ISSN: 2319-8753

International Journal of Innovative Research in Science, Engineering and Technology
Vol. 2, Issue 7, July 2013

PRODUCTION OF SELF-CLEANING CEMENT USING MODIFIED TITANIUM DIOXIDE

Jatinder Kumar[1], Anurag Srivastava[2], Ajay Bansal[3]

Assistant Professor, Department of Chemical Engineering, Dr. B.R. Ambedkar N.I.T, Jalandhar, India[1]

P.G. Student, Department of Chemical Engineering, Dr. B.R. Ambedkar N.I.T, Jalandhar, India[2]

Associate Professor, Department of Chemical Engineering, Dr. B.R. Ambedkar N.I.T, Jalandhar, India[3]

Abstract: The present work explores the applications of titanium dioxide and photocatalysis to produce self-cleaning cement. In the present study, self-cleaning cement was prepared using titanium dioxide and white cement. To enhance the performance, titanium dioxide was also doped with Ag, and further used for preparation of self-cleaning cement. The doped titanium dioxide was characterized using XRD and TEM. The surface of prepared cement samples were analyzed using SEM. The self-cleaning ability of the prepared cement samples were evaluated in a photocatalytic activity test under sun-light as well as artificial UV-light. It has been observed that prepared cement samples are able to clean their surfaces.

Keywords: $TiO_{2;}$ Photocatalysis; Cement; Doping; Sun-light

I. INTRODUCTION

The work of Honda and Fujishima in 1970s has led to diverse applications of TiO_2, particularly in the field of photocatalysis. Fujishima and Honda reported the photochemical dissociation of water using TiO_2 photoanode followed by Wrigton et al. [1,2]. TiO_2 is widely accepted photocatalyst because of its chemical and biological inertness, and economically feasible production. Among the three forms of TiO_2, anatase is most photoactive [3]. The photocatalytic activity of anatase TiO_2 can be further improved by incorporation and impregnation methods using metal and non-metals [4]. In the range of higher temperature 600-700 °C, anatase is irreversibly converted to rutile due to its lower thermal stability [3, 5]. Development of the stable anatase TiO_2 at higher temperature is especially one of the biggest challenges, especially with respect to application of self-cleaning coating on ceramic materials such as sanitary wares, glass and tiles, which are produced at higher temperature.

The main applications of photocatalytic anatase TiO_2 include anti-bacterial, self-cleaning and anti-soiling coatings. In practice, surface cleaning of building materials like tiles, fascades and glass panes cause considerable trouble, high consumption of energy and chemical detergents, which results in high expenditure. Ceramic materials coated with cement containing TiO_2 are considered to be very effective against organic contaminants and bacteria [6, 7]. Applications of TiO_2 photocatalysts to construction materials began towards the end of the 1980s. Development of TiO_2 - cementitious binders providing self-cleaning has been carried out in order to enhance aesthetic durability of cementitious materials, particularly those based upon white cement. Most of the external building walls get soiled from automobile exhaust gases, and other pollutants. By coating building walls with TiO_2, the dirt of the wall can be easily washed away by rain due to super-hydrophilic nature of TiO_2, keeping the external building walls clean for a very long time. TiO_2 can also photocatalytically degrade the other pollutants that come in contact with it. In order to verify self-cleaning performances of photocatalytic cements and concretes, tests involving organic substances have been set up mainly based upon the degradation of colour in dyes. Folli et al. (2012) worked on Rhodamine B to check self-cleaning effect in concrete. In the present study, self-cleaning cement was prepared by using titanium dioxide and white cement. To enhance the performance, titanium dioxide was also doped with Ag, and further used for preparation of self-cleaning cement. The self-cleaning ability of prepared cement samples were evaluated in a photoactivity test.

II. EXPERIMENTAL

A. Chemicals

The photocatalyst, titanium dioxide powder, aeroxide© P-25 (mean particle size = 21 nm, and surface area= 55±15 m^2/g) was obtained from Evonik Industries, Germany. Silver Nitrate was obtained from Qualigens Fine Chemical

Limited, Mumbai. Birla White was taken as white cement from local market. Azo dye amaranth ($C_{20}H_{11}N_2O_{10}S_3Na_3$) was purchased from S. D fine-Chem. Limited, Mumbai.

B. Preparation of modified TiO_2 nanoparticle

Impregnation method was used for the modification of titanium dioxide nanoparticles [8]. Modified titania catalyst were prepared with two different concentrations of Ag, 0.2% and 2%. For the preparation of titania doped catalyst with 0.2% Ag, 0.002 moles of silver was dissolved in 50 ml of distilled water in porcelain bowel and 0.998 moles of titanium dioxide was added to the solution. For the preparation of titania doped catalyst with 2% Ag, 0.02 moles of moles silver was dissolved in 50 ml of distilled water in porcelain bowel and 0.98 moles of titanium dioxide was added to the solution. The solutions were stirred well and allowed to settle for 24 hr, the contents were heated well to evaporate all the water. The dried solids were first ground and then calcined at 400 ^{O}C for 6 hrs in muffle furnace.

C. Preparation of cement samples

Total six different types of cement samples were prepared with varying ratio of TiO_2 to cement. TiO_2 was used in doped as well as non doped form. Cement slabs of dimensions 75 × 25 × 5 mm were prepared using white cement, titanium dioxide, and water. The composition of prepared cement samples along with nomenclature is presented in **Table 1.**

TABLE I

COMPOSITION OF CEMENT SAMPLES

TiO_2 to cement ratio (w/w)	**Titanium dioxide**		**Name of sample**
	Nature	**Percent Ag (w/w)**	
0.1	Non-doped	__	C1
0.2	Non-doped	__	C2
0.1	Doped	0.2	C3
0.1	Doped	2.0	C4
0.2	Doped	0.2	C5
0.2	Doped	2.0	C6

D. Characterization

The crystallinity of the titanium dioxide was analyzed with a X-Ray diffractometer (XPERTPro) using Cu-Kα radiation operated at 40 mA and 45 kV at an angle of 2θ from 20-80°. High resolution images of doped and non-doped TiO_2 were obtained using transmission electron microscope (Hitachi 7500). Surface images of cement samples were obtained by scanning electron microscope (JSM 6610 LV).

E. Photocatalytic activity test

The self-cleaning capability of the photocatalytic cement surface was tested both in laboratory photocatalytic reactor (under artificial UV light) and open environment under sunlight. The experiments in photocatalytic reactor were carried out in a reaction chamber of dimension 59 × 28 × 56 cm as shown in **Fig. 1.**

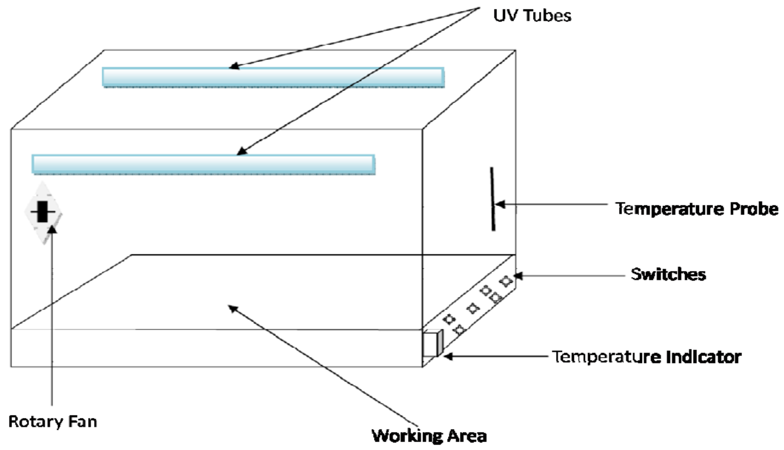


Fig. 1 Photocatalytic reactor

III. RESULT AND DISCUSSION

A. Characterization

XRD analysis was performed to understand the crystal structure of the doped and non-doped TiO_2. Major peaks occurred at $2\theta = 25.32, 27.45, 37.92, 48.14, 54.34, 55.18, 62.94$, and 69.12 in all the XRD patterns as shown in **Fig. 2.** These major peaks correspond to diffraction maxima of anatase. It can be inferred that after modification in P-25 the modified particles are able to retain their anatase form.

TEM was used to further examine the crystallinity and morphology of modified TiO_2 samples. It can give a real space image on the distribution of particles, their surface and shape. **Fig. 3** shows the TEM images of pure TiO_2, TiO_2 doped with 0.2% of Ag, and TiO_2 doped with 2% of Ag. The distribution of silver is shown in the TEM images with the arrows. It has been revealed that the TiO_2 powders in rutile phase consist of both spherical and rod shapes but the particles of TiO_2 powders in anatase phase are mostly of spherical morphology [9]. It can be seen from **Fig. 3** that the particles are mostly of spherical shape, which is an indication of anatase form.

SEM analysis was also performed. **Fig. 4** shows the SEM images of surface of cement slabs of pure white cement, TiO_2 and white cement in ratio of 0.1 and 0.2. The distributions of TiO_2 were shown by the circles in the SEM images. Surface image of pure cement implies that the particles were very closely packed, and some dust and small cracks were observed on the surface. Sample of cement slab with TiO_2 to cement ratio of 0.1 and 0.2 show even distribution of photocatalyst throughout the surface. The cement was well settled along with the photocatalyst. The photocatalyst was very well distributed on the surface.

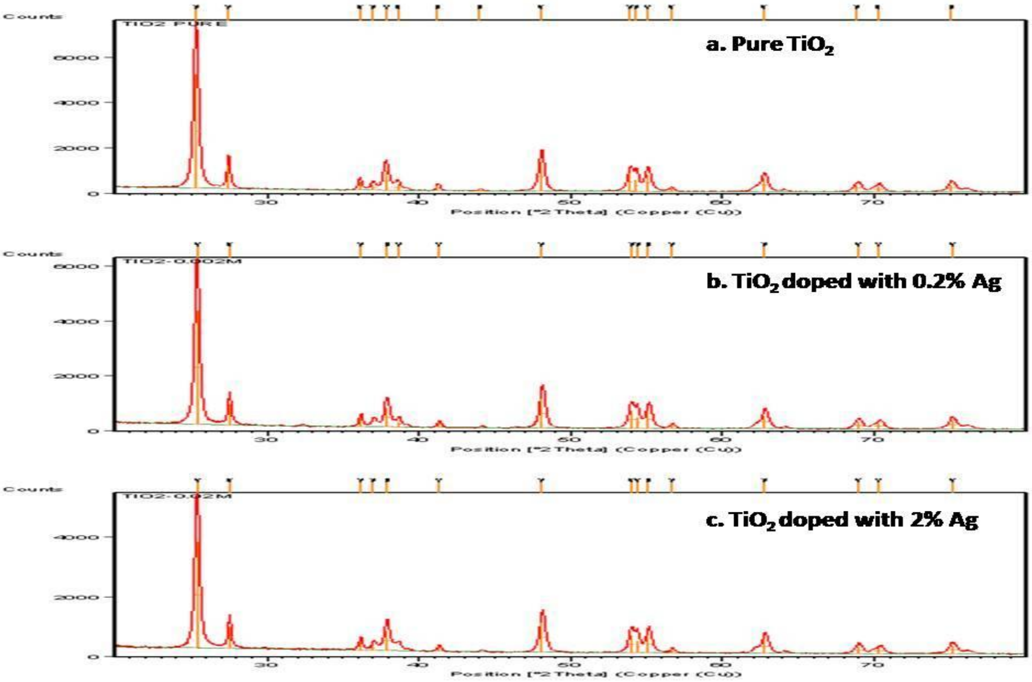
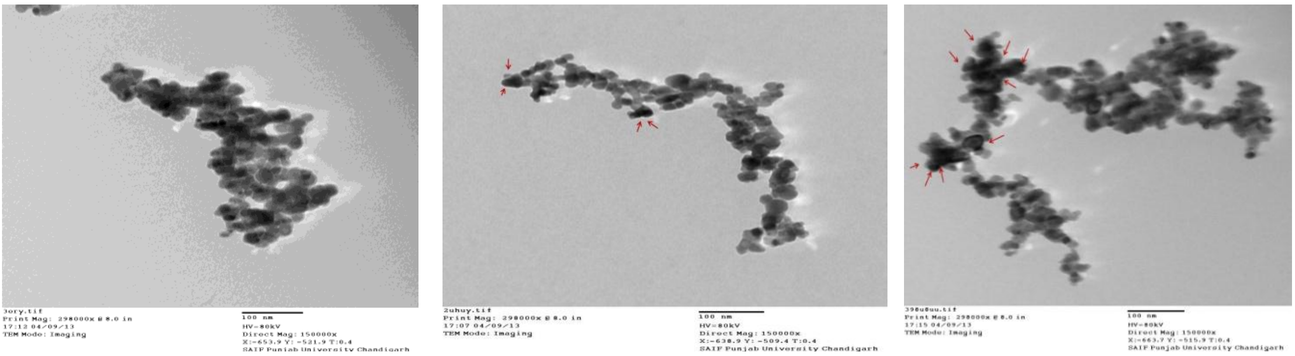
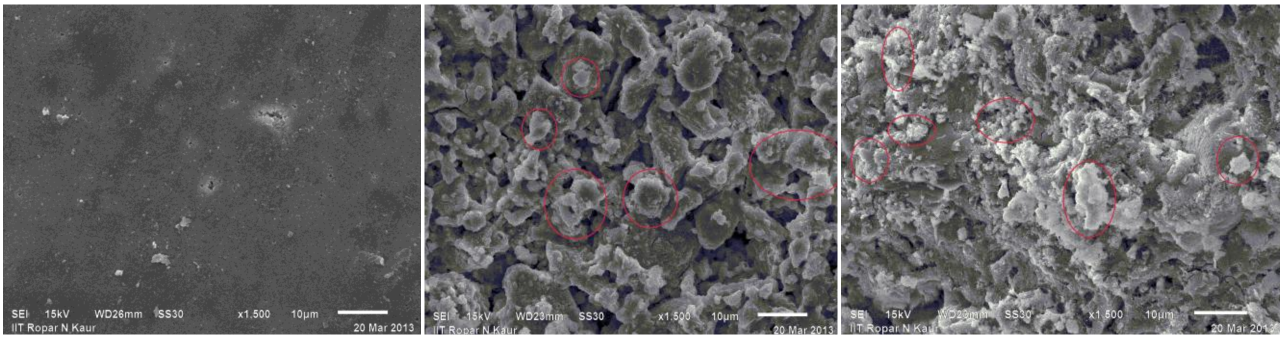


Fig. 2 X-Ray diffraction spectra of (a) Pure TiO_2 (b) TiO_2 doped with 0.2% Ag and (c) TiO_2 doped with 2% Ag



(a) (b) (c)

Fig. 3 TEM images at 150000x of (a) pure TiO_2 (b) TiO_2 doped with 0.2% silver (c) TiO_2 doped with 2% silver.



(a) (b) (c)

Fig. 4 SEM images at 1500x of (a) Cement slab made up of white cement only (b) Cement slab made-up of TiO_2 to white cement ratio of 0.1 (c) Cement slab made-up of TiO_2 to white cement ratio of 0.2

B. Photocatalytic activity test

Total six different types of cement samples were prepared with varying TiO_2 to cement ratio using doped and non doped TiO_2. These prepared cement samples were used to form cement slabs of dimensions 75×50×5 mm. The prepared cement slabs were used to degrade amaranth dye for evaluating degradation efficiency and self-cleaning capability. Degradation of the dye was observed under UV light as well as sun light. **Fig. 5** shows the time effect on degradation of dye using different cement samples under UV light (UV) and sun light (SL).

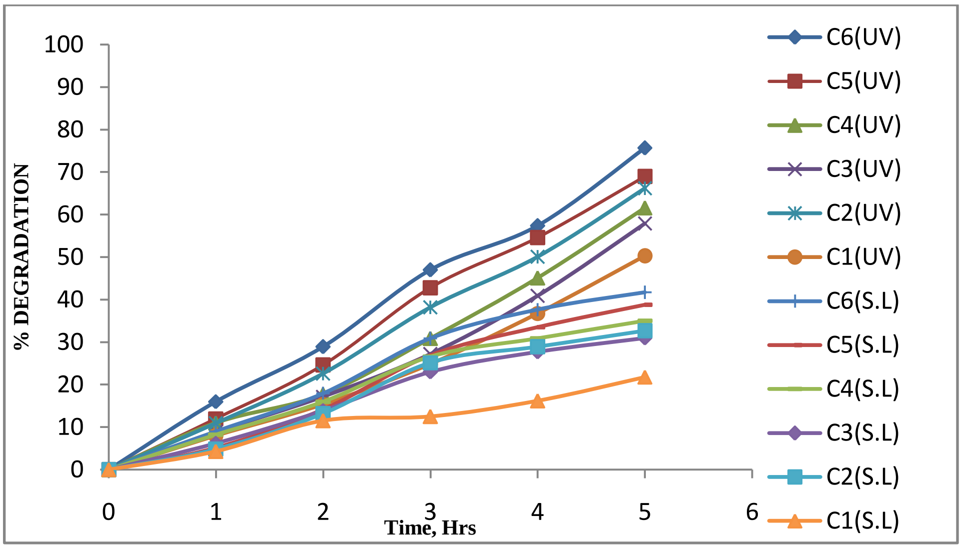


Fig. 5 Percent degradation in doped and non doped samples under sun light (SL) and UV light (UV) with time

Table 2 shows the half-life time and rate constant obtained in all the cement samples. It can be observed from Figure 5 that the undoped samples C1 and C2 show degradation of 50 and 66%, respectively under UV light. Under sun-light C1 and C2 samples show degradation of 22 and 32% respectively. The degradation is more in case of C2 sample having more amount of titanium dioxide. The degradation efficiencies particularly depend on the amount of TiO_2 distributed on the surface. The distribution of TiO_2 in cement slabs having TiO_2 to cement ratio 0.2 (C2) was more prominent than in cement slabs having ratio 0.1 (C1), resulting in the increase in degradation efficiency in case of C2 sample. Degradation of 58, 62, 69, and 76% has been observed in case of doped samples C3, C4, C5, and C6, respectively. It can be observed that cement samples containing doped titanium dioxide (C3, C4, C5, C6) show better degradation than sample containing undoped titanium dioxide (C1, C2) under UV light as well as sun-light. The doping of titanium dioxide with silver prevents the recombination of holes and electrons, which results in better photocatalytic activity. As a results cement samples containing doped titanium dioxide present better degradation. TiO_2 gets active only in UV light due to its larger band gap (3.2 eV). So, the degradation efficiencies were found to be greater in UV light as compared to sun-light (as shown in Figure 5) because sun-light contain very less amount of UV light.

TABLE II
KINETIC DEGRADATION COEFFICIENTS FOR DIFFERENT SAMPLES

	Under Sun-light			**Under UV-light**		
Type of Sample	**RateConst. K (hour^{-1})**	**Half-life $t_{1/2}$ (hours)**	**Correlation coefficient (R^2)**	**Rate Constant K (hour^{-1})**	**Half-life $t_{1/2}$ (hours)**	**Correlation coefficient (R^2)**
C1	0.04	17.33	0.973	0.13	5.33	0.951
C2	0.08	8.66	0.972	0.21	3.30	0.956
C3	0.07	9.90	0.986	0.16	4.33	0.927
C4	0.09	7.70	0.986	0.17	4.07	0.928
C5	0.10	6.90	0.983	0.23	3.01	0.967
C6	0.11	6.30	0.986	0.26	2.66	0.948

Degradation on TiO_2 surface take place by photocatalytic mechanism (TiO_2 sensitized photoreaction) as well as dye sensitized pathway [10]. In the first mechanism light activates TiO_2 through promotion of electrons from valence band to conduction band. Adsorbed water and oxygen react with valence band positive holes and conductance band electrons, respectively to generate hydroxyl radicals, HO·, which ultimately degrade the adsorbed dye. In the dye sensitized mechanism, electrons in the HOMO (Highest occupied molecular orbital) level of the dye undergo transitions to the LUMO (Lowest unoccupied molecular orbital) level, and these electrons subsequently injected into the conductance band of TiO_2. These electrons are then used by oxygen to generate oxidative species, which degrade the already partially reacted dye. Dye – sensitised pathways are predominant when the system TiO_2/amaranth is irradiated with visible light. The lower energies available from visible light are insufficient to induce photo-activation of TiO_2, but they can lead to dye sensitisation and degradation of colour by this mechanism.

IV. CONCLUSION

The current work explores the feasibility of development of a self-cleaning cement surface. It has been observed that nanoparticles of TiO_2 retain their anatase form after doping with silver. Cement sample containing doped TiO_2 shows better degradation efficiency than cement samples having non-doped TiO_2 in case of sun-light as well as UV light. Cement slab having TiO_2 (doped with 0.2% Ag) to cement ratio of 0.2 show the maximum degradation of 76%. TiO_2 also enhances the degree of whiteness of the white cement. TiO_2-Cement slabs having TiO_2 (doped with 2% Ag) to cement ratio 0.2 shows maximum efficiency of degradation of colour on the surface as compared to other samples. Application of TiO_2 photocatalysis to white cement provides an efficient strategy to obtain self- cleaning cement surface, which works simply with the support of sun-light, atmospheric oxygen and water present as humidity or rain water as well.

ACKNOWLEDGEMENT

The authors thank Evonik Industries, Germany for kindly providing P-25 TiO_2 for the present research work.

REFERENCES

[1] Fujishima, A., and Honda, K., “Electrochemical photolysis of water at a semiconductor electrode”, Nature., Vol. 238, pp. 37-38, 1972.
[2] Wrigton, M. S., Ellis, A. B., Wolczanski, P. T., Morse, D. L., Abrahamson, H. B., and Ginley, D. S., “Efficient photoassisted electrolysis of water at zero applied potential”, American Chemical Society, Vol. 98, pp. 2774-2779, 1976.
[3] Periyat, P., Divya, A. S., and Warrier, K. G. K., “Photocatalytic cement by TiO_2 addition”, Material Science Forum., Vol. 712, pp. 65-72, 2012.
[4] Behnajady, M. A., Modirshahla, N., Shokri, M., and Rad, B., “Enhancement of photocatalytic activity of TiO_2 nanoparticles by silver doping: Photodeposition versus liquid impregnation methods”, Global Nest Journal, Vol. 10, pp. 1-7, 2008.
[5] Pillai, S. C., Periyat, P., George, R., McCormack, D. E., Serry, M. K., Hayden, H., Colreavy, J., Corr, D., and Hinder, S. J., “Synthesis of high temperature stable anatase TiO_2 photocatalyst”, Journal of Physical Chemistry C., Vol. 111, pp. 1605-1611, 2007.
[6] Zaleska, A., “Doped-TiO_2: A Review”, Recent Patents on Engineering, Vol. 2, pp. 157-164, 2008.
[7] Folli, A., Pade, C., Hansen, T. B., Marco, T. D., and Macphee, D. E., “TiO_2 photocatalysis in cementitious cement: Insights into self cleaning and depollution chemistry”, Cement Concrete Research, Vol. 42, pp. 539-548, 2012.
[8] Sahoo, C., Gupta, A. K., and Pal, A., “Photocatalytic degradation of Crystal Violet (C.I. Basic Voilet 3) on silver ion doped TiO_2”, Dyes and Pigments, Vol. 66, pp. 189-96, 2005.
[9] Thamaphat, K., Limsuwan, P., and Ngotawornchai, B., “Phase characterization of TiO_2 Powder by XRD and TEM”, Natural Science, Vol. 42, pp. 357-361, 2008.
[10] Rehman, S., Ullah, R., Butt, A. M., and Gohar, N. D., “Strategies of making TiO_2 and ZnO visible light active”, Journal of Hazardous Materials, Vol. 170, pp. 560–569, 2009.