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Removal of Bats' Excreta from Water-Soluble Wall Paintings Using Temporary Hydrophobic Coating

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ABSTRACT

The removal of bats' excreta from the decorative surfaces of India's Ajanta cave (2nd BCE to 5th CE) was always feared due to the water solubility of the plaster and the binding glue in the paint layer. Although the caves are now free from bats, their heavy discharge in the past is having a telling impact in the form of damage to painted plasters and basaltic rock surfaces. Studies undertaken through FTIR, Raman spectroscopy, SEM-EDS, ion strip tests, etc. showed guano seeped deep into the earthen support through the paint layer. In the present work Cyclododecane (CDD), a volatile binder and reversible consolidant, was utilized to protect the infested paint layer from any water ingress and the surface was successfully cleaned with phytagel and de-ionized water. The two-step process cleaned guano from water-sensitive painted surfaces by selective masking with CDD which sublimed in few months leaving no visual residues on the substrate. This hydrophobic process of cleaning is certainly advantageous to other aqueous methods that may cause damage to the proteinaceous binder, found mixed in the paint and earthen plaster layers at Ajanta. The process can now be successfully applied to similar other sites in India and elsewhere for guano removal.

RÉSUMÉ

On a toujours craint de retirer les excréments de chauve-souris sur les surfaces décoratives des grottes d'Ajanta en Inde (IIe siècle av. J.-C. au Ve siècle apr. J.-C.) à cause de la solubilité à l'eau de l'enduit et du liant à la colle animale dans la couche picturale. Bien que les grottes soient maintenant exemptes de chauve-souris, les lourdes déjections du passé endommagent de façon évidente les surfaces peintes des enduits et de la pierre basaltique. Les études qui ont été menées à l'aide de l'IRTF, la spectroscopie Raman, le MEB-EDS, les bandelettes réactives pour ions, etc., indiquent que le guano a pénétré profondément dans l'enduit de terre au travers de la couche picturale. Dans le présent travail, le cyclododecane (CDD), un liant volatil et un consolidant réversible, a été utilisé pour protéger la couche picturale infestée de toute pénétration d'eau, et la surface a pu être nettoyée avec succès avec du phytagel et de l'eau déionisée. Le processus en deux étapes a permis de nettoyer le guano des surfaces peintes sensibles à l'eau par masquage sélectif avec du CDD qui s'est ensuite sublimé en quelques mois sans laisser de résidus visuels sur le substrat. Ce processus de nettoyage hydrophobe est certainement avantageux pour d'autres méthodes aqueuses qui pourraient endommager le liant protéique qui, à Ajanta, se retrouve à la fois dans les couches de peinture et d'enduit de terre. Le processus peut maintenant être appliqué avec succès à d'autres sites similaires, en Inde et ailleurs, pour l'élimination du guano. Traduit par Elisabeth Forest.

RESUMO

A remoção dos excrementos de morcegos das superfícies decorativas da caverna de Ajanta na Índia (Século 2 AEC ao século 5 EC) sempre foi temida devido à solubilidade em água do gesso e do adesivo aglutinante da camada de tinta. Embora as cavernas estejam agora livres de morcegos, a descarga pesada de excrementos no passado está causando um impacto significativo na forma de danos a rebocos pintados e superfícies de rochas basálticas. Estudos realizados através de FTIR, espectroscopia Raman, SEM-EDS, testes de tira iônica, etc., mostraram que o guano penetrou profundamente no suporte aterrado através da camada de tinta. No presente trabalho, o Ciclododecano (CDD), um aglutinante volátil e um consolidante reversível, foi utilizado para proteger a camada de tinta infestada de qualquer entrada de água, e a superfície foi limpa com sucesso com Phytagel e água deionizada. O processo de duas etapas limpou o guano das superfícies pintadas sensíveis à água, através de uma máscara seletiva com CDD, que sublimou em poucos meses, sem deixar resíduos visuais no substrato. Esse processo hidrofóbico de limpeza é certamente vantajoso para outros métodos aquosos que podem causar danos ao aglutinante proteico, encontrado misturado nas camadas aterradas de gesso e tinta de Ajanta. Este processo pode agora ser aplicado com sucesso em outros locais semelhantes na Índia e em

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outros lugares para a remoção de guano. Traduzido por Millar Schisler.

RESUMEN
Siempre hubo temor de la eliminación de la excreta de murciélagos de las superficies decorativas de la cueva de Ajanta en la India (II Siglo AC a V Siglo EC) debido a la solubilidad en agua del yeso y el pegamento aglutinante de la capa de pintura. Aunque las cuevas ahora están libres de murciélagos, su fuerte descarga en el pasado está teniendo un impacto revelador en forma de daños a los yesos pintados y las superficies de roca basáltica. Los estudios realizados a través de FTIR, espectroscopía Raman, SEM-EDS, pruebas con tiras iónicas, etc. mostraron que el guano se filtró profundamente en el soporte de tierra a través de la capa de pintura. En el presente trabajo se utilizó Cyclododecano (CDD), un aglutinante volátil y un consolidante reversible para proteger la capa de pintura infestada de cualquier penetración de agua y la superficie se limpió exitosamente con phytagel y agua des ionizada. El proceso de dos pasos limpió el guano de las superficies pintadas sensibles al agua mediante un enmascaramiento selectivo con CDD que se sublimó en pocos meses sin dejar residuos visuales en el sustrato. Este proceso de limpieza hidrofóbico es ciertamente ventajoso para otros métodos acuosos que pueden causar daños al aglutinante proteico que se encuentra mezclado en las capas de pintura y yeso de tierra en Ajanta. El proceso ahora se puede aplicar con éxito a otros sitios similares en la India y en otros lugares para la eliminación del guano. Traducción: Amparo Rueda.

Introduction

Ajanta is a great surviving monument of paintings created by Buddhist faith and fervor in a land that gave birth to this religion. Although many caves were discovered in India, none is so spectacular with beautiful artworks as Ajanta (Spink 2014). Ajanta murals not only offer some of the most important masterpieces of Indian art but also give a comprehensive picture of about 700 years of ancient Indian life and traditions (Singh and Arbad 2013a). Chiaroscuro technique (giving three-dimension effect to painting and sculptures) was first practiced in Ajanta from second century BCE to fifth-century CE and later the technique spread to other Asian countries, making Ajanta the first monument in India to be incribed to the World Heritage list by UNESCO (Singh and Arbad 2013b). Therefore, Ajanta is a very important link to discover 700 years of great Indian culture and history. The Ajanta paintings also preserve a unique record of ancient Indian religious thoughts, social life, and artistic skill. There are 30 excavated caves at Ajanta consisting of viharas and chaitya-grihas (rock cut halls, prayer halls or shrines) from two distinct phases: The Hinayana (earlier period) and The Mahayana (later period) (Yazdani 1930; Spink 2011; Singh and Arbad 2013a). The caves were excavated in the middle of basaltic rock scrap in the crescent shape bordering Wagora River (Figure 1). The paintings are exclusively executed in tempera technique on a mud/lime plaster ground. The Ajanta Cave was excavated from a fine-grained basalt rock called Deccan traps, which is massive, vesicular with amygdular formations (Rao and Rao 1972). The rock is fine-grained and dense and a thick massive overlies the roof of the caves.

Figure 1. Schematic diagram showing the location of various rock-cut caves at Ajanta.

The paintings have been executed on earthen plaster supports. From the visual examinations, it is observed that two layers of earthen plasters have been applied to roughly chiseled basaltic rock. The initial layer is more coarse and serves as a leveling layer. The upper finer layer provides a smooth plaster surface for the painted layer (Singh and Arbad 2015). The thickness of the lower layer varies from 5 to 35 mm depending on the roughness of the wall. The thickness of the second upper layer varies from 2 to 2.5 mm. The mud used in these plaster layers is similar to the alluvial deposits of the Wagora River that flows in front of the Ajanta caves. Studies undertaken through polarizing microscope, laser particle size analyzer, sieve analysis, XRF, XRD, CHN, FTIR, and SEM techniques on the plaster samples extracted from different caves showed that the properties of high silt (<75%) and low clay (≅15%) soils sourced from the Waghura river bank have been

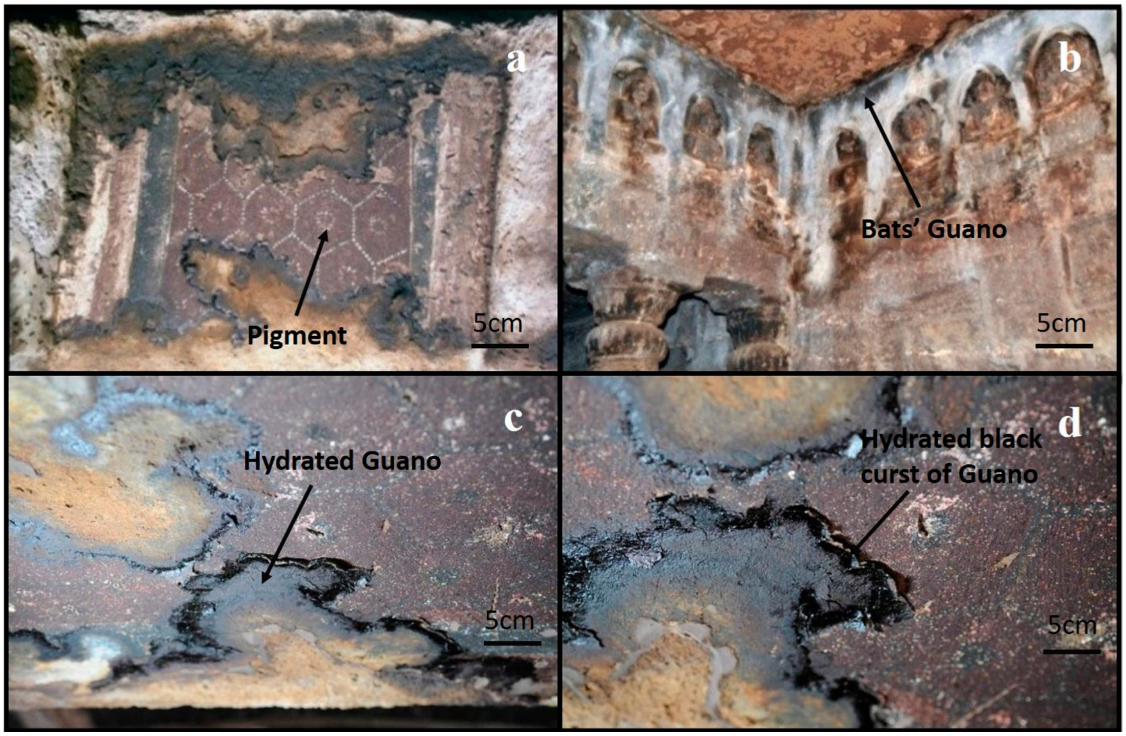


Figure 2. (a) Damage observed on the paintings at one of the beams of Cave No. 2; (b) sculpted wall, First Floor, Cave No. 6. (c) and (d) Close-up view of damage observed on painted beams due to bats' excreta, Cave No. 2.

modified by the addition of slaked lime and proteinaceous additives to enhance the plaster's cementing characteristics (Singh and Arbad 2015). The sandy loam soils sourced from the river bank consist of mixtures of coarse to fine sand and clay with the inclusion of celandonite and zeolite to allow the earthen plaster to receive the colors (Singh and Arbad 2015).

The plasters were mixed with vegetable fibers and plant seeds to improve the properties of preparatory layers at Ajanta. The FTIR spectra of the earthen plaster showed the inclusion of coarse black ferruginous silicate probably bound together with proteic materials (amide bands) that over time have partially transformed to calcium oxalate (Singh and Arbad 2015). Calcium oxalate is a byproduct of oxidative degradation of proteinaceous adhesives. The presence of calcium oxalate tends to indicate the use of organic additives which function as a binder for the earthen plaster.

Around two-thirds of the Ajanta paintings were coated with unbleached shellac varnish by Italian restorers in 1920. The varnish has now oxidized to an orange-red color masking the true color of the paintings and affecting the breathability of the painted plaster layers. In addition, the most ancient second century BCE paintings present in caves 9 and 10 have been covered with many layers of varnishes for copying in the past which has completely concealed the paintings. This has caused the formation of ridges, gaps, lacuna, and sometimes loss of Ajanta's decorative artwork. The conservation issues at the site are both intrinsic and extrinsic. Water infiltration through the stone joints, environmental parameters (Cacace et al. 2008), insect activity and biodeterioration (Dhawan, Garg, and Mishra 1991; Dhawan, Garg, and Pathak 1992) bat excrement, earlier conservation materials, shellac varnishes, and degradation of the components of the paintings are some of the factors causing damage to stone works and murals.

Damage due to bat excrement was identified as one of the major conservation issues since the cave was discovered in 1819. In fact, John Griffiths, the principal of J.J. School of Arts, Bombay, noticed damage and loss of painted material between 1872 and 1895 due to an infestation of bats and insects in the caves. Griffiths was dismayed to notice that much of the paintings remaining on his first visit in 1872 had been lost when he revisited Ajanta in the year 1895 (Griffiths 1896). The evidence of biological agencies causing decay to this heritage element from the caves could be determined from the observations of scholars who visited the cave during different periods. Griffiths recommended the erection of wooden doors and shutters to prevent the entry of bats and to protect the cave paintings from further damage. However, and the damage continued. In 1920–1921 during their work at Ajanta caves, the Italian experts inferred one of the causes of damage to Ajanta paintings was the bats' excrement (Annual report of Archaeological Department of Nizam 1949). UNESCO experts Prof. Paul Coreman and J.J Plenderleith inspected the caves in 1965 and completed a report on the condition of the caves and their paintings which highlighted the decay from bat guano and recommended treatments for their conservation (UNESCO 1983).

Despite Griffiths's suggestion, no measure was taken for installing wooden doors and damage continued. However, in 1953 when the cave was brought under the custody of Archaeological Survey of India, wooden frames fitted with small wire mesh were installed at the doors and windows to prevent the entry of bats. However, the earlier discharge left on the ceilings, joints of ceilings, and upper parts of the wall were so heavy that they pose a problem even today, because of the guano's physicochemical properties. Recorded problems include detachment of painted plaster, damage to the architectural elements, loss of paint layers on the walls close to painting, plus an emanating foul smell (Figure 2(a–d)).

Presently the bats' excreta are slowly spreading sideways and downwards during the rainy season and is a matter of great concern at Ajanta. The repeated cycle of solubilization and crystallization of soluble salts under humid conditions has caused physical damage to the paintings. The black deposits are rich in organic matters and served as nutrients to microbiological activities causing biodeterioration of the murals (Sharma, Saxena, and Saxena 1995). The slow decomposition of urea, one of the primary constituents of bats' urine, creates favorable environments for insect activity (Tilak et al. 1970).

The paint layers in the caves are easily softened by water. This indicates the presence of a water-soluble binding medium in the paint. Dr. B. B. Lal (1969) analyzed the paint layers from several of the caves of Ajanta and found that animal glue was used as a binding medium. Dr. Paramasivan (1936, 1938) had similar findings from the analysis of other painted plasters of India. The addition of proteic materials as binding media in the paint layer has also been identified by FTIR along with the peak of calcium oxalate due to partial oxidation of proteinaceous additives (Singh and Arbad 2015). As the Ajanta paintings used a tempera technique with animal glue as a binding medium, water based solvents could not be used for cleaning.

Cleaning operations of bat' excreta

Water-soluble black deposits of bat guano are visible on the paint layer in the form of tidelines. As previously discussed the paint layers are susceptible to damage by water due to the use of animal glue as a binding medium. To avoid this damage cyclododecane in conjugation with phytagel was selected for a two-step cleaning process. These methods were adopted to ensure no contamination of constituents of paintings during cleaning, which also addresses conservation issues for the removal of bat excreta from the painted plaster.

Cyclododecane (CDD) is a solid, saturated dicyclic alkane, $C_{12}H_{24}$. As CDD sublimates at room temperature it is also called a volatile binder (Brückle et al. 1999). The low vapor pressure of CDD allows it to convert directly from a solid to a gaseous state (Stein et al. 2000). Its characteristic to sublime is utilized in the conservation of various objects as there is no need for any intermediate aqueous or chemical process for its removal from the substrate. CDD has mostly been used as a temporary adhesive and consolidant for the safe transportation of fragile objects. Other alternative resins like acrylic or polyvinyl acetate are considered to be reversible and have also been used for this purpose (Brown and Davidson 2010). However, the issues of their removal with solvents and the possibility of residue made their application unsuitable for this project so CDD was chosen.

Phytagel, composed of glucuronic acid, rhamnose, and glucose, was used as a substitute for agar. Phytagel congeals at a temperature of 27–31°C (Cremonesi 2012) and has a higher flexibility than agar gel. Phytagel also makes better surface contact with the substrate over the more rigid agar gel. Phytagel is also more transparent than agar which allows for better observation of the surface being cleaned. It is also more economical than agar and was easier to control than other poulticing methods. Therefore, phytagel was used to control and reduce the release of water for cleaning of bat excreta at Ajanta.

Materials and methods

The sample for analysis was obtained from the east wall of Cave no. 2 which was infested with guano on mud as

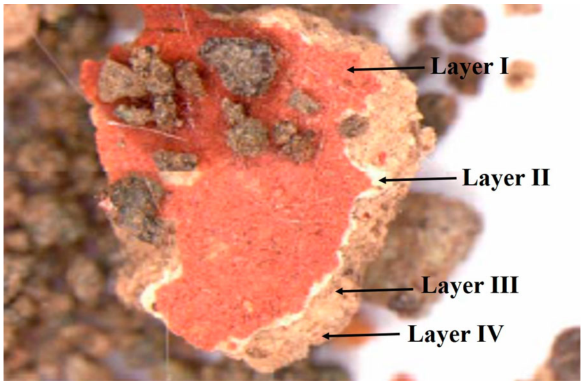
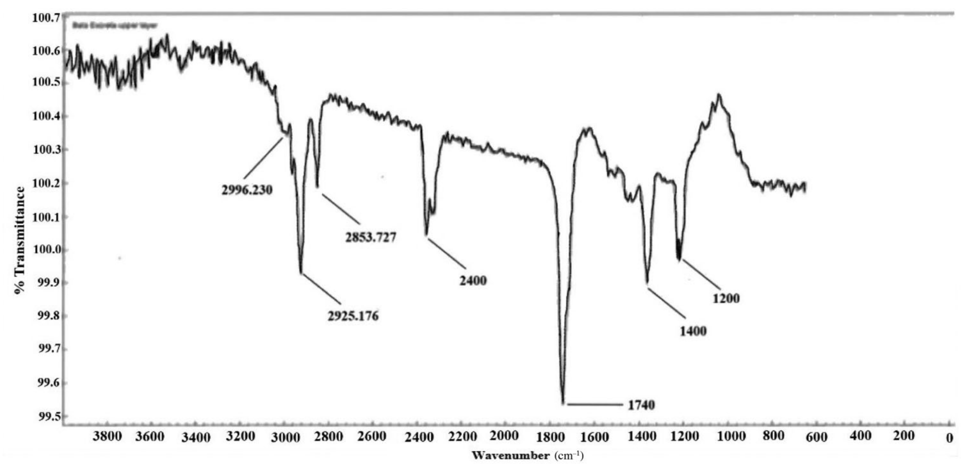
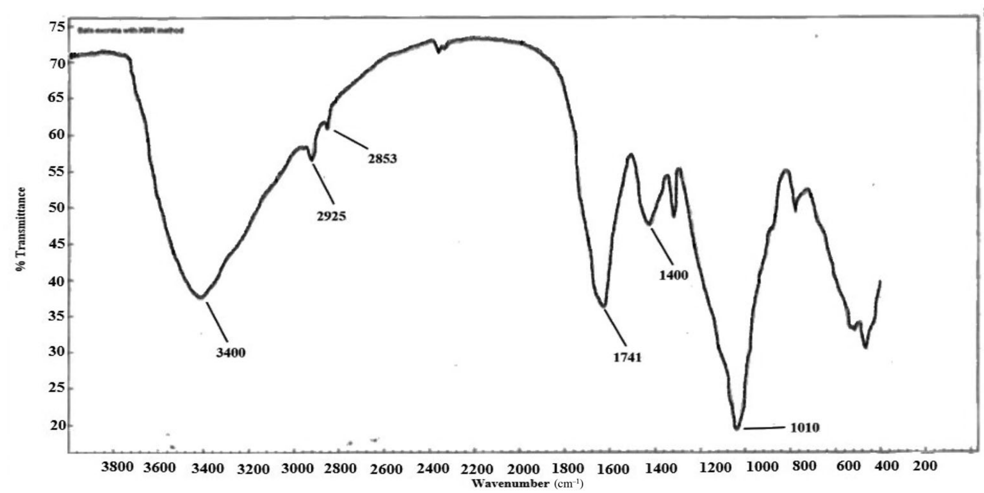


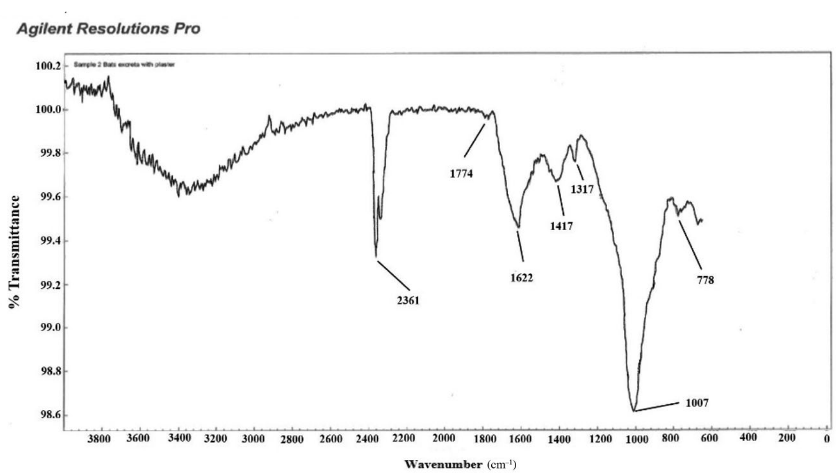
Figure 3. The stratigraphy of the painted plaster layer at Ajanta.



(a)



(b)



(c)

Figure 4. (a) FTIR spectra of bat excreta using the KBr pellet method. (b) FTIR spectra of bat excreta of upper layer using the ATR method. (c) FTIR spectra of the back side of earthen plaster with bat excreta using the ATR method.

well as on painted earthen plaster. The cleaning was conducted on a 10 to N 12 cm area which included both white and black guano deposits. For experimental studies, about 150–200 micron size samples were

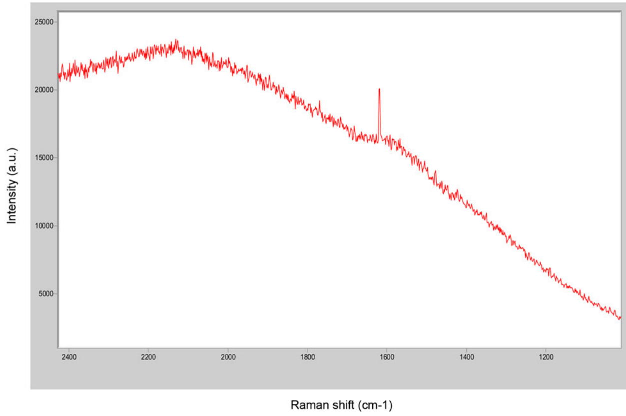


Figure 5. Raman spectrum of bat excreta present on mud plaster.

removed without causing any visual damage to the painted plaster. To understand the solubility characteristics, nature and composition of bats' excreta and the migration of the excreta into plaster layers, extensive examinations using Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, SEM-EDX, ion strip techniques, and visual observation were carried out.

FTIR analysis of the bats' excreta was carried out using an Agilent Carry 660 spectrometer with a liquid nitrogen cooled MCT detector and the peaks were identified using the RRuff database. Agilent inbuilt pro software was used to facilitate the data analysis. Mid-infrared spectra were recorded using the Attenuated Total Reflectance (ATR) Technique and using a Zn–Se crystal plate. Spectra were also generated using KBr pallet and captured over the range 4000–400 cm^{-1} using 32 scans with a resolution of 4 cm^{-1} and data collected as percentage transmittance (%T) values.

The Raman spectra of bats' excreta were recorded using a SEKI TECHNOS STR 150 instrument, equipped with a CCD Peltier cooled detector. The incident laser radiation was provided by a diode laser source with excitation wavelength at 532 nm. A 50X magnification was employed to focus the beam of the laser on to the sample, providing a spatial resolution of about 1–2 µm. The irradiating laser power was about 2 mW. Scattered light having a grating monochromatic with 1800 lines per millimeter was used. The spectra were recorded with a collection time of up to 10 s.

The examination of earthen plaster carrying bats' excrement was also undertaken with A TESCAN scanning electron microscope VEGA 3 LM coupled with Bruker Quantax X flash 6/10 energy dispersive X-ray spectrometry (EDX) with data analysis software ESPIRIT having features like real-time spectroscopy, light element analysis, hybrid map, and hybrid quantification.

White and black bat' accretions mostly affect the upper walls of the caves. The ion strip test was used on for a sample of excreta taken from the east wall of Cave No. 2 (Figure 1). The tested ions are phosphate, sulfate, nitrate, chloride, and ammonium. The pH was tested with pH paper. The ion strip test was again performed for the cleaned guano area after the sublimation of CDD to measure the concentration of ions present.

CDD was used in this study as a temporary hydrophobe to safeguard the paint layer from solvent water during the cleaning of bats' excreta. To set CDD in a solution form, it was kept in a container for 2–3 days without stirring at 20°C (40 parts of CDD was dissolved into 60 parts of petroleum ether) (Hangleiter 2000). When CDD is applied in the melted state without the addition of solvents, it solidifies quickly resulting in a thick uneven layer which increases the sublimation time. The mixing of solvent in hot molten CDD requires extra safety precautions as combustion is possible during mixing (Watters 2007). Therefore, all preventive measures were taken during mixing. The CDD solution was applied by brush to the infested paint layer. Brush application helped to form an even film on the surface which lowers the sublimation time. After application, the CDD solidified on the paint surface and formed a water impermeable film on the paint. The application of cyclododecane on the painted surface slowed down the rate of removal of guano, yet the guano was successfully removed in 2–3 applications.

The gel was prepared by mixing the phytagel powder slowly in cold de-ionized water and stirring rapidly until the particles are completely hydrated. This solution was heated on a hotplate for 1–2 min and was then allowed to cool. After cooling for two hours, the result was a transparent water-containing sheet type gel. Once cold, the gel was applied through Japanese tissue paper which served as a barrier layer. The black accretions were drawn into the tissue paper. The gel was left on the surface for about 5–6 min and then residual water along with the dissolved guano was removed using a dry cotton swab. The process was repeated 2–3 times depending on the stubbornness of guano.

Results and discussion

Micro samples of earthen plaster around 200 microns in size infested with bats' excreta were collected from the beam portion of the pillared central hall on the northeast side of Cave No. 2.

The micro sample was studied both by ATR and KBR techniques of FTIR. The spectra generated gave vital inputs with intense and medium peaks at different wavenumbers and the spectra were compared with published data.

The spectra generated by using the KBr technique were smooth (Figure 3(a)). The peaks observed in the region of 3200–3600 cm^{-1} are mainly due to the presence of moisture. The peak at 2900 cm^{-1} is due to C–H stretching vibration. The peaks observed in the region of 2200 and 2400 cm^{-1} are due to cyclic amide linkage (conjugate amide link). The peak at 1640 cm^{-1} indicates the presence of alpha, beta-unsaturated carbonyl compounds. The carbonyl stretching frequency is observed at 1630 cm^{-1}. The peaks observed at 1400 and 1200 cm^{-1} are due to aryl NH or cyclic amide stretching vibrations. The strong peaks at 1200 and 1000 cm^{-1} are due to phosphate stretching vibrations. The peak at 515 cm^{-1} is associated with phosphate (Figure 3(a)).

The spectra generated by the ATR technique were not as smooth as those recorded using the KBr technique (Figure 3(b)) However, the spectra showed both medium and strong peaks at different wavenumbers. The peak at 2925 cm^{-1} is due to C–H stretching vibrations caused by the uric acid of bat excrement. The peak at 2853 cm^{-1} is mainly due to carboxylic acid stretching vibrations,

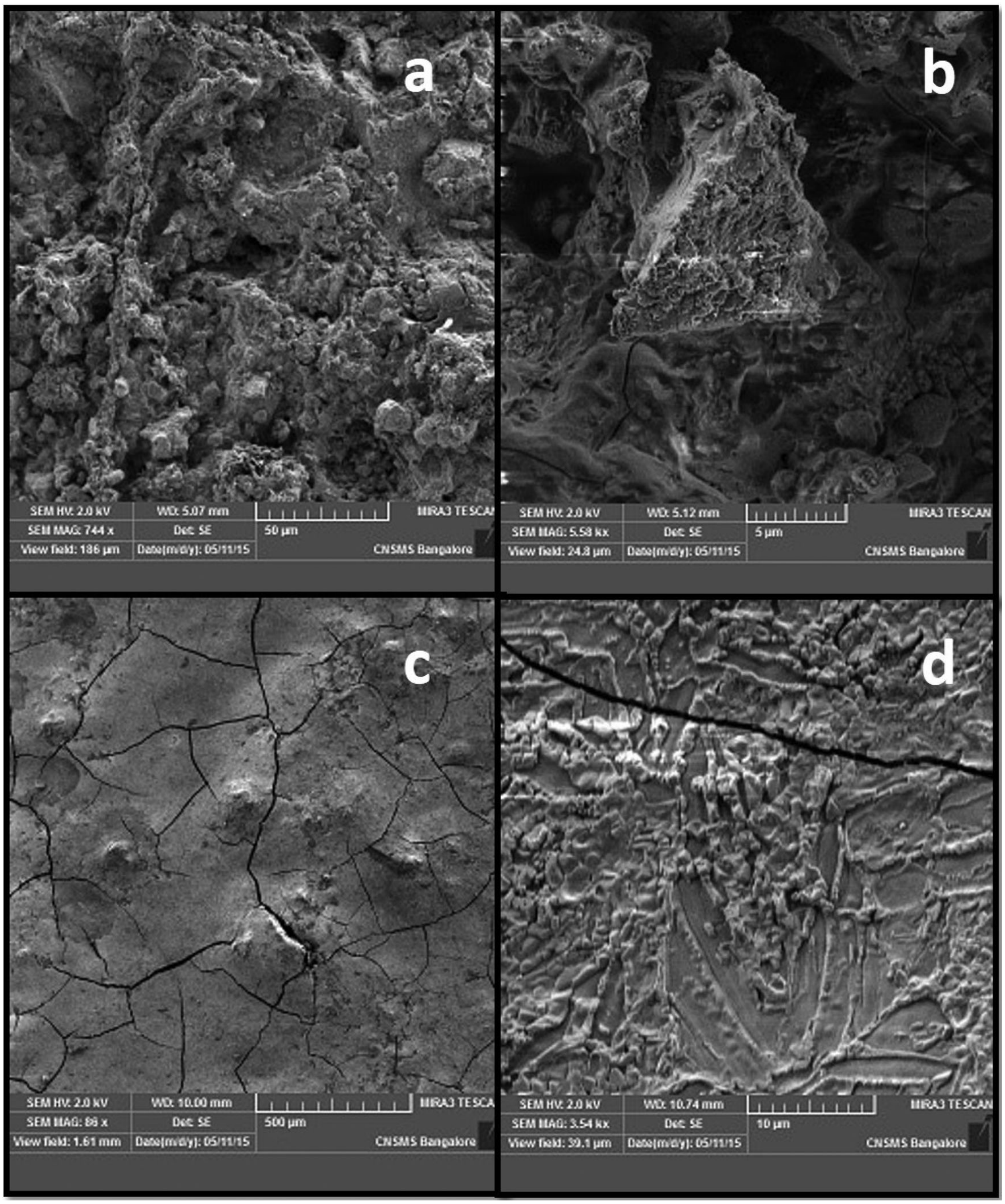


Figure 6. (a) and (b) SEM images of the back side of the mud plaster with bat excreta on the front (magnifications: (a) 744x: (b) 5.54 kx), (c) and (d) SEM images of the front side of the mud plaster carrying bat excreta causing cracks on the outer surface (magnifications: (c) 86x: (d) 3.54 kx).

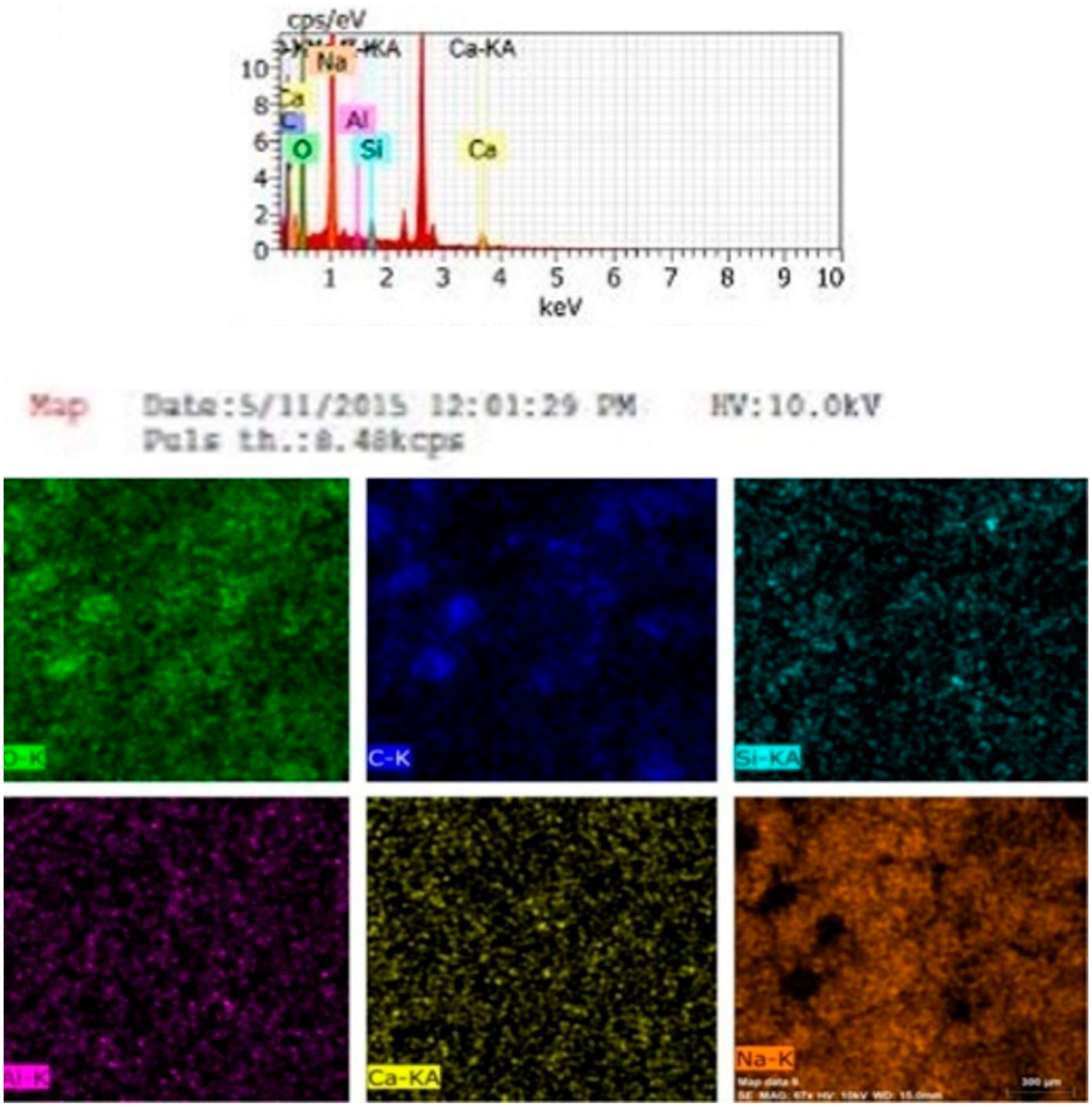


Figure 7. SEM-EDX of the front side of the mud plaster with bat excreta along with elemental mapping.

which are coming from the oxalate present in the excreta. A characteristic peak is observed at 1741 cm^{-1} due to carbonyl stretching vibrations that can be attributed to uric acid or oxalates present in the bats' excreta. (Figure 3(b)).

FTIR measurements from the back side of the earthen plaster with bats' excreta on the front were also carried out (Figure 3(c)). The spectra revealed broad peaks of moisture in the region 3200 and 3500 cm^{-1}. The peaks observed at 2200 and 2400 cm^{-1} are due to cyclic amide linkage (conjugate amid link is observed). Characteristic peaks due to carbonyl stretching vibrations are observed at 1774 and 1622 cm^{-1} and can be attributed to the uric acid or oxalates present in the bats' excreta. The peak observed at 1317 cm^{-1} is due to aryl NH or cyclic amide stretching vibrations. The peaks at 1417, 1007 and 778 cm^{-1} are due to the presence of earthen plaster that can be attributed to $CaCO_3$, Si–O linkage and Si–H stretching vibrations, respectively.

The cross section of the painted plaster is shown in Figure 4. The four layers that make up the paint and plaster can be described from bottom to top, as layer IV is the coarse labeling layer (IV) which is topped by the smothering layer of plaster (III), a lime wash (II) applied over the plaster, which serves as a primer for the painted tempera layer (I).

Thus, FTIR testing on the back of the plaster indicates that the excreta have migrated from the front through the porous earthen plaster to the back and therefore the process used for its eradication must not cause damage to the water-soluble binding media observed both in paint and mud plaster layers. The Raman spectra of bat excrement showed the presence of a peak at

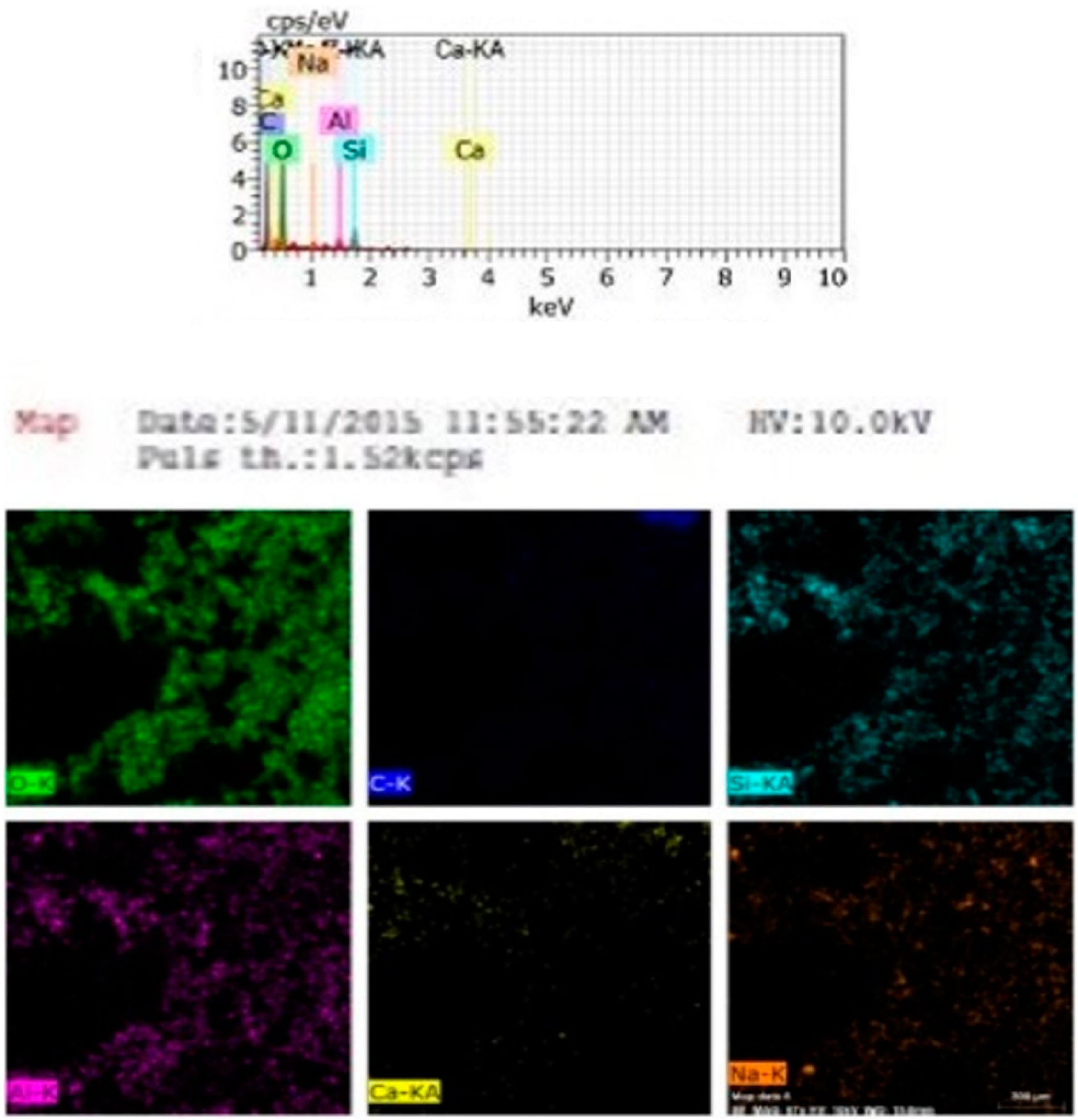


Figure 8. SEM-EDX of the back side of the mud plaster carrying bat excreta along with elemental mapping.

1619 cm^{-1} suggesting that the sample contains oxalates. The uric acid in bat excreta is broken down by fungi into urea and glyoxylic acid. The glyoxylic acid derived from fungal degradation of bird excreta tends to attack calcium-based construction materials through a process of acidolysis, which eventually lead to the formation of oxalic acid (Figure 5).

Two additional micro samples of earthen plaster collected from Cave No. 2 (around 200 microns in size) and affected by bat excrement were examined both front and back under SEM-EDS. The secondary electron images of both the surfaces for the two samples were recorded. The image of the front portion of the plaster suggested that the surface has become compact and non-porous with

Table 1. Ion strip tests of black and white deposits of bat excreta before and after cleaning.

Sl No	Parameter	Black/Brown deposits before cleaning	White deposit before cleaning	Black/Brown deposits after cleaning	White deposit after cleaning
1	pH	~6	~4	~6.5	~5.5
2	SO_4^{2-}	<200 mg/L	<1600 mg/L	<100 mg/L	< 800 mg/L
3	PO_4^{3-}	100–200 mg/L	>>500 mg /L	80–150 mg/L	>>300 mg /L
4	NO_3^-	Negligible	10–25 mg /L	Negligible	2–10 mg /L
5	Cl^-	500–1000 mg/L	Nil	300–600 mg/L	Nil
6	NH_4^+	60–100 mg/L	400 mg /L	20–60 mg/L	250 mg /L

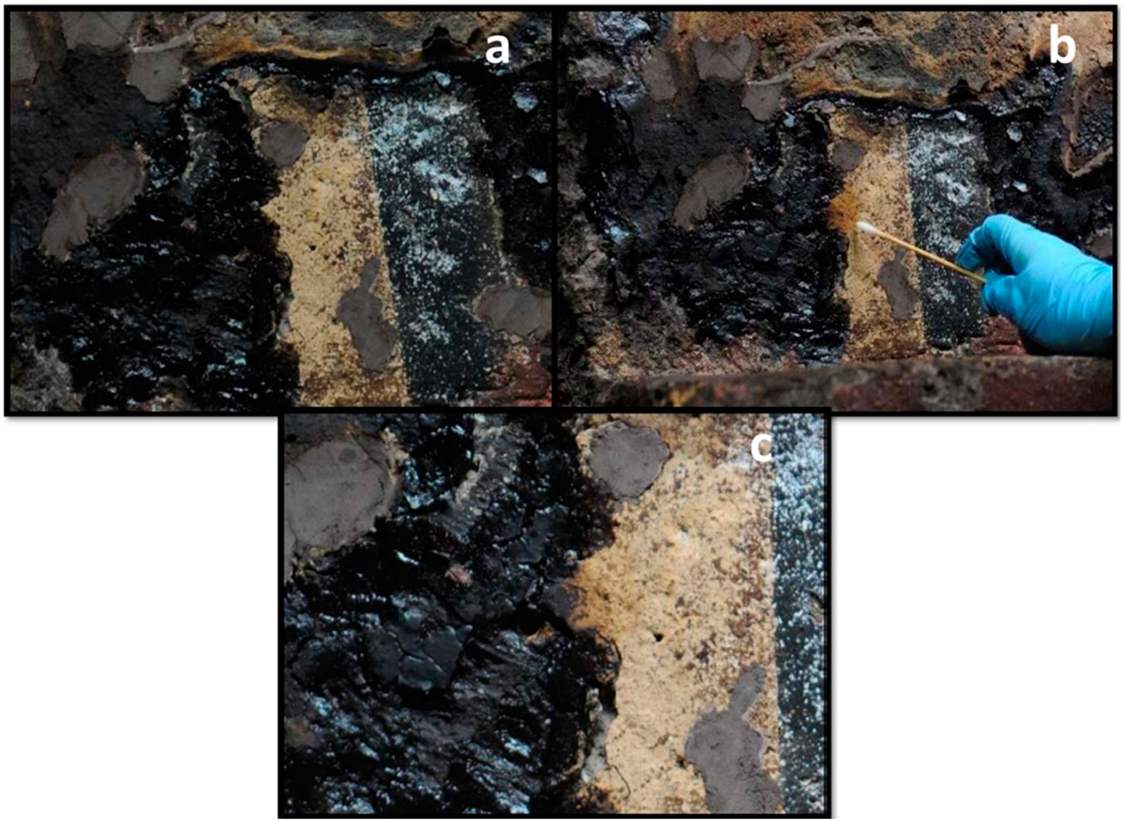


Figure 9. Cleaning trials for removal of bat excreta with de-ionized water after application of cyclododecane (CDD) (a) the initial application of CDD, (b) during the cleaning operations, (c) after cleaning of bat excreta.

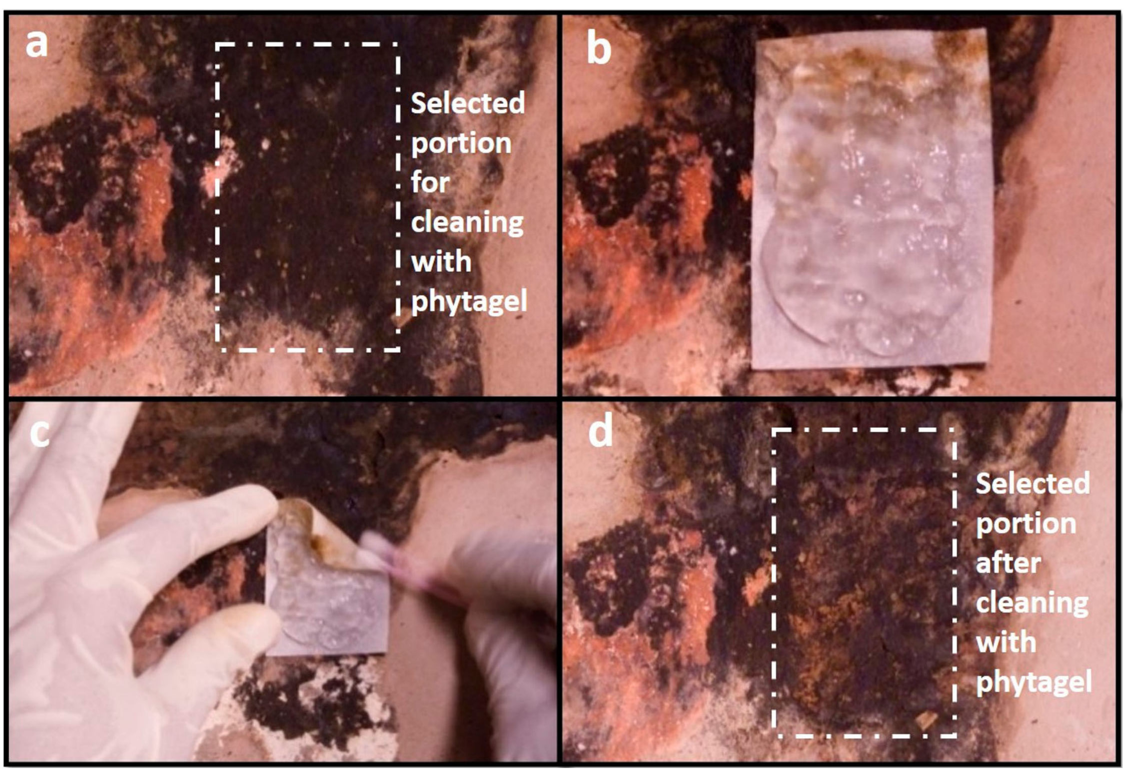


Figure 10. Cleaning trials for removal of bat excreta using phytagel.

some minor cracks. This was due to heavy discharge on the outer surfaces that has seeped deep into the porous plaster. The image on the back of the same plaster revealed that the surface is devoid of any kind of deposits. To further study the physical condition of the front surface of the earthen plaster, an additional SEM image was taken at higher magnification which showed clear deposition of bat excrement (Figure 6(a–d)).

The EDS of the guano-contaminated mud plaster led to the identification of elements present on the front and back sides. The elements identified were calcium, sodium, chloride, aluminum, carbon, and oxygen (Figure 7). These elements were also detected on the backside of the earthen plaster (Figure 8). The EDS analysis revealed the presence of a high percentage of chlorine and nitrogen, constituents of bats' excreta that were also confirmed by the qualitative specific reagent strip technique.

An ion strip test was carried out for a sample extracted from a damaged area of the east wall of Cave No. 2 to analyze various functional groups present in guano. The identified ions present in the excrement were phosphates, sulfates, nitrates, chlorides, and ammonium. The pH paper test result is shown in Table 1. Testing showed that the black/brown deposits have an excess of chlorides, whereas high quantities of sulfates are noted in the whitish accretions.

The cyclododecane layer protected the paint layer by forming a hydrophobic mask that allowed for the application of an aqueous medium for the removal of guano. This treatment not only helped in exposing the paintings underneath, but also allowed for the removal of the bat excreta. The CDD at the interface also prevented migration of water towards the adjacent and unaffected areas of paintings on account of its hydrophobic nature. Upon the completion of treatment, the samples continued to be observed for several months and it was found that the painted surface had ceased to behave as hydrophobic, which indicates the sublimation of CDD. The sublimation time might have been influenced by the thickness of the layer of CDD applied on the porosity of the painted surface (Figure 9). The removal of phytagel was also very simple as it formed a sheet on the surface which could be removed in one step and it did not leave any visible residue, due to the strong intermolecular bonding achieved after heating the phytagel polysaccharides. Phytagel sheets were very transparent and their application on the painted surfaces allowed much better visibility for observation of the painted surfaces during cleaning. (Figure 10).

For the application of CDD in the cleaning of bat excreta, an earthen plaster infested with black accretions, but devoid of any painting was first selected for intervention. The CDD was applied at the interface of the earthen plaster and a cleaning trial was undertaken with de-ionized water applied with a cotton swab. This method had a satisfactory result. Subsequently, the cleaning operation was extended to contaminated painted plaster. While the CDD stayed in the plaster preventing migration of the water towards the paint, the brown accretion of the bat excreta was successfully cleaned with de-ionized water (Figure 9).

After cleaning, the ion strip test was again performed on the sample. The data obtained are shown in Table 1. It can be observed that the values for sulfate, phosphate, nitrate, chloride, and ammonium have reduced considerably on the cleaned surface in comparison to the uncleaned surface (Table 1). This shows the effectiveness of the cleaning operation undertaken in this study and that the methodology can be extended to other areas or sites to safeguard water-sensitive painted plaster from the damaging effect of guano.

Conclusion

The cleaning of bat guano from decorative surfaces of India's Ajanta cave is a major conservation concern. A study using SEM-EDX, FTIR, Raman, and ion strip techniques was carried out to understand the composition and properties of the guano. Based on the characteristic features, CDD was applied to remove the guano of the painted plasters. Physical observation of the cleaned surface showed total sublimation of CDD in a 2–3 months period. The goal of the cleaning was to reduce the thickness of bats' guano to restrict its flow to the fresh unaffected painted surface during high humidity periods inside the cave. The process also restored the breathability of the contaminated surface. The cleaning continued until the surface no longer showed brownish soluble excreta on the tissue paper. The cleaned area was observed regularly for the reappearance of any stains over a period with satisfactory results and the method can now be extended for the safe removal of guano from water-sensitive mural arts at Ajanta and elsewhere.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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References

Annual Report of Archaeological Department of Nizam. 1949. “The Preservation and Maintenance of Cave Temple of Ajanta.” Annual Report of Archaeological Department of Nizam, 1–6.

Brown, M., and A. Davidson. 2010. “The Use of Cyclododecane to Protect Delicate Fossils During Transportation.” *Journal of Vertebrate Paleontology*, (30): 300–303.

Brückle, I., J. Thornton, K. Nichols, and G. Strickler. 1999. “Cyclododecane: Technical Note on Some Uses in Paper and Objects Conservation.” *Journal of the American Institute for Conservation* 38 (2): 162–175. doi:10.1179/019713699806113501.

Cacace, C., E. Giani, A. Giovagnoli, M. P. Nugari, and M. Singh. 2008. “The Mural Painting of Cave No. 17 Ajanta, the Environmental Studies and Geographical Information System (GIS) of Collected Data.” ICOM Committee for Conservation. 15th Triennial Conference, Vol. II, 2, 726–734. New Delhi, September 22–26.

Cremonesi, P. 2012. “Rigid Gels and Enzyme Cleaning,” *Smithsonian Contributions to Museum Conservation*, 3 (November 2010), 179–183.

Dhawan, S., K. Garg, and A. Mishra. 1991. “Effect of Temperature on Some Fungal Isolates of Ajanta Wall Paintings,” In Proceeding of the International Conference on Biodeterioration of Cultural Property, edited by O. P. Agrawal, and S. Dhawan, 339–352. Lucknow.

Dhawan, S., K. Garg, and N. Pathak. 1992. “Microbial Analysis of Ajanta Wall Painting and Their Possible Control InSitu.” In Proceeding of the 2nd International Conference on Biodeterioration of Cultural Property, edited by K. Toishi, H. Arai, T. Kenjo, and K. Yamano, 245–262. Tokyo: International Communications Specialists.

Griffiths, J. 1896. *The Paintings in the Buddhist Cave-Temples of Ajanta, Khandesh, India*. London: W. Griggs. Available at: https://books.google.co.in/books?id=WJIrNAAACAAJ.

Hangleiter, H. M. 2000. “Temporary Protection of Sensitive Surfaces about the Usage of Volatile Binding Agents,” in *DRV-Conference Berlin*. Hangleiter.

Lal, B. 1969. *The Murals: Their Preservation*, Ajanta Murals, Gosh, New Delhi, 56–59.

Paramasivan, S. 1936. “Technique of the Painting Process in the Cave Temples of Ajanta,” In *Annual Report of the Archaeological, H.E.H. the Nizam’s Dominions*. Calcutta.

Paramasivan, S. 1938. “Techniques of Painting Process in the Kailashnatha and Vaikuntha Perumal Temples in Kancheepuram.” In *Nature* CXL VII: 757.

Rao, A. S., and N. K. Rao. 1972. “The Petrogarphy and Petrochemistry of Deccan Traps of Ajanta Area.” *Journal of Indian Academy of Geo-Science* 15 (1): 67–81.

Sharma, R., K. Saxena, and V. Saxena. 1995. “Biodeterioration of Cave Paintings Due to Bat’s Excrement, Biodeterioration of Cultural Property,” in Proceeding of the 3rd International Conference on Biodeterioration of Cultural Property. Bangkok, Thailand, July 4–7.

Singh, M., and B. Arbad. 2013a. “Architectural History and Painting Art at Ajanta: Some Salient Features.” *Arts* 2 (3): 134–150. doi:10.3390/arts2030134.

Singh, M., and B. Arbad. 2013b. “Chemistry of Preservation of Ajanta Murals.” *International Journal of Conservation Science* 35 (10): 161–176.

Singh, M., and B. R. Arbad. 2015. “Characterization of 4th-5th Century A.D. Earthen Plaster Support Layers of Ajanta Mural Paintings.” *Construction and Building Materials.* 82: 142–154. doi:10.1016/j.conbuildmat.2015.02.043.

Spink, W. M. 2011. *Ajanta: History and Development: The End of the Golden Age*, Vol. 1. Brill. Available at: https://books.google.co.in/books?id=n4ChtgAACAAJ.

Spink, W. M. 2014. *Ajanta: History and Development, Volume 6 Defining Features*. Brill. Available at: https://books.google.co.in/books?id=PdlXAwAAQBAJ.

Stein, R., J. Kimmel, M. Marincola, and F. Klemm. 2000. “Observations on Cyclododecane as a Temporary Consolidant for Stone.” *Journal of the American Institute for Conservation* 39 (3): 355–369. doi:10.2307/3179979.

Tilak, S. T., B. R. N. Sharma, S. R. SenGupta, and R. L. Kulkarni. 1970. “The Deterioration and Microbiological Studies of Ajanta and Ellora Paintings, Conservation of Cultural Property in India.” *Indian Association for the Study of Conservation of Cultural Property* 5: 77–82.

UNESCO. 1983. “Periodic Reporting on the Application of the World Heritage Convention Section II”, 2.

Watters, C. 2007. “Cyclododecane: A Closer Look at Practical Issues.” *Anatolian Archaeological Studies* 16: 195–204.

Yazdani, G. 1930. *Guide to Ajanta Frescoes*. Archaeological Department H.E.H. The Nizam’s Government. Available at: https://books.google.co.in/books?id=MDrrAAAAMAAJ.