

Synthetic polymer nano-film coating efficacy evaluation in prevention of chemicals induced corrosion of monuments

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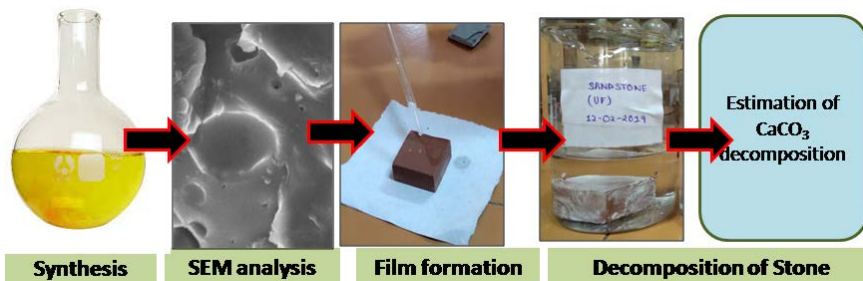
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Article

ABSTRACT

One of the most notable adverse effects of acidifying air quality is damage to materials exposed to the atmosphere. Systematic fields and laboratory experiments have been done to understand the mechanisms underlying the impacts of pollutants on the measurement of damage and estimate the cost of damage. In this study, authors have synthesized nano polymer film, which is transparent, resistant to acids and flexible. The as-synthesized nano polymer film was characterized using UV-Visible Spectroscopy, FTIR Spectroscopy and Scanning Electron Microscope (SEM). Coating of the nano polymer film was done onto various monuments stone samples and studied their corrosion in the presence of acids



Keywords: Nanofilms, Stone, Corrosion, Air pollution, Material protection

INTRODUCTION

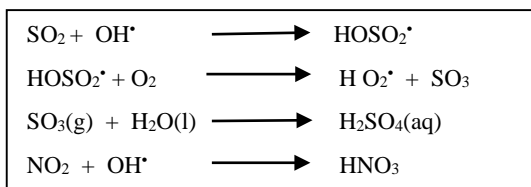
Pollution effects are not only confined to the environment but they have a damaging impact on historical monuments and buildings. One of the most destructive forms of pollution is acid rain (Figure 1), which when falls on the surface of limestone or marble causes a chemical reaction and corrodes the stone.¹

The impact of acid deposition on stone monuments made of marble and limestone and on building materials composed of mainly carbonates has been recognized for over a century and many research works have addressed the effect of acid deposition on stone materials of historic buildings and monuments.²⁻³ Acid rain is any form of precipitation with a pH of less than 5.7, which results from high levels of atmospheric nitric and sulfuric acids that get washed down to earth.⁴

Acids have a corrosive effect on limestone or marble buildings or sculptures.⁵ It is well established that either wet or dry deposition of sulfur dioxide significantly increases the rate of corrosion in limestone, sandstone and marble. Wet deposition

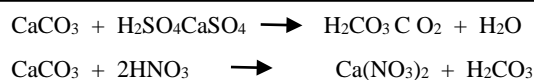
results from the deposition of acids produced in the raindrops or by precipitation removing the acids either in clouds or below clouds. Dry deposition occurs when particles and gases stick to the ground, plants or other surfaces.

Chemical Processes: Combustion of fossil fuels produces sulfur dioxide and nitric oxides.



Gas phase chemistry: In the gas phase sulphur dioxide is oxidized by reaction with the hydroxyl radical via an intermolecular reaction, which is followed by oxidation further. In the presence of water, sulfur trioxide is converted rapidly to sulfuric acid, Nitrogen dioxide reacts with OH radical to form nitric acid.⁶⁻⁷

Reaction of acid with marble: The sulfuric acid and nitric acid then further reacts with the limestone in a neutralization reaction.



The calcium sulfate and calcium nitrate is soluble in water and hence the limestone /marble dissolve and crumbles, as shown above.

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Figure 1: a) Effect of acid rain on the statue of George Washington b-c) Pollution in river Yamuna d) Mud therapy on the walls of Taj Mahal, Washington and e) The Acropolis of Athens and f) Restoration project of The Acropolis of Athens.

Case Study of Taj Mahal: The Taj Mahal is an ivory white marble mausoleum on the south bank of the Yamuna river (as shown in **Figure 1d**), in the Indian city of Agra. Declared as one of the seven Wonders of the World, this masterpiece is facing some major threat from acid rain which is making the white marble discoloured (making it go yellow) and the material is peeling off. The main cause of acid rain is attributed to the emission of sulfur dioxide and nitric oxides from automobile exhaust and the Oil Refinery situated in Mathura. In fact, work done at the National Environmental Engineering Research Institute at Nagpur has revealed that SO_2 and other emissions from refineries and foundries can certainly effect not only marble but even the red sandstone buildings of the tomb of Etmad-ud-daulah, the Fatehpur Sikri complex, and the Red Fort.⁸ The crude oil intended to be processed in the refinery is estimated to contain up to about 2 percent sulfur. This is oxidized to SO_2 and will be emitted from the chimney of the refinery. Thereafter in the moist atmosphere it is converted to dilute acid which causes decay (cancer) of stone and marble.⁹ The Taj Mahal is also threatened by dropping water tables and bacteria from the Yamuna River. Due to water pollution of the Yamuna River algae proliferates and with them a harmful local variety of mosquitoes, the chironomids are generated. Now, these mosquitoes make green droppings, the color of the algae they feed on which is turning the mausoleum brown. The Archaeological Survey of India, in an effort to preserve the grandeur of the Taj Mahal, started applying Fuller's earth (multani mitti) on discolored portion of the monument in 1994. The treatment involved the application of a 2mm-thick layer of lime-rich clay on the affected portions. The

clay was left to dry and later washed off with distilled water. Fuller's earth consists primarily of hydrous aluminium silicates of varying composition. As a good absorbent, it removes dust, dirt, impurities and stains from the surface and replenishes the shine of the marble (as shown in **Figure 1(d)**).

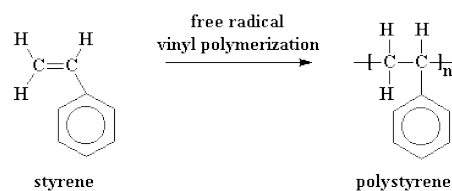
Case Study of the Acropolis of Athens: The Acropolis of Athens is an ancient citadel located on a rocky outcrop above the city of Athens and contains the remains of several ancient buildings of great architectural and historic significance. The buildings on the Acropolis are constructed using Pentelic marble. This is an extremely good building material under 'normal' circumstances.⁷ It is dense, has a fine structure, is low in porosity and is almost pure calcium carbonate. Air pollution is causing catastrophic damage to the priceless treasures on the Acropolis (as shown in **Figure 1(e)**).

The pollutants causing most of the damage to the Acropolis structures are sulphur dioxide (SO_2) and sulphur trioxide (SO_3). Most of the sulphur oxides come from the burning of oil from space heating in the densely populated Athens area. Two types of oil are currently used: distillate (or diesel oil, as it is called in Athens) containing up to about 1% sulphur, and heavy residual oil (or mazut) contains approximately 3.5% sulphur. Much of the brown discoloration one sees around joints in the marble on the Parthenon, other than simple soot, is probably Iron oxide. Some of this comes from the corroding of the iron reinforcing pins introduced by Belanos during restoration between 1902 and 1908.

The restoration project (as shown in **Figure 1(f)**), began during 1975 but as of 2017 it almost ground to a halt. The goal of the restoration was to reverse the decay of the centuries of attrition, pollution, destruction stemming from military use, and misguided past restorations. The project included collection and identification of all stone fragments, even small ones, from the Acropolis and its slopes and the attempt was made to restore as much as possible using reassembled original material, with new marbles from Mount Penteli being used sparingly. Restoration of the Temple of Athena Nike was completed in 2010 from a combination of cutting-edge modern technology and extensive research.

Materials used for coating Monuments

Polystyrene: Polystyrene is a synthetic aromatic hydrocarbon polymer made from the monomer styrene. It is an inexpensive resin per unit weight. Polystyrene can be naturally transparent, but can be colored using colorants. As a thermoplastic polymer, polystyrene is in a solid (glassy) state at room temperature but flows if heated above about 100°C , its glass transition temperature.¹⁰ Polystyrene is chemically very inert, being resistant to acids and bases but is easily dissolved by many chlorinated solvents, and many aromatic hydrocarbon solvents. The only commercially important form of polystyrene is *atactic*, in which the phenyl groups are randomly distributed on both sides of the polymer chain. While Ziegler-Natta polymerization can produce an ordered *syndiotactic* polystyrene with the phenyl groups positioned on alternating sides of the hydrocarbon backbone. This form is highly crystalline with a T_m of 270°C



Urea-Formaldehyde Resin: Urea-formaldehyde was first synthesized in 1884 by Holzer, who was working with Bernhard Tollens.¹¹ It is a non-transparent thermosetting resin or polymer. Urea-formaldehyde resin's attributes include high tensile strength, flexural modulus, and a high heat distortion temperature, low water absorption, mould shrinkage, high surface hardness, and volume resistance. Urea-formaldehyde is also used in agriculture as a controlled release source of nitrogen fertilizer. Health effects occur when urea-formaldehyde based materials and products release formaldehyde into the air. Generally, there are no observable health effects from formaldehyde when air concentrations are below 1.0 ppm.¹²

Polymer Nanotechnology:

Polymer nanoscience is the study and application of nanoscience to polymer-nanoparticle matrices, where nanoparticles are those with at least one dimension of less than 100 nm. Polymer nano composites (PNC) consist of a polymer or copolymer having nano particles or nano-fillers dispersed in the polymer matrix. These may be of different shape (e.g., platelets, fibers, spheroids), but at least one dimension must be in the range of 1–50 nm. These PNC's belong to the category of multi-phase systems (MPS, viz. blends, composites, and foams) that consume nearly 95% of plastic production. These systems require controlled mixing/compounding, stabilization of the achieved dispersion, orientation of the dispersed phase, and the compounding strategies for all MPS, including PNC, are similar. The transition from micro- to nano-particles leads to change in its physical as well as chemical properties. Two of the major factors in this are: the increase in the ratio of the surface area to volume, and the size of the particle. The increase in surface area-to-volume ratio, which increases as the particles get smaller, leads to an increasing dominance of the behavior of atoms on the surface area of particle over that of those interior of the particle¹³. This affects the properties of the particles when they are reacting with other particles. Because of the higher surface area of the nano-particles, the interaction with the other particles within the mixture is more and this increases the strength, heat resistance, etc. and many factors do change for the mixture.¹⁴⁻¹⁵ An example of a nano polymer is silicon nano spheres which show quite different characteristics; their size is 40–100 nm and they are much harder than silicon, their hardness being between that of sapphire and diamond.¹⁶⁻¹⁷

RESULT AND DISCUSSION

The as-synthesized product of polymer films (polystyrene and urea-formaldehyde) were analyzed by various characterization techniques such as UV-Visible spectroscopy, FTIR and morphology and topography of film were analyzed by scanning electron microscopy.

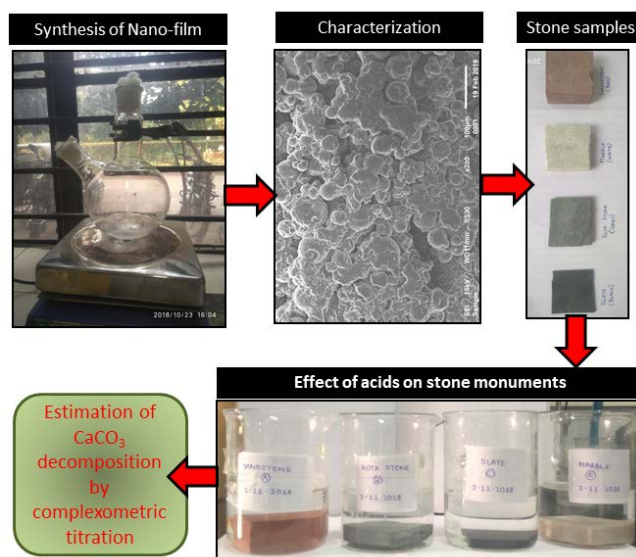


Figure 2: Schematic view of work done.

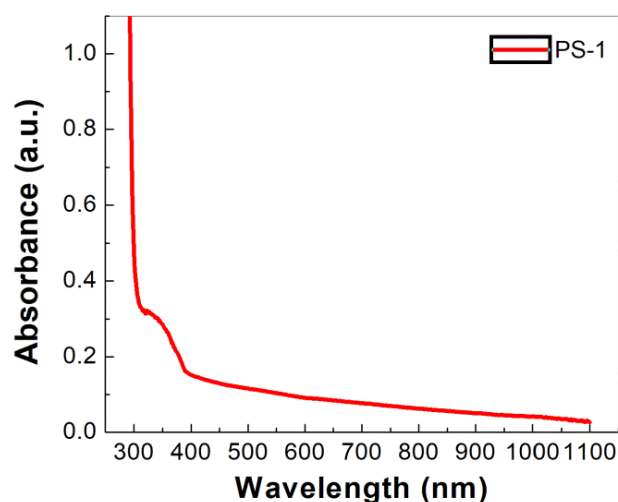


Figure 3: UV-Visible spectra as synthesized Nano-film of polystyrene.

Though spectral analysis of polystyrene can be done in far IR region, here we are showing characteristic absorption shoulder in UV-Visible region shows the formation of polystyrene. **Figure 3** shows the UV-Visible spectra of as-synthesized polystyrene film. The spectrum was recorded in region of 250 nm to 1100nm. Moreover slight shift on the absorption pattern further confirms the nano particle size of as-synthesized polystyrene. **Figure 4z** shows the FTIR spectrum of as-synthesized polystyrene films (PS-1 and PS-2). Spectrum was recorded in region up to 4000 cm^{-1} . The characteristic stretches of polystyrene and urea formaldehyde were observed from the FTIR pattern, polystyrene shows peaks at 3441, 2915, 1667 1031 and 493 cm^{-1} whereas urea formaldehyde shows peaks that were at 3325, 1625 and 1019 cm^{-1} . All these peaks were found to be well matched with standard pattern respectively.

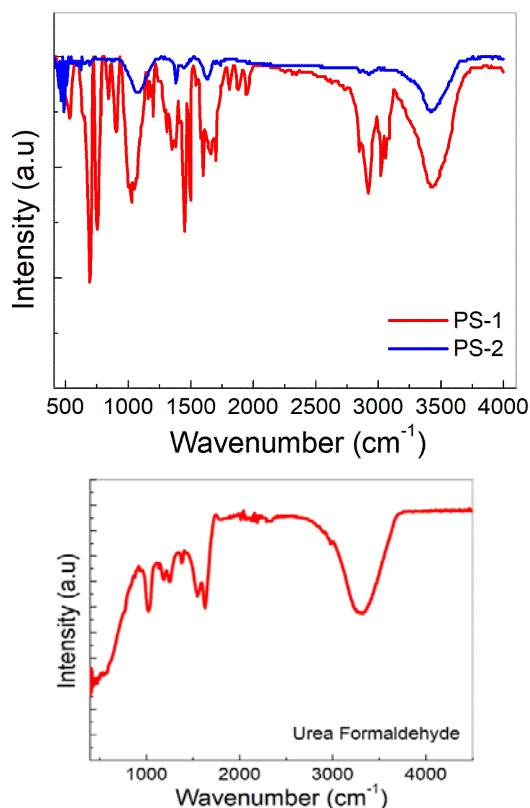


Figure 4: FTIR patterns-synthesized Nano-film of polystyrene (left) and urea formaldehyde (right).

Figure 5 shows SEM images of as-synthesized Nano-film of polystyrene at various scales. Panel “a” and Panel “b” shows the globules polymer film formation which may be due to high concentration of sample deposition over glass film during the analysis. However at small scale more magnified images as shown in panel “c and d” shows single layer of polystyrene. The thickness of layer observed below 100 nm so we can confirm formation of polystyrene nano-film from synthesis. Hence these nano-films will have more surface area and show high resistivity density towards acid when they are coated over various stones.

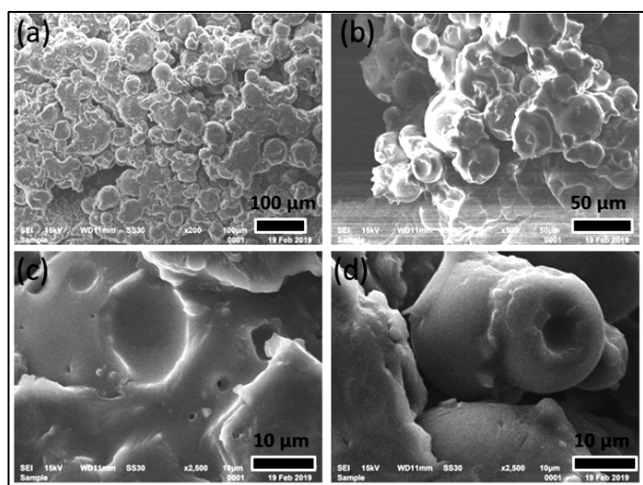


Figure 5: SEM images of as-synthesised Nano-film of polystyrene at various scales.

Study of Effect of Chemicals on Stone Monuments

Four types of stone specimen: Marble, sandstone, slate and kota stone were collected and cut into pieces having surface area of 4cm x 4cm (as shown in **Figure 6(b)**). These stone specimens were soaked in distilled water for 24 hours. A sulphuric acid solution of pH 5.5 was prepared and the four stones (marble, sandstone, slate and kota stone) were dipped in four different beakers of 250 mL, each containing 100mL of sulfuric acid. The beakers were labeled and covered to prevent it from any type of contamination (as shown in **Figure 6**).

Estimation of Calcium Decomposition of various Stones in Acid Without Coating of Nano-film: However as Sandstone, Kota Stone and Slate does not contain calcium carbonate, as they all are silicates, respectively, did not show any result for detection of Calcium ions in the sulphuric acid solution of pH-5.5.

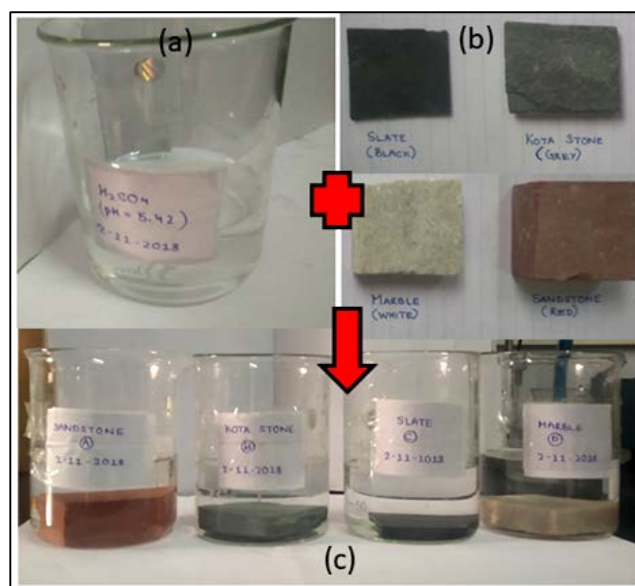


Figure 6: (a) Sulphuric acid solution of pH – 5.5 (b) Different specimen of stones (c) Stone specimens dipped in sulphuric acid solution

Estimation of Calcium Decomposition of various Stones in Acid Without Coating Dipped in Equinormal Solution of Acids (1:1:1 of H₂SO₄: HNO₃: HCl): An equinormal solution of 1:1:1 ratio of sulphuric acid, nitric acid and hydrochloric acid of concentration 10⁻⁵ mol L⁻¹ was prepared and three specimen of stones (marble, sandstone and slate) were dipped in three different beakers each containing 150mL of the equinormal mixture as shown in Figure 7.



Figure 7: Stones dipped in equinormal solution of acids (1:1:1 of H₂SO₄: HNO₃: HCl).

Table 1: Change in concentration of Ca^{2+} in sulphuric acid without coating of polymer on stones

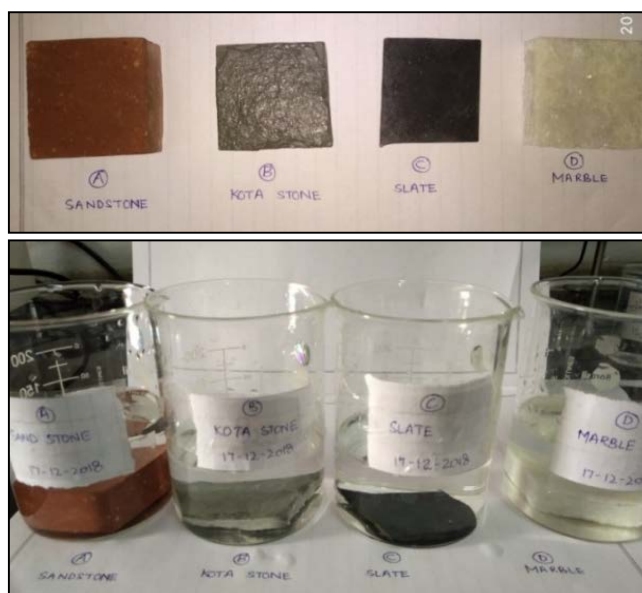
Stone Specimen	Acid Solution	pH	Duration	Conc. of Ca^{2+} (ppm/cm ²)
Marble	sulphuric acid	5.55	15 days	2.29
Sandstone	sulphuric acid	5.55	15 days	0
Slate	sulphuric acid	5.55	15 days	0
Kota Stone	sulphuric acid	5.55	15 days	0
Marble	sulphuric acid	5.55	30 days	3.34
Sandstone	sulphuric acid	5.55	30 days	0
Slate	sulphuric acid	5.55	30 days	0
Kota Stone	sulphuric acid	5.55	30 days	0
Marble	sulphuric acid	5.55	45 days	4.58
Sandstone	sulphuric acid	5.55	45 days	0
Slate	sulphuric acid	5.55	45 days	0
Kota Stone	sulphuric acid	5.55	45 days	0
Marble	sulphuric acid	5.55	60 days	8.75
Sandstone	sulphuric acid	5.55	60 days	0
Slate	sulphuric acid	5.55	60 days	0
Kota Stone	sulphuric acid	5.55	60 days	0
Marble	Equinormal solution		10 days	2.29

Estimation of Calcium Decomposition of various Stones in Acid With Coating of Nano-film of polystyrene: A sulphuric acid solution of pH 5.8 was prepared and the four stones (marble, sandstone, slate and kota stone) were dipped after coating them with Polystyrene-I(PS-I) in four different beakers of 250mL, each containing 100mL of sulfuric acid. The beakers were labeled and covered to prevent it from any type of contamination as shown in **Figure 8**.

Titration of Marble dipped in acid coated with Polystyrene-I (pH-5.80): No change in concentration of H_2SO_4 solution when Marble coated with Polystyrene dipped in it for 15, 30 and 45 days. Sandstone, Kota Stone and Slate did not show any result for detection of Calcium ions in the sulphuric acid solution of pH – 5.80(coated with Polystyrene-I).

Estimation of Calcium Decomposition of various Stones in H_2SO_4 Acid With Coating of UREA-formaldehyde resin

Also, other three specimens of stones (marble, sandstone and slate) were coated with Urea-Formaldehyde resin and dipped in three different beakers each containing 150mL of H_2SO_4 acid, as shown in **Figure 9**. No change in concentration of H_2SO_4 acid solution when Marble coated with urea formaldehyde was dipped in it for 15, 30 and 45 days.

**Figure 8:** Stones coated with Polystyrene – I (PS-I) (above) and Stone specimens coated with PS-I dipped in Sulphuric acid.**Table 2:** Change in concentration of Ca^{2+} in sulphuric acid with polymer coating on stones

Stone Specimen	Acid Solution	pH	Polymer Coating	Duration	Conc. of Ca^{2+} (ppm/cm ²)
Marble	sulphuric acid	5.80	PS-1	15 days	0
Sandstone	sulphuric acid	5.80	PS-1	15 days	0
Slate	sulphuric acid	5.80	PS-1	15 days	0
Kota Stone	sulphuric acid	5.80	PS-1	15 days	0
Marble	sulphuric acid	5.80	PS-1	30 days	0
Sandstone	sulphuric acid	5.80	PS-1	30 days	0
Slate	sulphuric acid	5.80	PS-1	30 days	0
Kota Stone	sulphuric acid	5.80	PS-1	30 days	0
Marble	sulphuric acid	5.80	PS-1	45 days	0
Sandstone	sulphuric acid	5.80	PS-1	45 days	0
Slate	sulphuric acid	5.80	PS-1	45 days	0
Kota Stone	sulphuric acid	5.80	PS-1	45 days	0
Marble	Equinormal solution	-	UF	10 days	0
Sandstone	Equinormal solution	-	UF	10 days	0
Slate	Equinormal solution	-	UF	10 days	0

Estimation of Calcium Decomposition of various Stones Dipped in Equinormal Solution of Acids (1:1:1 of H_2SO_4 : HNO_3 : HCl) With Coating of Urea-formaldehyde resin

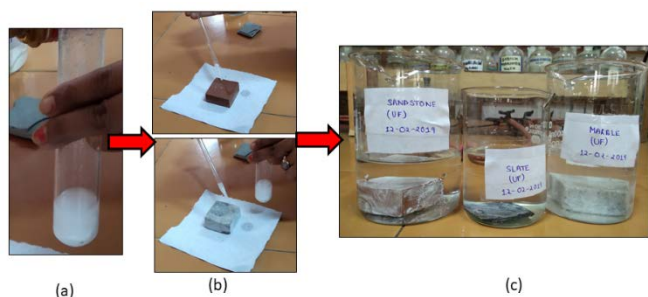


Figure 9 (a) As-synthesized urea formaldehyde (UF), (b) Stones coated with UF (c) Stone specimens coated with UF dipped in Sulphuric acid.

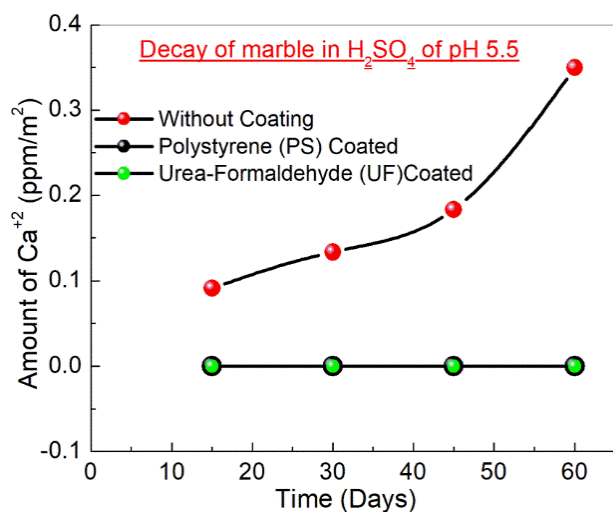


Figure 10: Comparison of decomposition of calcium of marble dipped in acid with or without coating.

EXPERIMENTAL DETAILS

Synthesis of various nano materials by green method to synthesize such materials to inhibit marble decomposition in presence of acid or by the action of other pollutants is discussed in this section.

Chemicals used: Styrene (ALFA ASER), Potassium persulfate (Merk), Sodium dodecyl sulphate, (Merk), Polyvinylpyrrolidone (ALFA ASER), Urea (Merk), Formaldehyde (Thomas baker).

Preparation of Polystyrene polymer (PS-I): Polystyrene was prepared from styrene, using potassium persulfate (KPS) as polymerization initiators, in the presence of polyvinyl pyrrolidone (PVP) as surfactant agent. 0.05g of potassium persulfate was dissolved in 20mL of ethanol in a beaker of 100mL and in another beaker 2g of PVP was dissolved in 10mL of water. 7.63g of styrene was poured into a 2-neck round flask along with PVP dissolved in water and the flask was kept on a magnetic stirrer with a temperature controller. The mouth of the flask was plugged with cotton in order to remove oxygen from the reactor. The temperature was increased up to 60°C, and then the initiator dissolved in an aliquot of ethanol was added to the reactor (as shown in **Figure 11**). The polymerization was carried

out for 5 hrs. After completion of this time, the solution was stored in the form of dispersion in ethanol.

Preparation of Polystyrene polymer (PS-II): PS-II was prepared from styrene, using Potassium persulfate (KPS) as polymerization initiator, in the presence of Sodium dodecyl sulfate (SDS) as surfactant agent. 0.024g of potassium sulfate was dissolved in 10 mL of ethanol in a 100mL of beaker and in another beaker 1g of SDS was dissolved in 5mL of water. 3.844g of styrene was mixed with the SDS solution dissolved in water and the reaction mixture was poured into a 2-neck round flask with its mouth plugged with cotton. The flask was kept on a magnetic stirrer and temperature was increased to 60°C. After 10 mins, KPS dissolved in ethanol was added to the reaction mixture and the polymerization was carried out for 14hrs. After the completion of this time, the latex was washes with ethanol and stored in the form of dispersion in ethanol.



Figure 11: Synthesis of Nano-film of polystyrene (PS-1).

Preparation of Urea-Formaldehyde resin: 10mL of 40% aqueous formaldehyde solution was taken in a 100mL beaker and 4g of Urea was added to it. The mixture was stirred with a glass rod to make a saturated solution. To this added few drops of conc. sulfuric acid and stirred vigorously till a white solid mass was formed. The residue was filtered and washed with distilled water several times to remove any acid.

Complexometric Titration: Pipetted out 5mL of the marble dipped acid solution in a 100mL conical flask. 2.5mL of Mg-EDTA complex was added to it followed by 2mL of NH₃-NH₄⁺ buffer (PH-10) and few drops of Eriochrome black T indicator. The solution was titrated with EDTA solution of concentration 10⁻³mol/L till the colour changed from wine red to blue. The procedure was repeated to get three concordant readings¹⁸⁻²⁰.

Instrumentation: Scanning electron microscopy (SEM) measurements were performed with a JEOL JSM 6610 at 20 kV, width distance 10 mm and spot size 30.. FT-IR spectra of as prepared samples were recorded directly in a Perkin Elmer FT-IR2000 spectrophotometer. UV-Visible spectra were recorded with Perkin Elmer instrument.

CONCLUSION

In conclusion of this project report we observed that nano-film of polystyrene and urea-formaldehyde was prepared. The detailed study of calcium decay of various types of monument stones in acidic media shows that there will be up to 8.5 ppm of calcium in 60 days in acidic media of pH 5.5 which can be prevented by nano-film of polystyrene and urea-formaldehyde polymer. Comparison is shown in **Figure 10** and in **Table 1** and **Table 2**.

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