollutions of air can be shortened because self-cleaning contributes to the termination of VOC's that present in the atmosphere. These days, air pollution is a significant problem in the urban environment that affects the health of living beings. Thus, self-cleaning concrete is a productive substitute to provide a cleaner environment and maintain appearance building. All the time, the growth of cementitious material, radiation of UV from the sun represents one of the solutions to the issues of pollution. In termination, it can be used in the different solicitation, especially cementitious materials, which put up to eco-friendly and towards a green environment. A detailed study and research are required for self-cleaning geopolymer concrete. The researcher has to take mandatory steps to extract sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) solution from the chemical industries waste so that the cost of alkaline solution prescribed for the concrete with geopolymer will be reduced.

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