

PHYSICO-CHEMICAL ASSESSMENT OF BIODETERIORATED AND BIODEGRADED ARCHIVAL PAPER

Salgo Merin JACOB, Jenifer RASEETHA, Varsha KELKAR-MANE*

Department of Biotechnology, University of Mumbai; Vidyanagari, Kalina, Santacruz (E), Mumbai-400098, India

Abstract

Archival preservation has always been important for mankind to transfer knowledge to the posterity. Their degradation/deterioration and preservation has been studied with a view to aid in their restoration and conservation. The present work employs analytical and microbial methods to understand the physico-chemical deterioration and degradation of a 19th century colored map and two 20th century photocopied map. Irrespective of the era, analysis revealed that all the three samples were acidic in nature with rosins as sizing agent, were high in organic matter primarily cellulose with high moisture levels. The degraded/deteriorated regions of the paper were subjected to Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) to further elucidate the type of effect. The estimates of microbial count efficiently co-related with the physico-chemical changes observed in the archival documents. It can thus be concluded that irrespective of the era biodeterioration and biodegradation of archival documents follow a similar pattern.

Keywords: Archival documents; Biodeterioration and biodegradation; Cellulose support; FTIR; SEM

Introduction

Cultural property preserved in indoor environments, such as libraries and archives, are subject to a particularly high risk of biodeterioration effects of the physical state of the artefact and, respectively, biodegradation effects of the chemical nature of the component materials [1, 2]. The two effects of historic paintings, wood, paper, glass, textiles, metals, waxes, stone, polymers and coatings by microbial action is a well documented phenomenon; no material is completely immune to microbial attack [3]. Our history is primarily stored in the form of written texts, an asset indispensable for our present and future. These historical records are our heritage to future generations [4]. Archives once lost cannot be replaced, and usually reconstruction is impossible. Archives allow us to establish communications between past and future generations [5]. Libraries and archives worldwide face the growing concern regarding the biodegradation of ancient documents and books [5]. Degradation of paper-based materials is mainly due to the alteration of cellulose caused by a number of factors, such as chemical attack due to acidic hydrolysis, oxidative agents, light, air pollution and biological attack due to the presence of microorganisms like bacteria and fungi [6-10]. Study of documentation reveals that various methods were used for manufacture of paper. Paper largely contained lignin and

* Corresponding author: drvkelkar@mu.ac.in salgotmerin@gmail.com

cellulosic material embedded with fillers and sizing agents of different kind. In 19th century process of photozincography was more popular for printing more copies whereas in 20th century colored printing using inks and pigments was in vogue hence differences in paper quality were expected [7].

Enzymes of microbial origin such as cellulases, proteases, etc cause structural alterations within the matrix of the paper [11-13]. These enzymes are synthesized by microorganisms which compound the frailty of paper leading to its ultimate deterioration. Additionally essential additive components such as plasticizers, adhesives, organic glues, inks, pigments and bindings are susceptible to microbial attacks [11, 12, 14] which cause extensive damage to distinguishing features of documents rendering them unusable.

India is a country with a rich history; one can trace its origins to the Stone Age [15]. India boasts of one the world's oldest and largest collection of intact ancient manuscripts. The culture and literary heritage in India lie distributed at different institutions, libraries and private collections. These relics are becoming victims to deterioration, never to be seen again. Approximately 20-25 percent of the manuscripts surveyed is cataloged and preserved reliably [15-19]. In addition to this, India is a tropical country and the rate of deterioration is greatly affected by the environmental factors like heat, humidity, salinity due to the proximity to the sea [20]. This encourages and supports the growth of macro as well as micro organisms like insects molds, bacteria etc. Deterioration and degradation of such documents across diverse countries has been recognized in terms of the changes in their physical as well as chemical characteristics [27-31]. Many antifungal/antibacterial methods are used to prevent and/or stop biodeterioration and biodegradation. These methods can go from limiting the access to water by the fungi, to the application of chemical products in the gaseous or liquid state, or physical methods like extreme temperatures, radiation or current. A proper antifungal method for materials should have a broad activity spectrum, good chemical stability, low cost, should not be toxic to humans, and should have no adverse effects on the treated material. Several authors have measured pH of historical paper as it plays an important role to explain the mechanism of deterioration [27-29]. *C. Ververis et al.* [30] and *G. Abdel-Maksoud* [6] used chemical analysis for the estimation of hemicelluloses, lignin, and ash content. Additionally detailed methods have been utilized such as analytical techniques like Fourier transform infrared spectroscopy (FTIR) for the identification of the matrix as well as other components used in paper manuscripts [31-35]. Microbiological studies and examination of the surface morphology have also been evaluated in order to determine the degree of biodeterioration and biodegradation [35-40].

Taking into account these aspects, the objectives set for this study were to assess biodeterioration and biodegradation of archival documents belonging to the 19th and 20th century by biological as well as chemical analysis. A photozincographed map copy from the 19th century and two colored maps from the 20th century were selected for studying their degradation patterns. For characterization of the paper and to understand the degradation of these documents several non-invasive and micro-invasive techniques were used, observations were made using optical microscopy and, Scanning electron microscope (SEM). Chemical tests were carried out to identify the composition in terms of the structural matrix components and the additives used as binders or fillers for archival documents. The examination using Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) complemented the chemical analysis enabling the evaluation of difference in the matrix components of the paper.

Materials and Methods

Sample selection

Archival materials from the 19th and 20th centuries, ie maps belonging to the states of Hyderabad and Mumbai, were used as a source for the study. The maps belonging to the 19th century was a photozincographed map, whereas the other two maps belonging to 20th century were colored maps. These maps were collected from a private personal collection in Mumbai. The maps were stored in open racks in an open room. These documents are fumigated using Para-dichloro benzene and Carboxide (Mixture of Carbondioxide and Ethyleneoxide = 9:1) once in 3-6 months. In order to minimize the damage caused to the text and figures of the map the paper samples were taken from the peripheral region.

Investigation of the surface morphology by optical microscopy and SEM

The observations using optical microscope constituted the first step in identifying the alterations in the paper structure caused due to staining, mineralization and microbial growth. A light microscope, Leica DM750 was used for the direct examination of the paper samples. A scanning electron microscope, FEI-ESEM Quanta 200, was used for the elucidation of the surface morphology of the map paper.

Isolation of micro organisms

Sterile cotton buds were used to swab the surface of the papers in order to isolate the microbial load, especially from the contaminated area characterized by foxed and typically discolored areas. The cotton bud was then swabbed on to Nutrient agar surface for bacteria and Sabouraud's agar for fungi. The plates were incubated at 28°C for 2-3 days. The number colonies present on the plates were counted after the period of incubation. The colonies were screened for cellulolytic activity using Carboxy Methyl Cellulose (CMC) Congo-red agar. The bacteria which showed cellulolytic activity were subjected to preliminary identification through gram staining and biochemical characterization. The fungal isolates showing cellulolytic activity, obtained from both these techniques, were identified based on their cultural and morphological characteristics

Chemical analysis of paper

pH measurement

The measurement of the pH of the paper during this study was in accordance with TAPPI standard T 529 om-04 [41] with required modifications. Briefly, a 200 μ L drop of distilled water was placed on the surface of the manuscript, and the surface combined pH electrode pressed against it. The pH values were read after being constant for 30s.

Ash content

The percent ash content was estimated following TAPPI standard T 211 om-02 [42]. A test specimen was ignited in a muffle furnace at 525°C. The resulting weight of ash is used to calculate the percentage ash present at 525°C on a moisture-free sample basis.

Moisture content:

The percent moisture content was determined following the TAPPI standard T 550 om-08 [43]. The percentage of moisture in a sample was determined by drying the sample to a constant weight.

Lignin content

The lignin content was estimated by TAPPI standard T 222om-02 [44] for Acid-insoluble residue (AIR) and TAPPI UM 250 [45] for Acid-soluble lignin (ASL). To determine the AIR the carbohydrates in the paper pulp are hydrolyzed and solubilized by sulfuric acid; the

acid-insoluble lignin is filtered off, dried, and weighed. ASL is determined from the filtrate by spectrophotometry at 205nm.

Cellulose content

Alpha-, beta- and gamma-cellulose in paper pulp was estimated using TAPPI standard T 203 cm-99 [46]. The pulp was extracted consecutively with 17.5% and 9.45% sodium hydroxide solutions. The soluble fraction consisting of beta- and gamma-celluloses is determined volumetrically by oxidation with potassium dichromate, and the alpha cellulose, as in insoluble fraction, is derived by difference.

Spot/Qualitative tests

The qualitative analyses were based on color reactions and were carried out to identify the presence of organic and inorganic constituent. These reactions occur directly on small areas of the paper surfaces. The presence/absence of rosin glue by the Raspail test, gelatin by the Tannin test, and fillers i.e. Test for Sulfite, Sulfides, Carbonate using TAPPI standard T 421 om-97 was carried out.

FTIR Analysis

The FTIR spectra were obtained in Attenuated total reflection mode (ATR) using the FTIR – 460 plus, Jasco, equipped with a single reflection ATR cell and ZnSe crystal. All the spectra were acquired in the range of 4000-650cm⁻¹ at a resolution of 4cm⁻¹. The background measurement was recorded in order to eliminate the effect of the atmospheric carbon dioxide and water vapor.

Validation of scaled down methods and Statistical analysis

The physico- chemical analysis was carried out using TAPPI standards as described above. However, considering the sample quantity all the methods were validated to 1/10th of the original recommendation. The scaled down method was validated using standard whatman paper no 1. All the validations were carried out in replicates. The values obtained did not show any statistical difference when the sample quantity was reduced to 1/10th of recommended method. All experiments were performed in replicates. Mean and SD values are represented.

Results and Discussions

Investigation of the surface morphology by Optical & SEM microscopy

Under microscopic observation (Fig. 1.) random distribution and erosion of fibers was observed on all the samples. Foreign particles present between fibers could be most likely filler material or artifacts, contaminations from stains and dust. Physical damage in form of bores, deformations and micro tears in the strata of the fibers could be attributed to macroorganisms like silverfish and other insects.

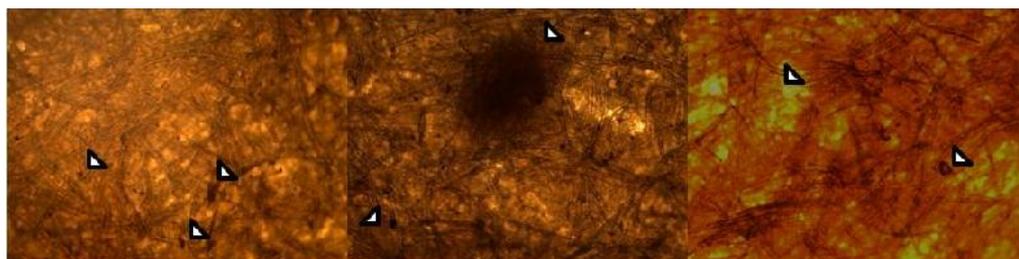


Fig. 1. Optical Microscope images of areas from the maps showing signs of deterioration

SEM analysis of the three maps showed severe microbial infestation in and around the cellulose fibers (Fig. 2). The presence of organic materials possibly of microbial origin, such as fungi and bacteria, were detected on the entire surface of the paper samples. Their presence was heterogeneous, crowded in some areas and limited in others. At areas with high microbial infestation the cellulose fibers were not visible because of the biological matter. The biodiversity of microflora on the paper was confirmed from the microbial samples collected and cultured from the paper surface. The greater reflection in few of the SEM images could be suggestive of mineralization. Microbial linked mineralization is reported in degrading paper material by *F. Pinzari et al.* [37]. Therefore it is likely that the mineralized areas observed in the present study could be due to microbial activity. The SEM observation of the morphology of paper fibers suggests that the material comes mostly from cotton.

Isolation of micro organisms

It was observed that bacterial isolates were larger in number on the documents whereas larger number of fungi was isolated from areas which showed signs of deteriorations. The bacterial cultures isolated were more diverse with gram positive rods and cocci along with few gram negative rods/coccobacilli. Fungi isolated mainly from areas which were foxed and bleached were dominated by *Aspergillus* species (Table 2). The Table 1 gives the colony counts of each of the archival document. Earlier study undertaken by this lab [13] showed a similar trend where in it was observed that areas with high fungal density had invariably low bacterial count and vice versa.

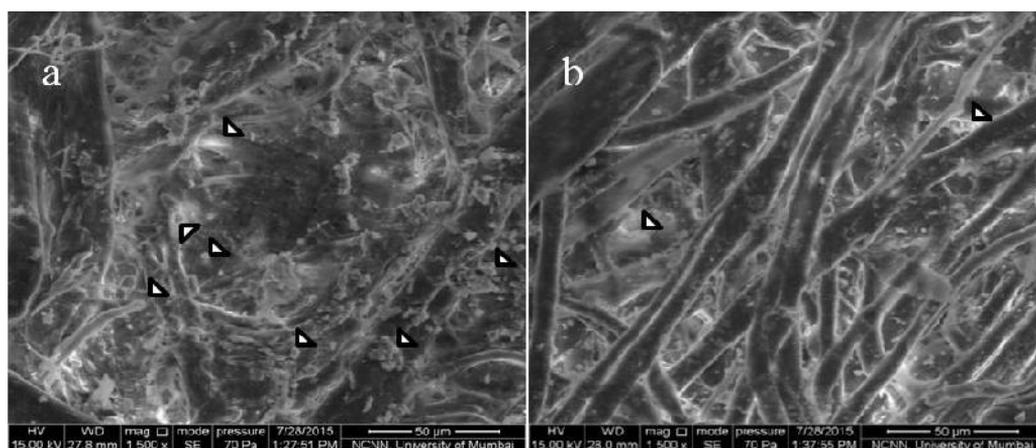


Fig. 2. SEM images of map (a) Area with high microbial infestation (b) Area with low microbial infestation

Table 1. Colony counts of bacteria and fungi isolated from each map

Sample	No. of bacterial colonies	No. of fungal colonies
Map 1	12	9
Map 2	17	7
Map 3	15	6

Chemical analysis of paper

The data on various parameters of the chemical analysis are presented in Table 3. The pH measurements revealed that the archival documents studied ranged from near neutral acidic 6.1 to 5.1. When co-related with microbial load, it is observed that acidic pH supported larger

population of fungus with lower bacterial count whereas near neutral (pH = 6.1) supported larger population of bacteria with lesser number of fungi (Table 1). The differential acidity can also be attributed to the manufacturing process or due to absorption of pollutants such as sulfur dioxide and nitrogen oxides. Also, the presence of rosin, as detected by the *Raspail test* is known to contribute to the acidic nature of paper as rosin is acidic in nature [48].

Table 2. Fungi isolated from different areas of maps

	Sample	No. of fungal colonies	Genera of fungi
Map 1	Foxed area (1)	2	<i>Aspergillus</i> species
	Foxed area (2)	3	2 <i>Aspergillus</i> and 1 <i>Penicillium</i> species
	Bleached area (3)	3	1 <i>Aspergillus</i> , 1 <i>Cladosporium</i> and 1 <i>Penicillium</i> species
	Normal area	1	<i>Aspergillus</i> species
Map 2	Foxed area (1)	1	<i>Aspergillus</i> species
	Foxed area (2)	3	2 <i>Aspergillus</i> and 1 <i>Penicillium</i> species
	Bleached area (3)	2	<i>Aspergillus</i> species
	Normal area	0	
Map 3	Foxed area (1)	2	<i>Aspergillus</i> species
	Foxed area (2)	1	<i>Aspergillus</i> species
	Bleached area (3)	2	1 <i>Aspergillus</i> and 1 <i>Penicillium</i> species
	Normal area	1	<i>Aspergillus</i> species

Percentage ash content is high in map 2 and 3 as compared to map 1 which is indicative of higher inorganic content in those maps as compared to map 1 (Table 3). This is indicative of the differences in the manufacturing processes of the paper through the era. All the documents in the study showed higher moisture content ranging from 7.69 -11.9% than generally accepted for the commercial printing (2-7%) [49] which could be attributed to the environmental humidity where the maps were stored. Literature cites significant increase in the rate of paper degradation with increasing moisture content [28, 50, 51]. During this study the maps with higher moisture content supported higher bacterial load (Table 3).

Table 3. Chemical analysis of paper

Sample	pH	% Ash content	% Moisture content	Lignin Content			Cellulose Content			Raspail test	Test for Gelatin, Sulfite, Sulfides and Carbonate
				AIR mg/g	ASL mg/g	Total: mg/g	Alpha %	Beta %	Gamma %		
Map 1 19th century	5.15± 0.05	0.714 ± 0.01	7.67 ± 0.01	0.34 ± 0.01	3.6 ± 0.36	3.94 ± 0.35	80.45 ± 0.05	14.06 ± 0.01	5.48 ± 0.06	Rosin present	Absent
	6.15± 0.06	13.56 ± 0.01	10.52 ± 0.02	0.17 ± 0.01	7.5 ± 0.30	7.70 ± 0.31	85.36 ± 0.07	7.85 ± 0.08	6.78 ± 0.03	Rosin present	Absent
Map 3 20th century	5.80 ± 0.01	14.02 ± 0.01	11.76 ± 0.15	0.25 ± 0.01	7.3 ± 0.30	7.61 ± 0.29	85.36 ± 0.09	7.88 ± 0.13	6.74 ± 0.03	Rosin present	Absent

The documents used in the present study were low in lignin content and high in alpha cellulose contents. The high alpha cellulose content obtained in the study was indicative of pure cellulose being used in the manufacturing of the paper. SEM imaging also supports the same in the present study (Fig 2).

Map 1 showed highest amount of beta cellulose, which is a degraded form of alpha cellulose. A higher number of fungi, isolated from map 1, seem to be the responsible factor for the cellulose degradation. Similarly, the higher acidity of the paper could also be attributed to the fungal degradation of cellulosic material. Fungi are known to degrade cellulose in archival documents and a large number of fungal spores were also seen in the SEM analysis (Fig 2).

FTIR Analysis

It has been already reported that the FTIR analysis, particularly in Attenuated Total Reflectance (ATR) mode appears to be promising, for preliminary analysis of the composition of ancient paper documents. FTIR-ATR analysis allows a rough classification of paper materials by examining the infrared bands not masked by cellulosic components.

General trend that appeared in the FTIR spectra of the three maps was as explained in the Table 4. The broad band in the 3600-3100cm⁻¹ region is attributed to OH-stretching vibration. Changes were observed in the 1300-1500cm⁻¹ region where the numbers of bands are due to numerous mixed vibrations rather than to characteristic group frequencies. Thus, the bands in this range are mixtures of OCH deformation vibrations, CH₂ bending vibrations, CCH and COH bending vibrations. Table 4 represents IR spectra of three maps from normal as well as foxed/ bleached area. It is observed that significant shift in the wavelenghts 3366cm⁻¹ and 1649cm⁻¹ in map 2 and 3345cm⁻¹ in map 3 suggesting alteration in the structure of the matrix of map 2 and 3 no such deviation was observed in the spectra of map 1. Incidentally map 2 and 3 are from the same era. Vibrational spectra, presented in this work, conclude that the paper samples are almost pure cellulose. Due to the different state of degradation of cellulose (paper) differences in the intensities of the bonds (~3300, ~1600 and ~1000cm⁻¹) and O-H bonds (~3338cm⁻¹) are evident. The water absorption belonging to the C-O bond, which can be explained by hydrolysis and oxidation of cellulose. The most marked variation is the decrease in intensity of the O-H stretch hydrogen-bonded band at around 3300cm⁻¹. Biotic foxing is evident from the peak 1159cm⁻¹ present on all 3 map samples attributed to N-acetyl ester bonds, Amide II bands.

Table 4. IR spectra and structural assignments

		Peakposition cm ⁻¹						Peak assignment
Map1		Map 2		Map 3				
Normal	Foxed	Normal	Foxed	Normal	Foxed			
			662				C-C stretching	
1029	1030	1029	1029	1031	1024	1029	C-O Stretch in cellulose and hemicellulose, C-O of primary alcohol	
1053	1053	1053					Denoting the presence of the glucose ring	
1109	1108	1110	1105	1109		1108	C-O and C-C ring vibrational stretching	
							Nonsymmetric in-phase ring of amorphous cellulose	
1159	1159		1159		1153	1159	N-acetyl ester bonds, Amide II	
1317	1317	1316	1316	1317	1320	1316	CH ₂ wagging, which distinguished between amorphous and crystallised I cellulose	
1647	1637	1619	1649	1620	1647	1649	Adsorbed OH (water) and conjugated C=O	
2367			2363	2365			Alkynes C=C, C-O stretching	
2900	2897				2900	2895	C-Hn, CH, CH ₂ and intermolecular OH stretching vibrations	
3339	3337	3338	3366	3331	3345	3327	Intra molecular OH-stretching vibration	

Precaution should be taken to use agents to control damage from ultraviolet radiation, pollutant gasses, fungi and bacteria that themselves do not enhance archival degradation. To protect against biodeterioration and biodegradation archival repositories fumigate, expose to UV light archival documents as a common practice which is responsible to weaken the cellulose fibers and ad to deterioration. This study highlights that documents from all eras follow the same pattern for deterioration, as environmental and extrinsic factors play a major role in deterioration. Antimicrobial protective coatings on archival documents will be an advanced procedure for preservation which will evade biodeterioration and biodegradation, and also protect from other extrinsic factors. Further studies with other paper materials are in progress for a better understanding of the abiotic factors and microbial degradation of archival documents for the preservation.

Acknowledgments

The author Salgo Merin Jacob wishes to acknowledge University Grants Commission (UGC), India for the support provided through fellowship.

References

- [1] C. Pasquarella, E. Sacconi, G.E. Sansebastiano, M. Ugolotti, G. Pasquariello, R. Albertini, *Proposal for a biological environmental monitoring approach to be used in libraries and archives*, **Annals of Agricultural and Environmental Medicine**, **19**(2), 2012, pp. 209-212.
- [2] O.M. Bankole, *A review of biological deterioration of library materials and possible control strategies in the tropics*, **Library Review**, **59**(6), 2010, pp. 414-429.
- [3] R. Mitchell, J.C. McNamara, **Cultural Heritage Microbiology: Fundamental Studies in Conservation Science**, 1st ed., ASM Press, 2010.
- [4] R. Teygeler, G. de Bruin, B. Wassink, **Preservation of Archives in Tropical Climates: An Annotated Bibliography**, International Council on Archives, Netherlands, Algemeen Rijksarchief, Arsip Nasional Republik Indonesia, ICA, 2001.
- [5] A. Michaelsen, G. Piñar, F. Pinzari, *Molecular and Microscopical Investigation of the Microflora Inhabiting a Deteriorated Italian Manuscript Dated from the Thirteenth Century*, **Microbial Ecology**, **60**(1), 2010, pp. 69-80.
- [6] G. Abdel-Maksoud, *Analytical techniques used for the evaluation of a 19th century quranic manuscript conditions*, **Measurement**, **44**(1), 2011, pp. 1606-1617.
- [7] M.C. Area, H. Cheradame, *Paper aging and degradation: recent findings and research methods*, **BioResources**, **6**(4), 2011, pp. 5307-5337.
- [8] P. Begin, S. Deschâtelets, D. Grattan, N. Gurnagul, J. Iraci, E. Kaminska, D. Woods, X. Zou, *The effect of air pollutants on paper stability*, **Restaurator**, **20**(1), pp. 1-21.
- [9] J. Bogaard, P.M. Whitmore, *Explorations of the role of humidity fluctuations in the deterioration of paper*, **Contributions to the Baltimore Congress, 2-6 September 2002. Works of Art on Paper Books, Documents and Photographs: Techniques and Conservation**, **Studies in Conservation**, **47**(3), 2002, pp. 11-15.
- [10] S. Zervos, I. Alexopoulou, *Paper conservation methods: a literature review*, **Cellulose**, **22**(5), pp. 2859-2897.

- [11] S. Manente, A. Micheluz, R. Ganzerla, G. Ravagnan, A. Gambaro, *Chemical and biological characterization of paper: A case study using a proposed methodological approach*, **International Biodeterioration and Biodegradation**, **74**, 2012, pp. 99-108.
- [12] K. Sterflinger, *Fungi: their role in deterioration of cultural heritage*, **Fungal Biology Reviews**, **24**(1-2), 2010, pp. 47-55.
- [13] S.M. Jacob, A.M. Bhagwat, V.K.-Mane, *Bacillus species as an intrinsic controller of fungal deterioration of archival documents*, **International Biodeterioration and Biodegradation**, **104**, 2015, pp. 46-52.
- [14] F. Gallo, **Biological Factors in Deteriorations of Paper**, ICCROM, Roma, 1985.
- [15] K. Antonova, G. Levin-Bongard, G. Kotovsky, K. Judelson, **A History of India**, 1st ed., Progress Publishers, Moscow, 1979.
- [16] R.C. Gaur, M. Chakraborty, *Preservation and access to Indian manuscripts: A knowledge base of Indian cultural heritage resources for academic libraries*, **Proceedings of the International Conference on Academic Libraries, ICAL, 5-8 October, 2009, Vision and Roles of the Future Academic Libraries**, University of Delhi, New Delhi, 2009, pp. 90-98.
- [17] A.K. Jain, S. Kumar, S. Choudhury, K.B. Jain, B.K. Sharma, *Rare handwritten manuscript collection in Indic Languages at Scindia Oriental Research Institute (SORI), (India)*, **Proceedings of the 79th IFLA General Conference and Assembly by IFLA World Library and Information Congress, 17-23 august 2013**, Singapore, 2013.
- [18] J. Sahoo, B.S.M. Phil, B. Mohanty, N.K. Dash, *Indian manuscript heritage and the role of national mission for manuscripts*, **Library Philosophy and Practice (ejournal)**, 2013, Paper no. 984.
- [19] S. Kumar, L. Shah, *Digital Preservation of Manuscripts: A Case Study*, **Proceedings of 2nd Convention PLANNER – 2004**, Manipur University, Imphala, 4-5 November, INFLIBNET Centre, Ahmedabad, 2004, pp. 27-36.
- [20] * * * S.D. Attri, A. Tyagi, **Climate profile of India. Environment Meteorology - 01/2010, Contribution to the Indian Network of Climate Change Assessment (National Communication-II) Ministry of Environment and Forests**, India Meteorological Department, Ministry of Earth Sciences New Delhi, 2010.
http://www.indiaenvironmentportal.org.in/files/climate_profile.pdf
- [21] F. Poole, Some aspects of the conservation: problem in archives, **The American Archivist**, **40**(2), 1977, pp. 163-171.
- [22] S.F. Ibrahim, D.M. Essa, F.M. Tera, fast production of artificial mimic textile samples using uv/ozone treatment application in conservation and consolidation, **International Journal of Conservation Science**, **6**(1), 2015, pp. 15-22.
- [23] I.C.A. Sandu, C. Luca, I. Sandu, A study on the paintings cloth-supports ageing degradation, **Revista de Chimie**, **50**(12), 1999, pp. 902-908.
- [24] W. Noshyutta, E. Osman, M. Mansour, An investigation of the biological fungicidal activity of some essential oils used as preservatives for a 19th century Egyptian coptic cellulosic manuscript, **International Journal of Conservation Science**, **7**(1), 2016, pp. 41-56.
- [25] G.M. Simu, I.V. Ledeti, S.G. Muntean, A. Fulas, I.M. Citu, C. Soica, D. Onisei, G. Savoiu-Balint, I. Pinzaru, D. Ionescu, *Study of the Interaction of Some Pharmaceutical*

- Compounds with Different Cellulosic Supports*, **Revista de Chimie**, **65**(6), 2014, pp. 664-670.
- [26] T. Lech, A. Ziembinska-Buczynska, N. Krupa, *Analysis of the microflora present on historical textiles with use of molecular techniques*, **International Journal of Conservation Science**, **6**(2), 2015, pp. 137-144.
- [27] E. Menart, G. de Bruin, M. Strlic, *Dose-response functions for historic paper*, **Polymer Degradation and Stability**, **96**(12), 2011, pp. 2029-2039.
- [28] M. Strlic, I.K. Cigic, J. Kolar, G. de Bruin, B. Pihlar, *Non-destructive evaluation of historical paper based on pH estimation from VOC emissions*, **Sensors (Basel)**, **7**(12), 2007, pp. 3136-3145.
- [29] A. Joel, N. Indictor, J.F. Hanlan, N. Baer, *The Measurement and significance of pH in paper conservation*, **Bulletin of the American Group** (International Institute for Conservation of Historic and Artistic Works), **12**(2), 1972, pp. 119-125.
- [30] C. Ververis, K. Georghiou, N. Christodoulakis, P. Santas, R. Santas, *Fiber dimensions, lignin and cellulose content of various plant materials and their suitability for paper production*, **Industrial Crops and Products**, **19**(3), pp. 245-254.
- [31] W. Faubel, S. Staub, R. Simon, S. Heissler, A. Pataki, G. Banik, *Non-destructive analysis for the investigation of decomposition phenomena of historical manuscripts and prints*, **Spectrochimica Acta Part B: Atomic Spectroscopy**, **62**(6-7), 2007, pp. 669-676.
- [32] D. Agha-Aligol, F. Khosravi, M. Lamehi-Rachti, A. Baghizadeh, P. Oliyai, F. Shokouhi F, *Analysis of 19th-19th century's historical samples of Iranian ink and paper belonging to the Qajar dynast*, **Journal of Applied Physics A: Materials Science and Processing**, **89**(3), 2007, pp. 799-805.
- [33] K. Kavkler, N.G. Cimerman, P. Zalar, A. Demsar, *Deterioration of contemporary and artificially aged cotton by selected fungal species*, **Polymer Degradation and Stability**, **113**, 2015, pp. 1-9.
- [34] K. Kavkler, N. Gunde-Cimerman, P. Zalar, A. Demsar, *FTIR spectroscopy of biodegraded historical textiles*, **Polymer Degradation and Stability**, **96**(4), 2011, pp. 574-580.
- [35] M. Zotti, A. Ferroni, P. Calvini, *Microfungal biodeterioration of historic paper: Preliminary FTIR and microbiological analyses*, **International Biodeterioration and Biodegradation**, **62**(2), 2008, pp. 186-194.
- [36] T. Espejo, A. Duran, A. Lopez-Montes, R. Blanc, *Microscopic and spectroscopic techniques for the study of paper supports and textile used in the binding of hispano-arabic manuscripts from Al- Andalus: A transition model in the 15th century*, **Journal Cultural Heritage**, **11**(1), 2010, pp. 50-58.
- [37] F. Pinzari, M. Zotti, A. de Mico, P. Calvini, *Biodegradation of inorganic components in paper documents: Formation of calcium oxalate crystals as a consequence of *Aspergillus terreus* Thom growth*, **International Biodeterioration and Biodegradation**, **64**(6), 2010, pp. 499-505.
- [38] C. Schabereiter-Gurtner, G. Pinar, W. Lubitz, S. Rolleke, *An advanced molecular strategy to identify bacterial communities on art objects*, **Journal of Microbiological Methods**, **45** 2001, pp. 77-87.

- [39] A. Michaelsen, F. Pinzari, K. Ripka, W. Lubitz, G. Pinar, *Application of molecular techniques for identification of fungal communities colonising paper material*, **International Biodeterioration and Biodegradation**, **58**, 2006, pp. 133–141.
- [40] M. Buckova, A. Puskarova, M.C. Sclocchi, M. Bicchieri, P. Colaizzi, F. Pinzari, D. Pangallo, *Co-occurrence of bacteria and fungi and spatial partitioning during photographic materials biodeterioration*, **Polymer Degradation and Stability**, **108**, 2014, pp. 1-11
- [41] * * *, *Surface pH measurement of paper*, **TAPPI T529 om-04**, 2004.
- [42] * * *, *Ash in wood, pulp, paper and paperboard: combustion at 525°C*, **TAPPI T 211 om-02**, 2002.
- [43] * * *, *Determination of equilibrium moisture in pulp, paper and paperboard for chemical analysis*, **TAPPI T 550 om-08**, 2013.
- [44] * * *, *Acid-insoluble lignin in wood and pulp*, **TAPPI T 222 om-02**, 2006.
- [45] * * *, *Acid-soluble lignin in wood and pulp*, **TAPPI UM 250**, 1991.
- [46] * * *, *Alpha-, beta- and gamma-cellulose in pulp*, **TAPPI T 203 cm-99**, 1999.
- [47] * * *, *Qualitative (including optical microscopic) analysis of mineral filler and mineral coating of paper*, **TAPPI T 421 om-97**, 1997.
- [48] Y. Ito, D. Folmer, *Glycerol Ester of Wood Rosin - Chemical and Technical Assessment (CTA)*, 2013. http://www.fao.org/fileadmin/user_upload/agns/pdf/CTA_GEW_77.pdf
- [49] * * *, **Properties of Paper - PaperOnWeb**, <http://www.paperonweb.com/paperpro.htm> accessed on 18th November 2015
- [50] A.B.J. Du Plooy, The influence of moisture content and temperature on the aging rate of paper, **Appita**, **34**, 1981, pp. 287–292.
- [51] E. Vänskä, M. Luukka, I. Solala, T. Vuorinen, *Effect of water vapor in air on thermal degradation of paper at high temperature*, **Polymer Degradation and Stability**, **99**, 2014, pp. 283-289.

Received: April 8, 2017

Accepted: December 3, 2017