



Comparative Studies on Polyacrylic Based Anti-Algal Coating Formulation with SiO₂@TiO₂ Core-Shell Nanoparticles

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Received: 13 January 2018;

Accepted: 28 February 2018;

Published online: 29 March 2018;

AJC-18852

In the present study, we developed anti-algal coating formulation with silica (SiO₂), titania (TiO₂) and silica-titania core-shell nanoparticles individually. This core-shell nanoparticle was formulated because of silica is a hard material that provides the mechanical strength and shell TiO₂ on core silica can impart the antimicrobial property of material. These nanoparticles were prepared through sol-gel process and peptization process and characterized by dynamic light scattering, UV-visible spectrophotometer and X-ray diffraction. Particle size was measured 90 nm for silica nanoparticle prepared through sol-gel process. TiO₂ nanoparticle size was measured 107 nm prepared through sol-gel synthesis and 77 nm prepared through peptization process. Particle size of silica-titania core-shell nanoparticle was measured 240 nm prepared through sol-gel process and 144 nm from peptization process. The coating formulation were developed with the above nanoparticles individually and nanoparticle concentration was maintained at 4 % (wt) in polyacrylic binder. These coatings were applied on bricks for anti-algal testing against green algae and mixed algae. Optical density was measured of these samples at 665 nm up to 120 h and observed that nano-coating developed with silica-titania core-shell nanoparticle prepared through peptization process has shown good anti-algal effect as compared to nano-coating developed with silica-titania core-shell nanoparticles prepared through sol-gel process.

Keywords: SiO₂@TiO₂ core-shell nanoparticle, Nanocoating, Polyacrylic, Algae.

INTRODUCTION

Man made surfaces like roof tiles, buildings, *etc.* is receiving increased attention as a major ecological and potential health problems [1-3]. The incorporation of biocidal agents into engineered polymer-based nanocomposites has led to the development of versatile antimicrobial materials that are useful for a wide variety of packaging, biomedical, coatings and general use applications [4,5]. Antimicrobial nanocomposites based on titania (TiO₂) have been actively investigated in recent years [6-9]. Upon photo-activation of the oxide component, the biocidal action is a result of modulation of charge (electron-hole) carriers at the interface of external surface of the material, yielding potent and long-lasting capabilities when the dispersion of the inorganic phase and organic-inorganic interfacial contact are optimally achieved [10-12]. Titania has substantial advantages over both chemical and metal based systems [13,14]. Titania nanoparticles have a broad spectrum of activity against microorganisms, including gram-negative and positive-bacteria, algae and fungi, which is of particular importance for multiple drug resistant strains [13,14]. More importantly, titania-polymer nanocomposites

are intrinsically environmentally friendly and exert a non-contact biocidal action. Therefore, no release of potentially toxic nanoparticles (with unpredictable effects on human health) to the media is required to achieve disinfection capabilities [15,16].

In this paper, we are aimed to analyze the anti-algal effect of polyacrylic (due to presence of poly-acrylic high durability implies resistance to the effects of UV degradation from the sun) based coatings that contained silica, titania and silica-titania core-shell nanoparticles individually. This core-shell formation improved antimicrobial property of coatings better than only titania coatings and makes this structure thermally stable. This core-shell structure improves the strength of the coating (due to high mechanical stability of silica nanoparticle) as well as anti-algal property. Only using TiO₂ nanoparticle is costlier than this silica-titania core-shell nanoparticle. This core-shell formation improves the surface area to kill algae. In present study, two type of procedure were used to form core-shell nanoparticle one is sol-gel and other is peptization process for better analysis purpose and peptization process gave better particle size at low processing temperature as compared to sol-gel synthesis [17-19].

EXPERIMENTAL

Titanium tetraisopropoxide (TTIP) and tetraethyl orthosilicate (TEOS) was purchased from Sigma Aldrich Chemicals Pvt. Ltd. (India). Ethanol was purchased from Merck (India). Acetone and isopropyl alcohol were purchased from Fischer Scientific (India). Ammonium hydroxide from Qualikems Fine Chemical Pvt. Ltd. (India) was purchased. Poly acrylic binder was purchased from Dalton Chemicals Pvt. Ltd. (India).

Particle size of prepared nanoparticles was measured by dynamic light scattering using Malvern instruments (Zetasizer Nano S-90). X-ray diffraction was carried out using Bruker D8 Focus. UV-visible spectrum of prepared nanoparticles have been analyzed using UV 1800 Shimadzu UV spectrophotometer. The algal growth (absorbance) was measured at 665 nm (A665 nm) using UV-visible spectrophotometer (Shimadzu UV-1650, Japan).

Preparation of silica nanoparticles using sol-gel method:

Tetraethyl orthosilicate (TEOS) was used as a precursor for preparation of silica nanoparticle. It was prepared from 8 mL of TEOS in 100 mL of ethanol and 35 mL of deionized water. This solution was stirred for 40 min and after that ammonium hydroxide was added dropwise to maintain pH at 10. This solution was kept for 1 day and centrifuged it at 8000 rpm for 5-10 min. After centrifugation material was dried at 100 °C overnight and calcinated at 650 °C for 2 h.

Preparation of titania nanoparticles using sol-gel method:

Titanium tetraisopropoxide (5 mL) was added in isopropyl alcohol and water 1:1 ratio. This solution was sonicated for 20 min, after this 5 mL of ammonium hydroxide was added dropwise under sonication for 40 min to maintain the pH of

solution at 9 and centrifuged at 8000 rpm for 10-15 min, white precipitate was obtained. This precipitate was washed with ethanol and acetone. After 1 h air dry material was dried at 100 °C overnight and calcinated at 500 °C for 4 h.

Preparation of titania nanoparticles using peptization method:

In a typical peptization process, a specific amount of titanium tetraisopropoxide (2 mL) was added to 50 mL of distilled water under constant stirring. Within a few minutes, a white suspension was formed and then coagulated titanium oxide was precipitated. To this titania gel, 1 mL of nitric acid was added. The resulting suspension was stirred for 4 h at 70 °C. After this, whole material was dried at 70 °C for overnight.

Preparation of silica-titania core-shell nanoparticles using sol-gel method:

Same procedure was followed as described above (preparation of titania nanoparticles through sol-gel process) for preparation of silica-titania core shell nanoparticles, in presence of 2 g of silica nanoparticle prepared through sol-gel process.

Preparation of silica-titania core-shell nanoparticles using peptization process:

For preparation of silica-titania core shell nanoparticles (peptization process), same procedure was followed as described above (preparation of titania nanoparticles through peptization process) in presence of 2 g of silica nanoparticle prepared by sol-gel process (Fig. 1).

Coating formulations: Polyacrylic coatings were applied on bricks with silica, titania and silica-titania core-shell nanoparticles individually prepared through both processes *viz.*, sol-gel and peptization. Nanoparticle concentration was maintained at 4 % (wt) in coating formulations (this concentration have shown best anti-algal effect) for anti-algal testing against green and mixed algae.

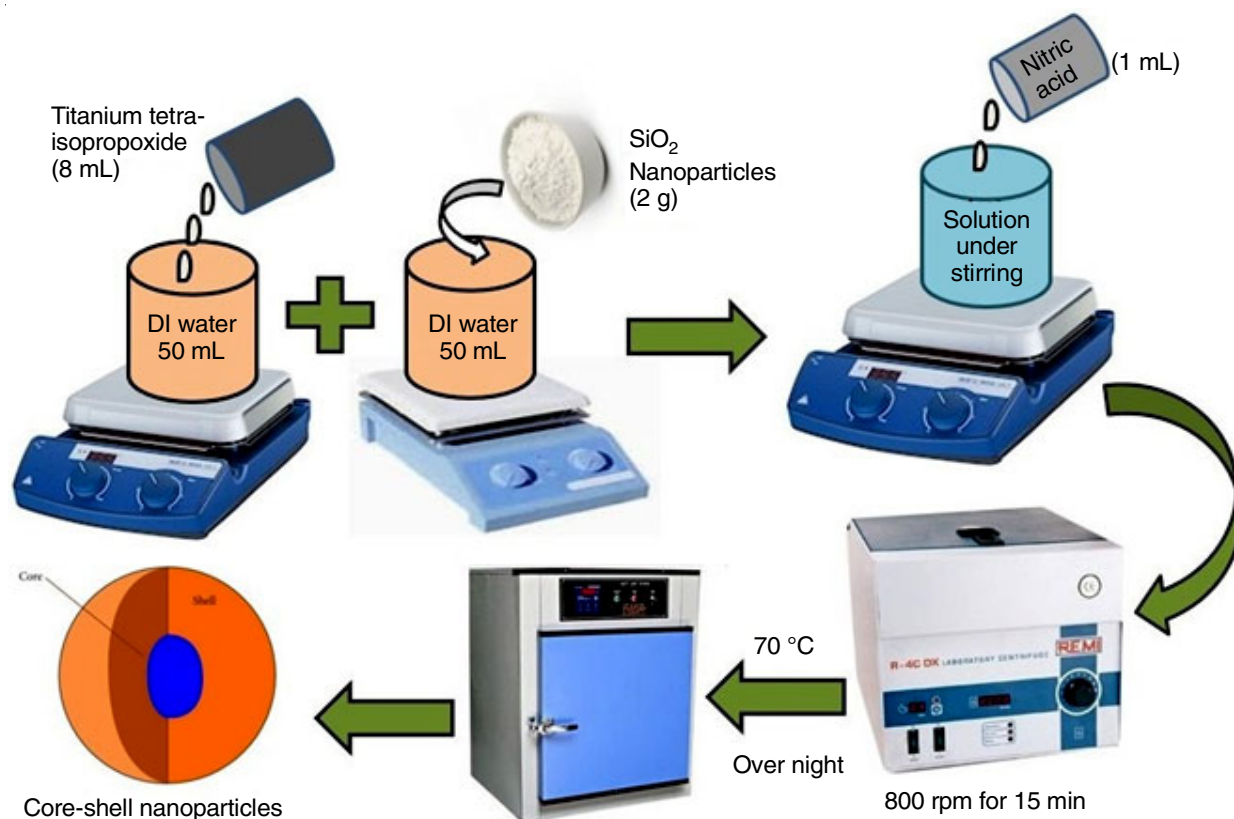


Fig. 1. Preparation of silica-titania core-shell nanoparticles (peptization process)

Algal biomass culture and growth conditions: A culture of green algae *C. pyrenoidosa* and combination of green algae (*C. pyrenoidosa* and *Oedogonium* sp.) were grown photoautotrophically in sterile Fogg's media. The cultures were grown in 1000 mL Erlenmeyer flasks with 500 mL medium at 25°C with fluorescent illumination (40 watt, white light). The algal growth was measured at 665 nm (A665 nm) using UV-visible spectrophotometer.

RESULTS AND DISCUSSION

Particle size of prepared core-shell nanoparticles were observed 240 nm using sol-gel synthesis and 144 nm from peptization process with silica particle (core) size of 92 nm. It indicates that thin coating of TiO₂ layer (26 nm) was formed on core-silica in peptization process as compared to sol-gel process. Even titania nanoparticles prepared individually through sol-gel and peptization processes produced the particle size (dia) of 107 and 77 nm (Fig. 2).

UV-visible analysis was carried out in the region of 200–700 nm and absorption peak at 330 nm was obtained for TiO₂ and SiO₂-TiO₂ core-shell prepared through sol-gel process and 310 nm for both in peptization process. This result confirms the coating of TiO₂ on core silica and thus formation of core shell structure (Fig. 3).

X-Ray diffraction (Fig. 4) also confirms the formation of core-shell nanoparticles in both methods, sol-gel and peptization. Silica nanoparticle have shown broad peak (amorphous nature) at $2\theta = 15^\circ$ ($hkl=100$) and titania nanoparticle have shown sharp peaks (crystalline nature) at $2\theta = 25^\circ, 37^\circ, 46^\circ, 55^\circ$ ($hkl = 110, 111, 211, 220$). In nano core-shell XRD, one broad peak was obtained at $2\theta = 15^\circ$ ($hkl = 100$) which shows the presence of core material silica and other sharp peaks at $2\theta = 25^\circ, 46^\circ, 55^\circ$ ($hkl = 110, 211, 220$), indicates the presence of TiO₂ nanoparticles.

Table-1 shows the absorbance peak of free nanoparticles at 665 nm (120 h) for anti-algal testing (Figs. 5 and 6). Coating formulation were developed with polyacrylic at different

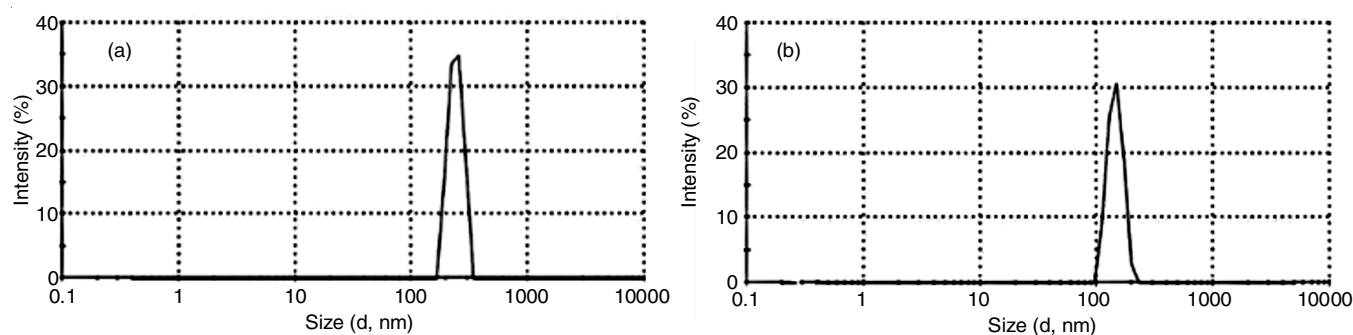


Fig. 2. Dynamic light scattering of silica-titania core-shell nanoparticles prepared through (a) sol-gel process (b) peptization process

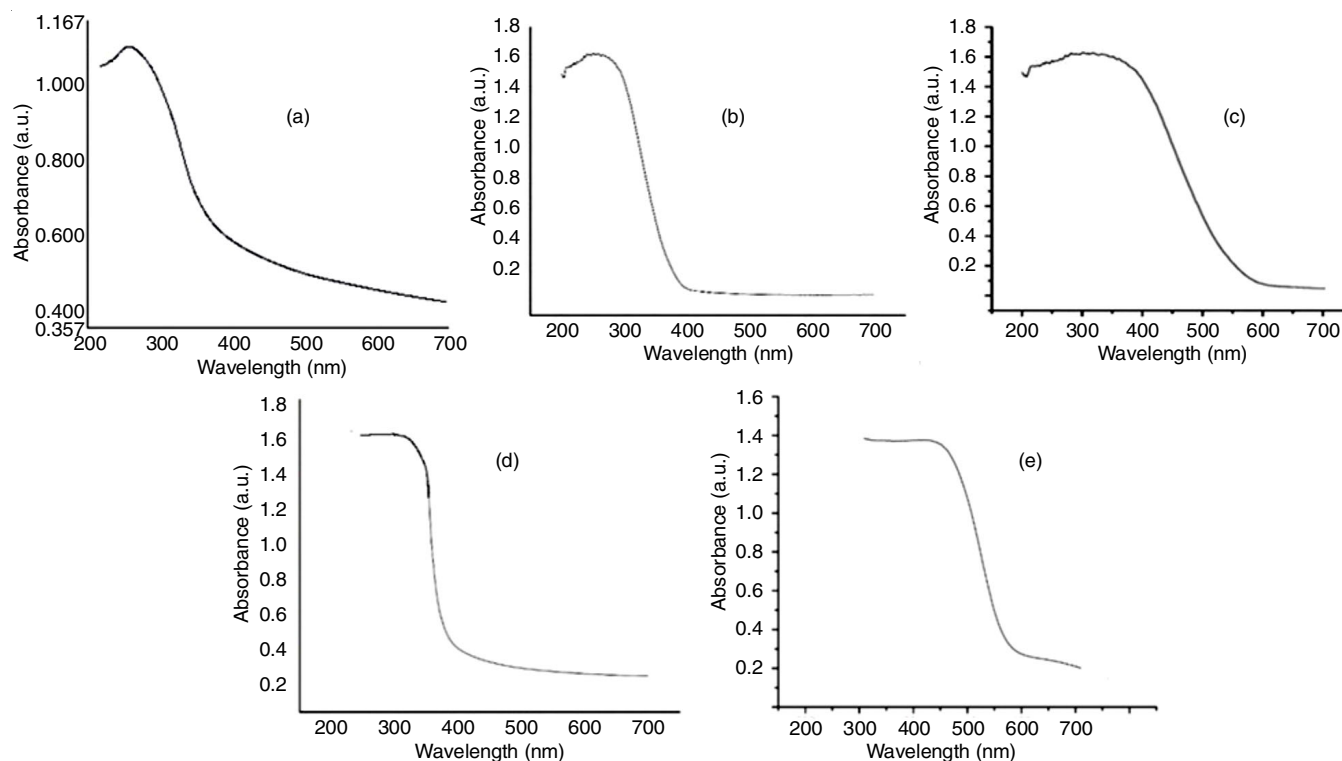


Fig. 3. UV visible spectrum of (a) silica nanoparticles (b) TiO₂ nanoparticles (peptization process) (c) silica-titania core-shell nanoparticles (peptization process) (d) TiO₂ nanoparticles (sol-gel process) (e) silica-titania core-shell nanoparticles (sol-gel process)

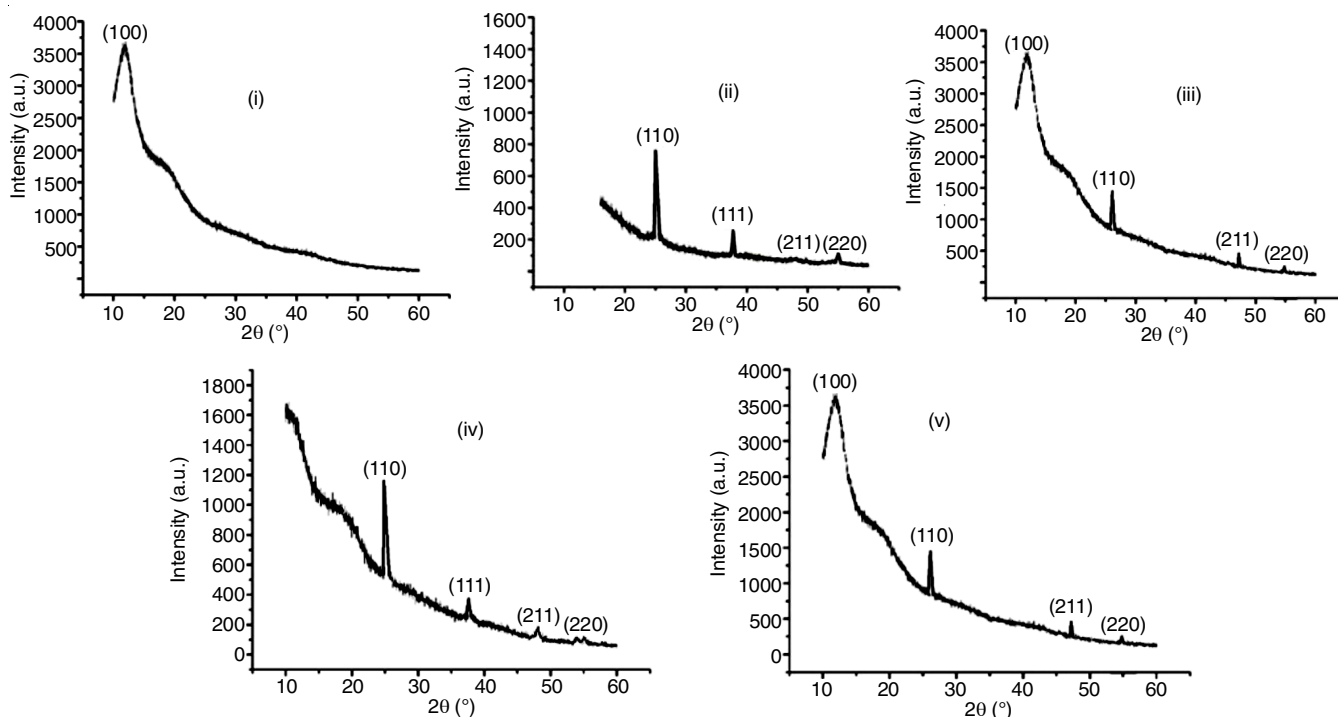


Fig. 4. XRD analysis of (i) silica nanoparticles (ii) titania nanoparticles (peptization process) (iii) silica-titania core-shell nanoparticles (peptization process) (iv) titania nanoparticles (sol-gel process) (v) silica-titania core-shell nanoparticles (sol-gel process)

TABLE-I
ABSORBANCE DATA OF ALL NANOPARTICLES IN ALGAE CULTURE MEDIA

Material (Algae)	Absorbance at 665 nm	
	Green algae (<i>C. pyrenoidosa</i>)	Mixed algae (<i>C. pyrenoidosa</i> + <i>Oedogonium sp.</i>)
Control	0.921	0.800
SiO ₂ nanoparticles	0.429	0.475
TiO ₂ (sol-gel) nanoparticles	0.380	0.430
Silica-titania core-shell (sol-gel) nanoparticles	0.334	0.389
TiO ₂ (peptization) nanoparticles	0.350	0.410
Silica-titania core-shell (peptization) nanoparticles	0.250	0.350

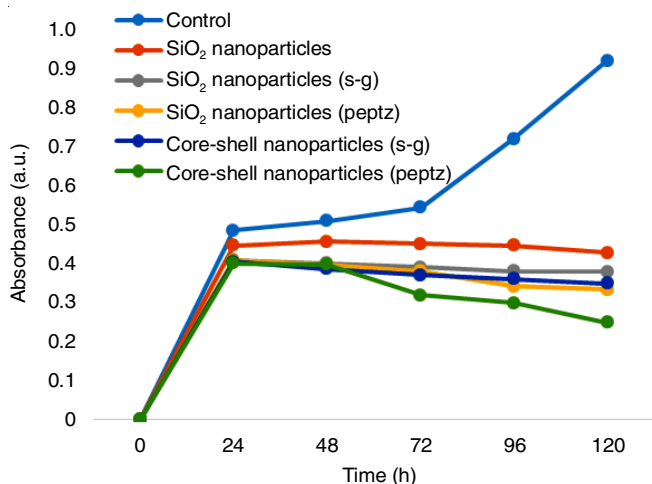


Fig. 5. Absorbance peak for all prepared nanoparticles against green algae represented by different colors in plotted graph

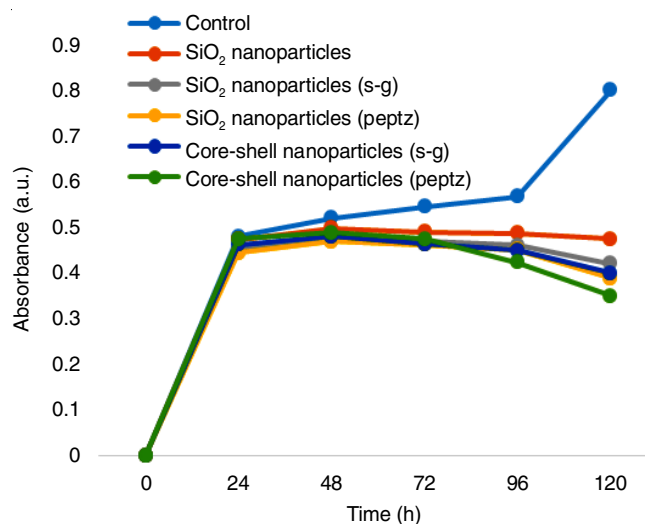


Fig. 6. Absorbance peak for all prepared nanoparticles against mixed algae represented by different colors in plotted graph

concentrations of nanoparticles on bricks and tested against green algae and mixed algae. Absorbance was checked at 665 nm of coated samples at 24 h interval upto 120 h. Table-2 showed the final absorbance value at 120 h for all coatings developed at 4 % (wt) concentration of nanoparticles. The best

anti-algal property was obtained in nano-coating developed with silica-titania core-shell nanoparticles at 4 % (wt) concentration prepared through peptization process against green algae and mixed algae (Figs. 7 and 8).

TABLE-2
ABSORBANCE DATA OF ALL COATINGS IN ALGAE CULTURE MEDIA

Material (Algae)	Absorbance at 665 nm	
	Green algae (<i>C. pyrenoidosa</i>)	Mixed algae (<i>C. pyrenoidosa</i> + <i>Oedogonium sp.</i>)
Control	1.50	1.200
Only brick	0.46	0.900
Pure polyacrylic (PA) coating	0.15	0.657
PA/SiO ₂ nano-coating	0.10	0.622
PA/TiO ₂ (sol-gel) nano-coating	0.07	0.420
PA/silica-titania core-shell (sol-gel) nano-coating	0.05	0.400
PA/TiO ₂ (peptization) nano-coating	0.04	0.380
PA/silica-titania core-shell (peptization) nano-coating	0.02	0.320

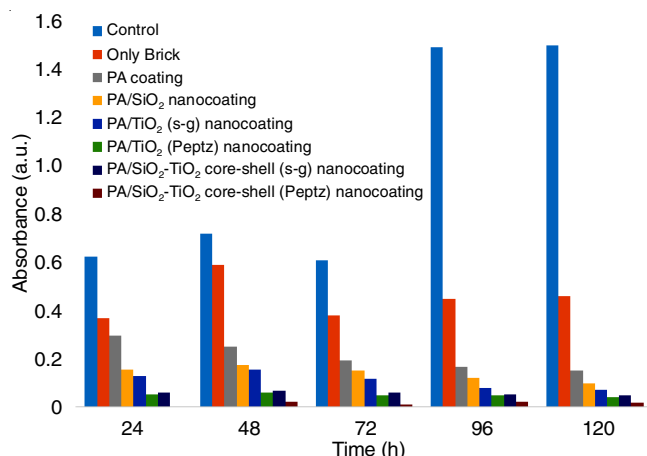


Fig. 7. Absorbance peak for poly-acrylic coated bricks containing all prepared nanoparticles as represented by different colors in plotted graph against green algae

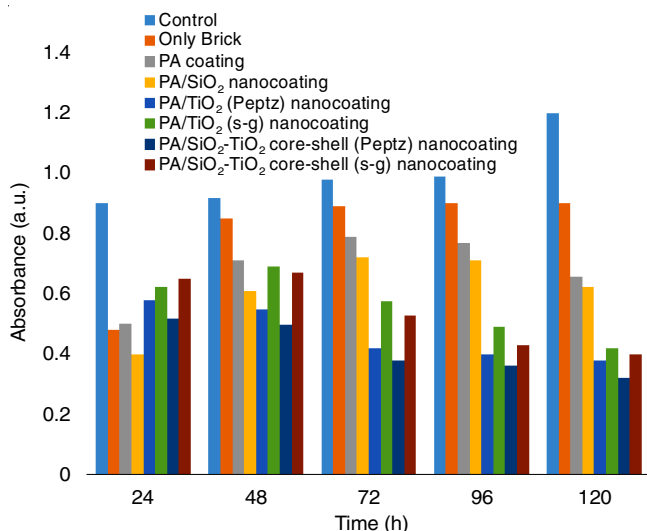


Fig. 8. Absorbance peak for poly-acrylic coated bricks containing all prepared nanoparticles as represented by different colors in plotted graph against mixed algae

Conclusion

We have successfully prepared silica, titania and silica-titania core-shell nanoparticles and characterized by dynamic light scattering, UV-visible spectrophotometer and X-ray diffraction. Polyacrylic coatings were developed with all nanoparticles. Anti-algal property of these coatings tested against green and mixed algae and silica-titania core-shell (peptization process) nano-coating has shown the best anti-algal effect.

ACKNOWLEDGEMENTS

The authors thank Prof. D.K. Avasthi, Director of Amity Institute of Nanotechnology, Amity University, Noida, India, for guidance, motivation and providing all research facilities. The author also acknowledge to IUAC, Delhi for XRD facility.

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