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Photocatalytic, hydrophobic and antimicrobial characteristics of ZnO nano needle embedded cement composites

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HIGHLIGHTS

- ZnO needles was prepared by using coprecipitation method.
- Homogenous cement-ZnO(%) composites were formed.
- Absorption study of Rhodamine 6G was performed to test photocatalytic ability.
- Contact angle method was used to view hydrophobic nature of cement-ZnO(%).
- Enhanced antimicrobial activity was demonstrated in cement-ZnO(%) composites.

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ABSTRACT

In this work, ZnO nanoneedles were synthesized employing a co-precipitation method. Further, white cement composites were prepared with ZnO filler of 5%, 10% and 15% by weight ratio. With the increasing concentration of ZnO in cement matrix the synergetic effect between ZnO and white cement matrix was observed through FE-SEM and UV–visible. We studied the photocatalytic degradation of pollutant (Rhodamine 6G) using ZnO nano-needles embedded in white cement matrix under ultraviolet irradiation (UV) along with enhanced hydrophobic nature and the antimicrobial property of the cement. The pseudo-first order kinetics was found in a photocatalytic process, and degradation rate constant was enhanced up to 0.147 min^{-1} for ZnO modified cement which was significantly higher than the pure cement (0.037 min^{-1}). Antimicrobial studies were performed using bacterial strains *Escherichia.coli* (JM109, Promega Gram negative), *Bacillus subtilis* (MTCC121, Gram-positive) and fungal strain *Aspergillus niger* (MTCC281) for all the composites. A significant improvement in bacterial and fungal degradation was observed in ZnO modified cement than control and pure cement in a dose-dependent manner.

1. Introduction

Development of functional cement based materials is a new approach towards making novel architecture which can function as antimicrobial, photocatalytic activity and hydrophobicity in addition to the improved mechanical strength [1–7]. Cement is a prime building material which is used for binding. Mostly cementitious structures are brittle and full of capillary voids and having porous space. Therefore, over a period, due to unexpected weather effects such as rainfall and severe conditions like regular temperature cycles which enable freezing and thawing; water infiltration starts to occur in the cementitious structures [8,9]. Continuous water intrusion for a long time into cementitious structures accelerates the gradual decay of the structures. In addition, water intrusion for a long time causes dampness. In the case of indoor environments, the dampness leads moisture and provoke the microbial infections like bacteria, fungi, and insects on the surfaces of cementitious structures. Microbial infections spread hazardous effect on the environment and responsible for adverse health diseases like upper respiratory (nasal and throat) symptoms, cough, wheeze, asthma [10]. Antimicrobial and water repellent/hydrophobic cementitious structures can avoid microbial infections and water intrusions. To built such cementitious structures, we need some specific modification in the cementitious materials by incorporating the suitable fillers in it. Researchers are attempting to improve the cementitious materials by adding or coating some fillers having the hydrophobic and/or antimicrobial and/or photocatalytic properties such that it would be used for sterilizing, deodorizing and self-cleaning without affecting its essential virtue

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which is strengthening the cementitious structures [11–13]. Hydrophobic and photocatalytic properties are widely exploited to improve the durability of different cementitious structures by resisting it from the water intrusion and self-cleaning property. Polyvinyl alcohol and waste paper sludge ash are the admixtures/fillers reported to improve the hydrophobic property of different cementitious materials [14,15]. TiO_2 incorporated cementitious materials have been extensively reported for photocatalytic oxidation and their applications [16]. Several building materials like tiles, glass, block, paints are widely fabricated with photocatalytic properties [17]. However, there are very few reports are available on antimicrobial cementitious materials [18,19]. Presently, sodium polyborate, dichlofluanid, and few others are the common antifungal admixtures which are used to avoid fungal infections in cementitious structures with very limited efficiency [20,21–24].

On the other side, ZnO has shown better antimicrobial efficiency with good photo chemical stability [25–27]. The better antimicrobial efficiency can be attributed to ZnO's superhydrophobicity and the high oxidizing power [28,29]. Under solar irradiation ZnO generate an electron-hole pair in an aqueous system which produces reactive oxygen species (ROS) and leads the microbial death. Different mechanisms are suggested for microbial death like cell membrane damage, lipid peroxidation, and nucleic acid degradation [30,31]. Other desired merits of ZnO are; a) it has high chemical stability under acidic and basic medium, b) biosafety, c) ecologically non-toxic, d) environmentally safe and e) relatively low cost [32]. Therefore, ZnO as a filler in cementitious materials could be a better option for promising functional building material with the solution to improve the hydrophobic and antimicrobial nature and self-cleaning activity under sunlight.

In this work, ZnO nano needles embedded with white cement has been fabricated by varying the ZnO amounts from 5 to 15 wt % in the dry (pre-set) mixture. Further, these cementitious compositions are investigated for hydrophobic nature (required to prevent water intrusion) and photocatalytic properties on carcinogenic pollutant (Rhodamine 6G in water). We believe, these ZnO needles along with the antibacterial and antifungal property in cement-ZnO composite, have a potential application for providing a simple, robust and economical solution.

2. Experimental

The conventional co-precipitation technique was employed to synthesize ZnO nano powder of desired quantity. Zinc nitrate [$Zn(NO_3)_2 \cdot 6H_2O$,(Merk, 99.0%)] of the 0.2 M solution was taken in a beaker. An aqueous solution of NaOH (Merk – AR) of 4 M was added drop wise with a constant stirring to the zinc nitrate solution till the pH 12 of the precipitation was attained. After filtering and washing the precipitate several times with distilled water, followed by acetone, a white powder was obtained. Finally, the powder was dried at 180 °C for 24 h in a vacuum oven. The mechanism of the reaction is given in equations as;

$$Zn(NO_3)_2 \cdot 8H_2O + 2NaOH \rightarrow Zn(OH)_2 \downarrow + 2NaNO_3 + 8H_2O \qquad (1)$$

$$Zn(OH)_2 + 2OH^- \rightarrow [Zn(OH)_4]^{2-} + 2H^+ \underset{\Delta(heat)}{\longrightarrow} ZnO \downarrow + 3H_2O \qquad (2)$$

Further, using the ZnO powder, four white cement-ZnO(%) composite pellets were prepared. In the composite, ZnO concentration was varied from 0, 5, 10, 15% by wt, respectively. During the preparation of composite pellets, first, we mixed ZnO and white cement in the appropriate amount by keeping the total weight of the mixture 1 gram. For homogeneous mixing, the mixture of ZnO and white cement was subjected to rigorous mixing by using mortar and pestle. In the next step, a small amount of water was added to the mixture, so that smooth paste of the composite was formed. Immediately the paste was transferred into the cylindrical cast moulds with the diameter of 12 mm and 2.5 mm height. The cement-ZnO(%) composite pellets were prepared following the procedure reported in SRPS EN 196-7:2010 slandered [33].

To investigate the photocatalytic performance of the white cement-ZnO(%) composite pellets, the solution of hazardous Rhodamine 6G in deionized water with concentration 5 ppm was used as a pollutant. All cement-ZnO(%) composite pellets were dipped into 15 mL of Rhodamine 6G solution, separately. Before starting the experiment, all containers of Rhodamine 6G solution accompanied with composite pellets were subjected to sonication for 2 h. This sonication was required to attain the equilibrium of adsorption-desorption process on the surface of composite pellets with Rhodamine 6G solution. At different time intervals, 1 ml of sample was removed by 1.5-mL Eppendorf tube. All isotherm measurements were made in the dark at 23 °C. During the photocatalytic experiment, we used a chamber with six tubes of Hitachi FL8BL-B light as UV source with the maximum emission of 350 nm and total intensity 210 lx. These lamps are uniformly distributed and fixed to the chamber's on the right, left and top walls at uniform distances. All four containers accompanied with the composite pellets were subjected together into the chamber such that each container equally exposed to the light. Humidity of the chamber was measured 67%.

The photocatalytic degradation process was initiated by exposing the containers with UV irradiation. At a different interval of time, 1 ml of sample was removed from UV chamber to 1.5 mL Eppendorf, separately, from each container. Before removing the sample, each container was sonicated for five minutes to obtain homogeneity in the solution. Finally, the UV–visible spectrophotometer was used for quantifying the degradation of the dye in solution with time subjected to UV irradiation.

The dried ZnO powders and white cement-ZnO(%) composite were characterized by X-ray diffraction (XRD) using a 9 kW rotating anode (Cu Kα) based Rigaku powder diffractometer. Samples were scanned with the scan rate of 2°/minute in the scanning range (2θ) starting from 20° to 80°. Raman scattering was performed on HORIBA (Model-LabRAMHR Evolution) with a grating of 1800 lines/mm, and a Peltier cooled charge-coupled device (CCD) detector working at −60 °C. The green laser (535 nm) was adopted as the excitation source. A microscope from HORIBA (Model-LabRAMHR Evolution) was attached with the spectrometer that focuses the laser light on the sample. The LabSpec-6 software was used for data collection. The micrographs were recorded with FE-SEM Inspect™ S50. Optical absorption and band gap calculation were estimated by using double beam UV–visible spectrophotometers SHIMADZU-2450. The contact angle was measured with a Ramé-Hart Goniometer model 250.

Two bacterial strains *Escherichia coli* (JM109, Promega, Gram negative), *Bacillus subtilis* (MTCC121, Gram positive) and *Aspergillus niger* (MTCC281, Fungal strain) were selected as the prototypical member of their respective class to evaluate the antimicrobial effect of prepared cement. Antibacterial and antifungal tests were performed as per the protocol proposed in the previously reported literature [34]. A stock inoculum was prepared by shake culture for 6 h in sterile LB (Luria Bertani) broth and Yeast extract dextrose for *A.niger*, (YEPD,LB). Working culture of 1×10^6 cells was obtained by diluting the stock with fresh LB media. Suspension (100 mg/ml) of ZnO cement was prepared in sterile water (autoclave). Two ml of microbial suspension was prepared in which ZnO cement suspension was present in 5 mg/ml concentration. A negative control was produced similarly except for ZnO cement. The suspension was allowed to shake for 24 h at 180 rpm in orbital shaking incubator for good contact between ZnO cement particle and bacterial cells. The suspension was dilution plated on after 24 h to assess the viable microbes in the form of colony forming