Development of anti-bio deteriorate sustainable geopolymer by SiO_2 NPs decorated ZnO NRs

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Abstract

In concrete industry, geopolymer acts as an alternative building material of ordinary cement and possess similar/greater mechanical strength and durability, fashioned by industrial by-product; fly ash with alkaline activator. Accompanied by the chemical corrosion, biogenic corrosion is a foremost obstruction in sewer systems, bridge piers, pipelines and offshore platforms. The present works has been given an effort to introduce an anti-bio deteriorate sustainable geopolymer (GM_{ZnO-Si}) through the decoration of spherical nano silica (Si) on zinc oxide Nano-rods (ZnO NRs) surface. XRD, Zeta potential, FESEM, EDS and XPS were hired for the characterization of ZnO-SiO_2 nanohybrid system and applicability of GM_{ZnO-Si} mortar was investigated against microbial species (*E. coli*, *S. aureus*, *A. niger*). MIC/MBC/MFC values, agar plating, Inner permeability assay and ROS generation results exhibited excellent mechanistic approaches, by showing its ability to resist the biogenic degradation. The mechanical and durability activities of the GM_{ZnO-Si} are found considerably higher in respect to conventional control samples. The experimental outcomes propose a promising way to inclusion of ZnO-SiO_2 modified geopolymer for biodeterioration-resistant structure with significant mechanical properties in near future.

Keywords: ZnO-SiO_2 nanohybrid, geopolymer, anti-microbial activity, durability, mechanical properties.

Introduction

Worldwide, concrete is utilized in construction technology from the past some decades where Portland cement is the main ingredient in larger amount. The production of the cement causes the increment of greenhouse gases in the environment (~8% of global CO_2 emission) [**1, 2**]. To overcome the problem, substitute structure composite, Geopolymer, mainly consists of industrial by-products with alkali activators have been introduced nowadays though it needs heat curing above 50 ^{0}C to achieve the desired strengths for longer periods [**3, 5**]. Beside this, the corrosion is the primary issues in any infra-structures (geopolymer, concrete) due to mainly chemical or biogenic process. Biogenic corrosion by different microbial attacks has an massive economic impact universal, meanwhile most water systems and pipelines, swear systems, marine constructions, bridges, tunnels which furthers severely compromises the structural integrity of these building composite components [**6, 7**].

The present study is aimed to prepare a zinc oxide-silica nanohybrid based geopolymer by synthesizing both nanomaterials individually and thereafter attachment of SiO_2 NPs on ZnO NRs surface. Later the ZnO-SiO_2 nanohybrids have been characterized by XRD, Zeta potential, XPS, FESEM equipped with EDS techniques. The consequences of the ZnO-SiO_2 nanohybrid on geopolymer have been further conducted to observe the changes in durability and sustainability with anti-microbial activities against the bacterial/ fungal strains (*E. coli*, *S. aureus* and *A. niger).*

Experimental program

Materials/ chemicals details

Class-F fly ash (FA), River sand (specific gravity 2.52, and fineness modulus 2.38), sodium hydroxide (NaOH), sodium silicate (Na_2SiO_3), deionized water have been used as main constituents of geopolymer mortar. 43 grade Ordinary Portland Cement was taken for control cement mortar. Nutrient Broth (NB) media and Sabouraud Dextrose (SD) media (peptone, beef extract, glucose, yeast extract, NaCl, agar) have been used for *E. coli* (MTCC 1652), *S. aureus* (MTCC 96) bacterial strains and *A. niger* (MTCC 1344) fungal strains growth. Zinc nitrate ($Zn(NO_3)_2$, $6H_2O$), hexamine ($(CH_2)6N_4$], tetraethyl orthosilicate (TEOS), colloidal nano silica and ammonia were taken for the synthesis of zinc oxide silica nanohybrid.

Material synthesis

Synthesis of $ZnO\text{-}SiO_2$ nanohybrid

About 0.04M mixture of zinc nitrate and hexamine was heated at 120°C temperature for 6h to synthesize of ZnO nanorods. A typical 5h sonication and 1h annealing process (450ºC) were carried out for the preparation of $ZnO\text{-}SiO_2$ nanohybrid by using TEOS-ethanol-ammonia solution in presence of pre-synthesized ZnO NRs.

Characterizations

The synthesized dried powder samples were taken under X-ray diffractometer (XRD, D8 Advanced Bruker) with Cu-Kα radiation of wavelength 1.5406°A at 55 kV and 40 mA to identify the phases. The Field emission scanning electron microscope (FESEM) and energy dispersive spectroscopy (EDS) were hired for the surface morphology and elemental analysis purposes. The XPS inspection was carried out using AXIS Supra (Kratos) instrument. The surface charge of the $ZnO\text{-}SiO_2$ samples were done by using Zeta Potential Analyzer (Brookhaven Instruments Corp. Holtsville, USA.

Synthesis of Geopolymer

The geopolymers ($GM_{ZnO\text{-}Si}$, GM_{Si}) were synthesized as following manners;

$GM_{ZnO\text{-}Si}$: FA + Sand + $ZnO\text{-}SiO_2$ + Alkali activator

GM_{Si} : FA + Sand + SiO_2 + Alkali activator.

The FA: Sand = 1:3, FA: alkali activator = 1:0.8 was affixed in both cases. The alkali Activator was made by using 10M NaOH and Na_2SiO_3 and their ratio was taken as 1:2. The $ZnO\text{-}SiO_2$ nanohybrid and nano silica were taken 6% of FA for $GM_{ZnO\text{-}Si}$ and GM_{Si} respectively. About 50mm x 50mm geopolymer mortar cubes were air cured for different days for the measurement of durability and mechanical strengths.

Mechanical Strengths and durability test

The compressive, flexural and tensile strengths were measured by international standard (IS) codes [**7-9**]. The durability in terms of Ultrasonic Pulse velocity (UPV), Rapid Chloride ion Penetration Test (RCPT), water absorption test were carried out by IS codes [**10-12**].

Anti-biogenic deterioration test

All geopolymer samples ($GM_{ZnO\text{-}Si}$, GM_{Si}) were treated with 1N carbonic acid solution until the pH of the sample be (< 8.0). Microbial growth kinetic study in the presence of geopolymer samples was carried out using *S. aureus*, *E. coli* bacterial and *A. niger* fungal strains. The growth kinetics of the bacterial (NB media) and fungal (SDB media) strains were estimated by the optical density (OD) measurements at λ = 620 nm and λ = 595 nm respectively. The Minimum Inhibitory Concentration (MIC), Minimum Bactericidal Concentration (MBC) and Minimum Fungicidal Concentration (MFC) were determined by using 0.1% to 5.0% w/v concentration of each geopolymers in bacterial/fungal growth medium (10^7 CFU ml^{-1}) distinctly. Membrane integrity and inner membrane permeability assay were investigated for *E. coli* (PUC 19 strain) by measuring the OD at λ= 420nm after GM_{Si} and GM_{ZnO-Si} treatment. Reactive oxygen species (ROS) were measured by using DCFHDA, SG (syber green) and PI (propidium iodide). The excitation and emission OD was taken at λ = 490 nm, 520 nm respectively using Fluorescence Spectrophotometer (Motic Image plus 2.0 software) as the ROS level is proportionally related to the intensity of the fluorescence.

Results and discussion

Fig. 1A displays well-defined peaks of $ZnO\text{-}SiO_2$ from XRD which can be indexed to the wurtzite structure of ZnO with lattice parameters of a = 0.325 nm and c = 0.521 nm (JCPDS No. 36–1451). Another appearing peaks at different 2θ, associated with reflecting planes (100), (002), (101), (102), (110), (103), (200), (112) and (201) suggests the formation of wurtzite. In contrast, a little hump is detected at 2θ ~20°, due to the amorphous silica in the hybrid. However, SiO_2 NPs don't influence on the crystallinity of the NRs after the surface modification so, no change is detected of the ZnO NRs characteristic peak position [**13**]. Hexagonal faceting characteristic of wurtzite structure of ZnO very regular spherical shaped silica NPs (~12 ± 3 nm) is decorated on its surface, reflected in the FESEM figure 1D. The elemental analysis confirms main constituents of the hybrid are silicon, oxygen and zinc. The XPS of the Zn 2p spectra of the ZnO and $ZnO\text{-}SiO_2$ in figure 1C suggest a shift in peak position and Zn 2p peak in the $ZnO\text{-}SiO_2$ is found to be shifted by ~ 1.4 eV in higher binding energy side than ZnO. This phenomenon and characterization validates the silica has been attached on the surface of the ZnO NRs which is corelated by other study [**14**].

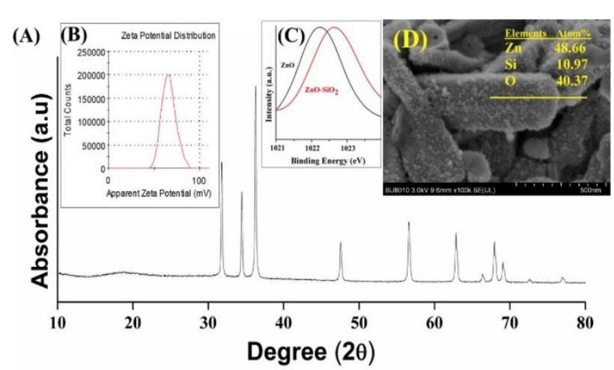

Fig. 1. (A) XRD (B) Zeta Potential (C) XPS (D) FESEM of $ZnO\text{-}SiO_2$ nanohybrid.

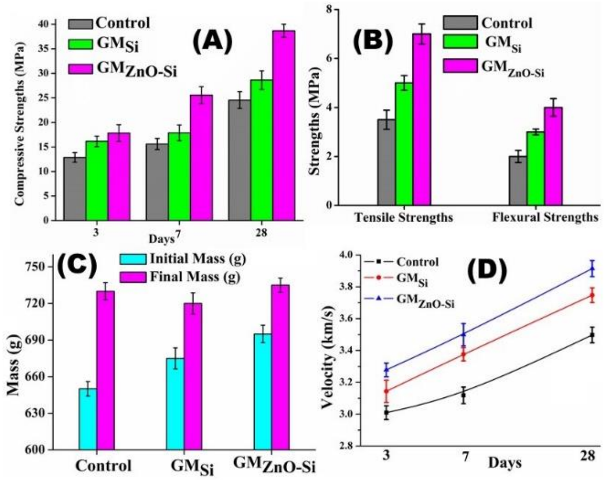

Fig. 2. (A) Compressive (B) Tensile and Flexural strength (C) Water absorption (D) UPV of geopolymers.

The compressive strengths, flexural strength and split tensile strength of the GM_{ZnO-Si} treated mortar samples are significantly enhanced than silica NPs treated GM_{Si} samples **(Fig. 2A & 2B)**. In case of water absorption test and UPV, similar results are observed for GM_{ZnO-Si} samples **(Fig. 2C & 2D)**. The ZnO NRs and the attached silica particle can react with the surrounding binders in interlocking orientation that further make a polymer sodium aluminosilicate in the composite. This long-chain silicate polymer in the matrix finally increased the mechanical strength as well as structural properties [**15**]. The RCPT test exhibits that the lower amount of chloride ions passed through the GM_{ZnO-Si} sample matrix that concludes the more durability **(Fig. 3)**. The results of growth kinetic for each microbial strain are displayed in **Fig. 4** Which demonstrates the populations of exponentially growing microbial strains (*E. coli, S. aureus and A. niger*) were reduced by 99% after 8 h, 6 h and 4 days after the treatment of GM_{ZnO-Si} respectively. The **Fig. 4C** showed the fungal growth inhibition (OD at λ= 595nm) within 72h by GM_{ZnO-Si} exposure. Large numbers of bacterial colonies are found in plate culture technique for GM_{Si} treated samples however, in case of GM_{ZnO-Si}, number of colonies are reduced. Similar result, a particular inhibition zone is also found for GM_{ZnO-Si} treated fungal strain **(Table 1, Fig. 5)**. The MIC, MBC and MFC values indicate very tiny quantity of GM_{ZnO-Si} (0.2mg) can eradicate the (>99%) bacterial and fungal populations **(Table 1)**. These observations also reveal that the MBC for GM_{ZnO-Si} treated bacterial cells are not more than 4 times their respective MIC values, while MFC value is about 0.29 mg for *A. niger* **(Table 1)**. The results indicate that the nano composites are bactericidal rather than bacteriostatic. The level of ROS generation of GM_{ZnO-Si} treated cells were about 4 times higher with corresponds to the control for microbial strains **(Fig. 6A)**. Such microbial growths prevention can be elucidated on the basis of high ROS generation. The optical density of GMZnO–Si treated *E. coli* strain is increased in inner membrane permeabilization assay (**Fig. 7A**) as compared to control and GMSi treated samples. Disturbance of proper transportation in plasma membrane increased ROS level, which influences the inner membrane permeabilization action, as bacteria/fungi, are sensitive to ZnO NRs. The presences of ZnO NRs in the microbial growth media carry on releasing peroxides covering the entire surfaces of the dead bacteria/fungi and this continuous peroxide release leads to higher bactericidal/fungicidal efficacy [**16-18**].

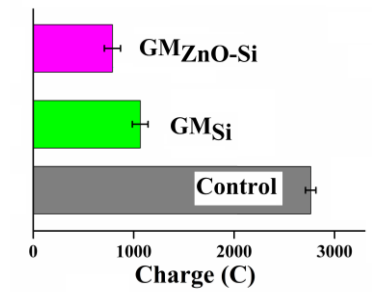

Fig. 3. RCPT result.

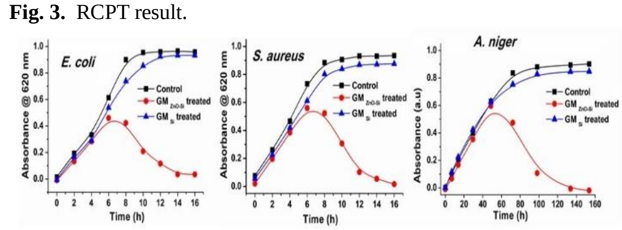

Fig. 4. Mortality studies of microbial strain (A) *E. coli*; (B) *S. aureus*; (C) *A. niger*.

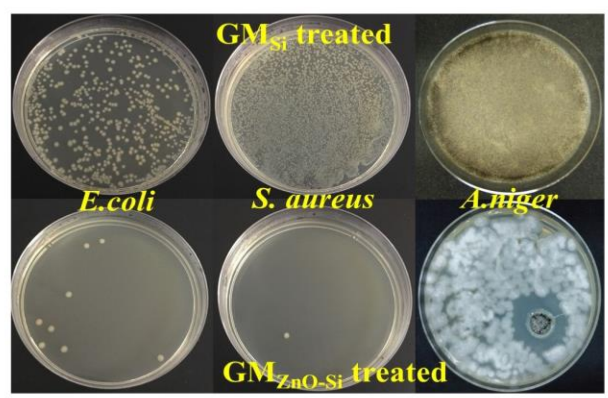

Fig. 5. Antimicrobial study by platting culture.

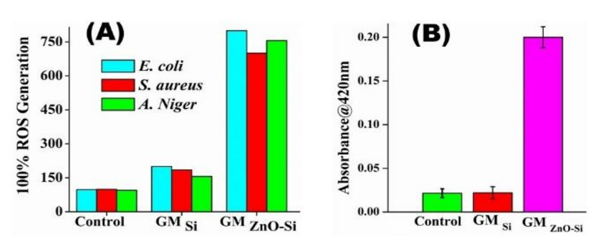

Fig. 6. (A) ROS generation (B) Inner permeability Assay.

Table 1. MIC, MBC and MFC values.

Microbes strains	**GM_{ZnO-Si} (mg/ml^{-1})**		
	MIC	MBC	MFC
E. coli	0.12	0.17	-
S. aureus	0.14	0.23	-
A. Niger	-	-	0.29

Conclusion

Incorporation of $ZnO-SiO_2$ nanohybrid (comprises of spherical shaped silica nanoparticles on the surface of the ZnO nano-rods) into fly ash based geopolymer, a sustainable building composite is established which exhibited high mechanical strength as well as efficient ability to protect from the biogenic corrosion. Conceivable pathway towards anti-microbial activity using GM_{ZnO-Si} has been demonstrated via mortality assay, plate culturing, inner permeability and ROS generation .Such implementation of GMZnO-Si could afford appreciated empathies to develop a new microbial incidence free cementitious composite by avoiding the bio-degradation in construction filed.

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Author's contributions

Dr. Manas sarkar and Dr. Moumita Maiti has degined the work and excuted this study. Professor Shilang Xu has given his valuable guidance. Mr. Malik helped to write manuscript. Authors have no competing financial interests.

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