INTERNATIONAL JOURNAL OF CONSERVATION SCIENCE

ISSN: 2067-533X Volume 7, Issue 4, October-December 2016: 1023-1030 www.ijcs.uaic.ro

EXPERIMENTAL STUDY ON THE CLEANING OF FOXING SPOTS ON THE OLD PAPER MANUSCRIPTS USING NATURAL PRODUCTS

Nadia Zaki SHABAN[1], Sawsan Said DAROUISH[2], Taha Ayman SALAH[*3]

[1] Biochemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt
[2] Conservation Department, Faculty of Archaeology, Cairo University, Cairo, Egypt
[3] Conservation Department, Faculty of Archaeology, Aswan University, Egypt.

Abstract

Many manuscripts and historical books contain a form of deterioration known as foxing or fox spots, a brownish stain which has the effect of altering aesthetic and visual appeal. The aim of this work is to study the role of the extracts of Water Cantaloupe (CE) and Water melon (WE) separately as natural products in removing foxing spots in various modern and old papers. Old papers and three types of modern papers made from cotton, linen and a mixture of cotton, linen and wood (1:1:1) were used for this purpose. Each type was divided into two groups, one of them was infected with foxing and the other was left as control (uninfected). Infected papers were treated with CE, WE and 2% sodium hypochlorite (as a traditional chemical bleaching) separately. Fourier Transform Infrared Spectroscopy (FTIR), Atomic Absorption Spectroscopy, Scanning Electron Microscopy equipped with Energy-Dispersive X-ray spectroscopy (SEM-EDX) in addition to some optical and mechanical properties were carried out to evaluate the Cantaloupe Extracts (CE) and Water Melon Extracts (WE) use in removing foxing stains compared to sodium hypochlorite. The results showed that CE removed foxing in different studied papers at pH = 7.4. In contrast, WE could not remove these foxing at any studied pH values.

Keywords: *Foxing; Natural products; Cantaloupe; Water melons; Paper; Cleaning*

Introduction

Foxing appears on the paper as stains of reddish-brown, brown or yellowish color, generally of small dimensions, with sharp or irregular edges, most of which, if excited with UV light, show fluorescence. Foxing is more pronounced on papers produced in the end of eighteenth up to the beginning of twentieth century [1, 2].

The causes of foxing are not yet completely understood, but they are usually ascribed to mould growth and/or heavy-metal-induced degradation of cellulose and sizing materials. Some foxing is clearly fungal in origin and other related forms of spotting are probably chemical, both resulting in a physical degradation of paper [3, 4].

There are three types of foxing: (1) *Bulls eye*: These spots are small and round, with a dark center and concentric rings. They are red/brown to yellow in color with rings of a paler color. Bulls eye foxing can be further subdivided by UV examination. (a) Centers do not fluoresce (appear dark blue/black), rings fluoresce yellow/orange and pale yellow. (b) Centers and rings do not fluoresce (appear dark blue/black). This type of foxing always has metal cores, which do not fluoresce and appear dark blue/black. (2) *Snowflake*: These are spots with

[*] Corresponding author: aymansalahtaha_1982@yahoo.com

scalloped edges and/or irregular shapes which can measure inches across. They are red/brown to yellow in color but sometimes are not visible in normal light. It is theorized that the advanced stage of foxing causes coloration while the younger or dormant stage may not be visible in normal light. This type of foxing gets its name from its white fluorescence and Snowflake – like appearance under UV. Snowflake foxing apparently has a higher iron concentration than the surrounding paper, but concentration may vary within foxing areas. (3) *Stain confused with foxing* (offset or migration): The following discoloration are seen by conservators to be staining rather than foxing [5, 6]. The nature of foxing stains can be studied by means of instrumental techniques FTIR, UV fluorescence X-ray analysis and SEM-EDX [7].

Some traditional methods were used to remove foxing stains such as mechanical cleaning; solvents and chemical bleaching but these methods damage the paper fibers [8]. The present study was designed to describe a novel technique using extracts of cantaloupe and watermelon as natural products for the suppression of foxing in old and modern papers. In addition, the chemical bleaching using 2% sodium hypochlorite was used in foxing suppression and all results were compared with each other's.

Materials and methods

Chemicals

Sodium monohydrogen and dihydrogen phosphate, α – naphthol, ammonium molybdate, sodium hypochlorite, sulphoric acid, iron(III) chloride, iron(II) sulphate, copper sulphate, ascorbic acid and hydroxypropylcellulose were obtained from Sigma Aldrich.

Plants

Cantaloupe (*Cucumis melo L.*) and Water melon [*Citrullus lanatus (Thunb.)*] were obtained from a local market in Egypt.

Preparation of Cantaloupe Extracts (CE) and Water Melon Extracts (WE)

The fruit was cut longitudinally into two halves and cut into small pieces after removing seeds and peels. The tissues were homogenized in sodium phosphate buffer (1:4 w/v) at different pH values (4, 5, 6 and 7.4) at 4ºC. The homogenit was then filtrated using a centrifuge at 4ºC and at 12,000g for 30 minutes. The supernatant was divided into portions and kept at 20ºC [9, 10] .

Paper

Synthesis of modern papers

Modern papers were made according to Technical Association of the Pulp and Paper Industry (TAPPI) T200 OS - 70. Three types of papers were made from cotton, linen and a mixture of cotton, linen and wood (1:1:1). The dimension of each paper was 5cm x 5cm and weighted 1.74g. Each type was divided into two groups, control and infected papers. Papers were infected with foxing according to the methods of Marian et Leslie [11]. In this way, six groups were prepared as follow: two groups of cotton {control (PCC) and infected (PCI)}, two groups of linen {control (PLC) and infected (PLI)} and two groups of mixer of (cotton, linen and wood) {control (PMC) and infected (PMI)}.

Old paper manuscripts.

Samples of old valuable manuscripts, Folder IV of the Encyclopedia of Description of Egypt, were obtained from the Central Library of Islamic Manuscripts Sayeda Zeinab - Cairo, Egypt. These old papers were made from linen. They were divided into two groups control (POC) and infected groups (POI).

Methods of application

Different extracts WE and CE were applied separately at different pH values (4, 5, 6 and 7.4) and at room temperature on different studied groups, (PCI), (PLI), (PMI) and (POI) using soft brush or cotton poultice (Fig. 1). All papers were left at room temperature till dryness. This method of cleaning was repeated several times. Finally, the papers were washed with distilled water using a soft brush. Then they were immersed in 5% hydroxy propyl cellulose solution to improve mechanical properties without affecting the optical properties [12]. All papers were weighted and photographed using Yashica Digital Camera (5031) f = 5.8-17.4mm. Each studied group was compared with its specific control.

Fig. 1. Application of the natural products on the foxing spots using:
a) soft brush, b) cotton poultice.

Cleaning the foxing using traditional method

Four groups of infected papers (PCI, PLI, PMI and POI) were cleaned using chemical bleaching sodium hypochlorite 2% then immersed in 5% hydroxylpropylcellulose (HPC) solution.

Investigation methodologies

FTIR

The changes of molecular structure occurring in the treated samples were monitored by BRUKER'S VERTEX 70 infrared spectroscopy (FTIR spectrometer) in the 650 – 4000cm^{-1} range with resolution of 4cm^{-1}. The vibrational bands that appear in the infrared spectra provide information about the chemical functional groups of a sample which leads to study the changes in characterization of the materials.

SEM

The surface morphology of the untreated and treated samples was investigated to show the changes to or the damage to the fibers. The microstructure of these samples was investigated under JSM –5300 - Joel Scanning Electron Microscope (SEM), equipped with EDX according to the method of Arai [13]. Images were acquired in backscattered mode (BSE).

AAS

Metal content of different papers were determined using atomic absorption Spectroscopy (Thermo elemental, Model 300VA 50 - 60HZ 100 – 240V) according to the method of Perkin-Elmer [14].

Mechanical and optical properties

Mechanical and optical properties of papers were tested using a Breaking Length (Instron Model 1011 - ISO 1974), the Mullen Tester (Perkins -Serial No: 10503 -Type: 18821-S.I : 2: 0 To 145- Frank), Elmendorf Tearing Tester (Type of set: Measuring of no. of Tears - Production Name: Loren Zone & Wetter "L.W" in Stockholm), and Opacity & Brightness (Hunter Lab Color - Type of Set: Measuring of Brightness and Opacity- Difference meter D. 25-2 - Serial No: 74064 - Range: 72, 84, 90 for magnesium oxide. All tests were done according to the method of Technical Association of the Pulp and Paper Industry (TAPPI) T 220 OS - 71.

Results and Discussions

Visual and SEM microscopy observation

The results of the present study showed that CE gave positive results at various studied pH values in removing the foxing stains on POI group with maximum cleaning at pH 7.4. However, WE at the same pH values didn't give any acceptable results (Table 1 and Figure 2). Table 2 showed that 3% of sodium hypochlorite gave the best cleaning effect on POI group while 2% was sufficient to remove foxing stains from all other modern papers.

The morphology of the POI surfaces and treated POT group by CE was investigated using SEM. Scanning electron micrographs were taken of selected samples to assess fiber fracture patterns and the damaged aspects on these fibers. Some types of fiber fracture patterns and damage were identified in POI groups. However, the surfaces of the treated old fibers were smooth with homogeneous appearances as shown in figure 4. This explained the increase in mechanical properties after treatment with CE as mentioned below.

Metal content

Metal analysis of treated and untreated papers of different groups using atomic absorption spectroscopy, confirmed with EDX, showed that untreated papers POI groups contain high contents of Cu and Fe and low contents of Mn and Zn. However their levels were lower in papers treated with CE (Table 3 and Figure 5) indicating that the presence of iron and copper plays an important role in the formation of foxing spots [15]. It was found that iron ions create yellow-brown spots and there is a trend for the darkness of the foxing spot to increase with increased iron content. When the metal concentration decreases due to cleaning process, the foxing spots become lighter and can be easily removed.

FTIR analysis

Infrared absorption spectra of infected old paper showed characteristic absorption bands assigned to the C-O, O-H & C=O stretching bands. Carbonyl groups found in foxing area resulted from catalytically oxidation of Cellulose in the presence of iron and copper compounds where carbon atom are occupying various positions in the ring of cellulose C_1, C_2…..C_6 gradually transformed by oxidation into various carbonyl groups. Spectrum of treated old papers using sodium hypochlorite in figure 6 showed an additional carbonyl band indicating that sodium hypochlorite accelerates cellulose oxidation. According to these results we can conclude that although sodium hypochlorite gave good results in removing foxing spots it should not be used if transition metal stains (e.g., iron or copper) are present since fiber damage is accelerated. While in case of CE treatment (figure 7), Band no.1 assigned to carbonyl group disappeared accompanied by increases in C-O and O-H bands, indicating the reduced effect of CE enzymatic contents.

Mechanical and optical measurements

Table 4 showed the properties of different studied groups before and after treatment with CE. As shown from the results, the tensile strength, burst resistance, tear resistance, brightness increased after treatment with CE, while darkness decreased. On contrary, tensile strength, burst resistance, tear resistance, darkness decreased after the treatment with 2% sodium hypochlorite (Table 5). From these results, we concluded that the treatment of foxing stain using CE is better than that using chemical bleaching with sodium hypochlorite. This indicates that the treatment with CE succeeded as a novel natural product in cleaning foxing spots in papers. This may be related to the effect of its contents such as antioxidants of vitamin C; antioxidants enzymes called superoxide dismutase (SOD); Glutathione reductase (GR); glutathione oxidoreductase; ascorbate peroxidase (APX); polygalacturonase (PG); β-galactosidase; galactanase and pectin methyl esterase (PME). SOD is a group of important enzymes in the free radical detoxification process. They are metallic-enzymes that catalyze the dismutation of superoxide radicals to oxygen and hydrogen peroxide according to the following reaction [16]:

$$2O_2^{\bullet} + 2H^+ \xrightarrow{SOD} O_2 + H_2O_2 \quad (1)$$

Glutathione reductase and glutathione oxidoreductase are important enzymes involved with glucose-6-phosphate dehydrogenase in the maintenance of a reduced intracellular environment. Ascorbate peroxidas (APX), polygalacturonase (PG), β-galactosidase and galactanase, pectin methylesterase (PME) produced Fe^{2+} by reduction of Fe^{3+} to Fe^{2+}[17].

Table 1. The results of cleaning with CE & WE at different pH values

pH	CE				WE			
	PCT	PLT	PMT	POT	PCT	PLT	PMT	POT
4	-ve	-ve	-ve	++ve	-ve	-ve	-ve	-ve
5	-ve	-ve	-ve	++ve	-ve	-ve	-ve	-ve
6	-ve	-ve	-ve	++ve	-ve	-ve	-ve	-ve
7.4	-ve	-ve	-ve	+++ve	-ve	-ve	-ve	-ve

- Ve uncleaning +ve A few cleaning ++ Medium cleaning +++ve good cleaning

Table 2. The results of cleaning with different concentrations of sodium hypochlorite

Conc.%	PCT	PLT	PMT	POT
1	+ve	+ve	+ve	+ve
2	++ve	++ve	++ve	++ve
3	++ve	++ve	++ve	+++ve

- Ve uncleaning +ve A few cleaning ++ Medium cleaning +++ve good cleaning

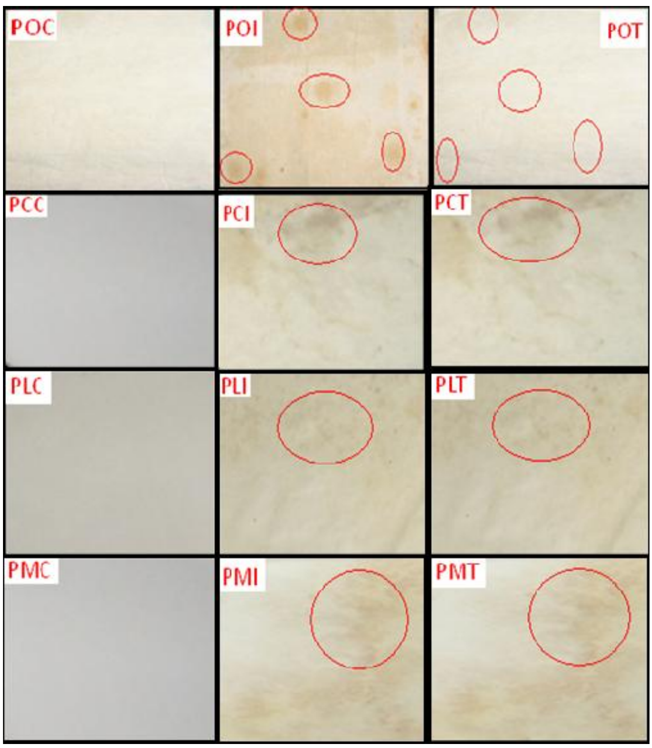

Fig. 2. Effect of CE at pH = 7.4 on foxing in different studied papers groups

Table 3. Metal contents in treated and untreated old papers using atomic absorption spectroscopy

	%	
Metal	(POT)	(POI)
Fe	2.5	4.4
Cu	3.4	5.6
Mn	o.13	0.25
Zn	0.10	0.16

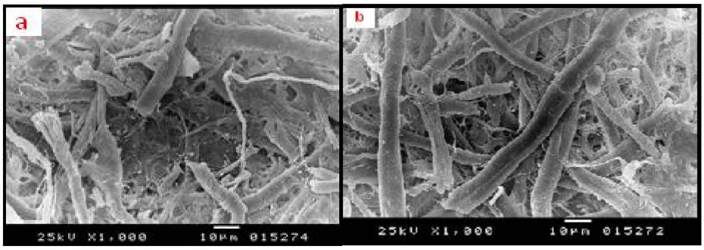

Fig. 4. SEM micrograph, 1000X, a) before, b) after treatment with CE

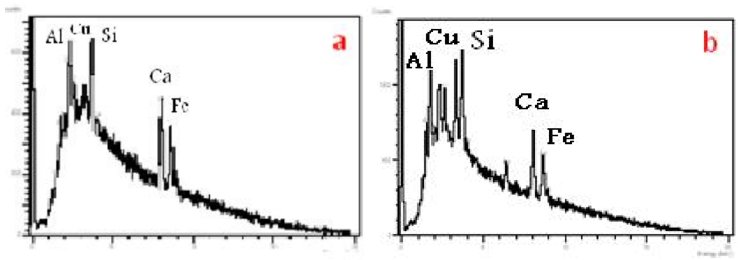

Fig. 5. EDX results, a) before, b) after treatment with CE

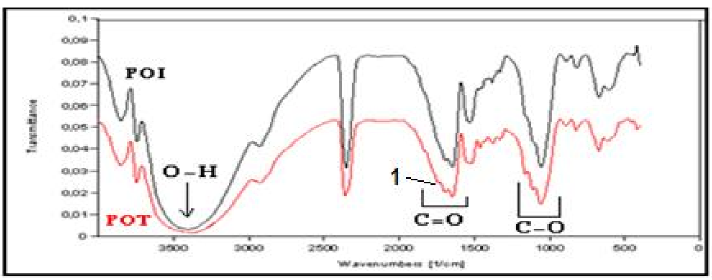

Fig. 6. FTIR spectrum of untreated and treated old papers using sodium hypochlorite, 1= additional carbonyl band

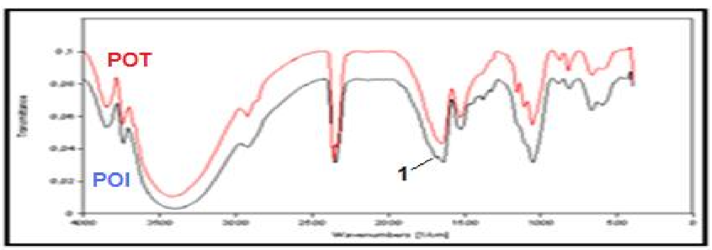

Fig. 7. FTIR spectrum of untreated and treated old papers using CE, band no.1 assigned to carbonyl group disappeared after CE treatment

Table 4. The effect of CE treatment on some mechanical and optical properties of various types of studied papers

Sample	Tensile strength Kg		Burst resistance k\ lbn		Tear Resistance g		Brightness **%**		Darkness **%**		Weight g	
	Value	Change %	Value	Change %	Value	Change %	Value	Change %	Value	Change %	Value	Change %
PCI	2.3	0.00	20.0	0.00	120.0	0.00	60.3	0.00	92.3	0.00	1.75	0.00
PCT	2.6	+13.0	22.3	+11.5	123.5	+2.83	77.6	+28.68	83.4	-9.64	1.76	+ 0.571
PLI	3.4	0.00	18.5	0.00	50.5	0.00	51.2	0.00	99.0	0.00	1.74	0.00
PLT	4.0	+17.64	20.2	+9.18	51.2	+1.38	64.4	+25.78	81.2	-17.97	1.78	+2.298
PMI	3.9	0.00	30.2	0.00	105.4	0.00	50.1	0.00	97.8	0.00	1.72	0.00
PMT	4.3	+10.25	31.5	+4.30	107.1	+1.61	54.2	+8.18	89.5	-8.48	1.75	+1.744
POI	0.243	0.00	2.5	0.00	16.0	0.00	36.1	0.00	78.4	0.00	0.292	0.00
POT	0.446	+83.53	4.3	+72	18.4	+15	68.4	+89.47	72.6	-7.39	0.297	+1.683

Table 5. The effect of sodium hypochlorite treatment on some mechanical and optical properties of various types of studied papers

Weight g		Darkness %		Brightness %		Tear Resistance g		Burst resistance k\ lbn		Tensile strength Kg		Sample
Change %	Value	Change %	Value	Change %	Value	Change %	Value	Change %	Value	Change %	Value	
0.00	1.75	0.00	88.7	0.00	60.8	0.00	160	0.00	24.6	0.00	3.7	PCI
+ 1.14	1.77	-7.21	82.3	+7.40	65.3	-25	120.0	-18.69	20.0	-37.83	2.3	PCT
0.00	1.74	0.00	95.0	0.00	51.0	0.00	54.4	0.00	10.1	0.00	4.0	PLI
+2.87	1.79	-5.26	90.0	+4.31	53.2	-7.16	50.5	-5.94	9.5	-15	3.4	PLT
0.00	1.72	0.00	80.7	0.00	50.2	0.00	114.9	0.00	33.0	0.00	4.5	PMI
+3.48	1.78	-13.50	69.8	+9.76	55.1	-8.26	105.4	-8.48	30.2	-13.33	3.9	PMT
0.00	0.292	0.00	81.4	0.00	44.3	0.00	19.5	0.00	4.2	0.00	0.473	POI
+2.39	0.299	-7.49	75.3	+50.11	66.5	-5.64	18.4	-11.90	3.7	-17.75	0.389	POT

Conclusions

This work studied the role of the extracts of Water Cantaloupe (CE) and Water melon (WE) separately as natural products in removing foxing spots in various modern and old papers, compared with sodium hypochlorite as a traditional material. The results showed that CE gave positive results at various studied pH values in removing the foxing stains on only old paper groups with maximum cleaning at pH = 7.4, accompanied by decrease in copper and iron levels. This finding proved that the iron and copper presence plays an important role in the formation of foxing spots. FTIR spectrum showed that carbonyl group of oxidised cellulose disappeared accompanied by increase in C-O and O-H bands indicating the reducing effect of CE enzymatic contents. Moreover, CE increased the mechanical properties of the old paper. On the other hand, we didn’t give any acceptable results at the same studied pH values. Sodium hypochlorite gave good results in removing foxing spots on both old and modern groups but it decreased the mechanical properties of paper and accelerated paper oxidation as proved from FTIR spectrum. So, we recommend that it should not be used if iron or copper stains are present since fiber oxidation and damage are accelerated.

Acknowledgements

This work was supported by Department of Biochemistry Laboratories, Faculty of Science, Alexandria University.

References

[1] M. Manso, S. Pessanha, M. Oliveira, **Characterization of Foxing Stains in Eighteenth to Nineteen the Century Drawing Using Non-Destructive Techniques**, © Springer-Verlag, 2009.

[2] M. Bicchieri, G. Pappalardo, F.P. Romano, F.M. Sementilli, R. de Acutis, *Characterization of foxing stains by chemical and spectrometric methods*, **Restaurator: International Journal for the Preservation of Library and Archival Material**, **22**(1), 2001, pp. 1-19.

[3] M. Bicchieri, S. Ronconi, F.P. Romano, L. Pappalardo, M. Corsi, G. Cristoforetti, S. Legnaioli, V. Palleschi, A. Salvetti, E. Tognoni, *Study of foxing stains on paper by chemical methods, infrared spectroscopy, micro-X-ray fluorescence spectrometry and laser induced breakdown spectroscopy,* **Spectrochimica Acta Part B: Atomic Spectroscopy, 57**(7), 2002, pp. 1235-1249.

[4] R. Buzio, P. Calvini, A. Ferroni, *Surface analysis of paper documents damaged by foxing*, **Applied Physics Materials Science and Processing, 79**(2), 2004, pp. 383- 387.

[5] A. Owen, J. Derow, *Foxing – Wiki*, **Book & Paper Conservation, Catalog,** BP Chapter 13 Foxing, Ed. Sarah Bertalan, 2009, pp. 1- 29.

[6] C.E. Cain, M.B. Stanley, W.H. Roberts, *Paper Foxing: Biochemical Effects of Fungal Infections of Paper*, **Journal of the Mississippi Academy of Science**, **32**, 1987, pp. 24-32.

[7] P. Choisy, *Non invasive techniques for the investigation of foxing stain of graphic art material*, **Restaurator, 18**(3), 1997, pp. 131-152.

[8] H. Anowska, R. Moomaw, *Laser stain removal of fungus – induced stains from paper*, **Journal of the American Institute for Conservation, 33**(1), 1994, Article 2, pp. 25- 32.

[9] O. Lamikanra, M. Watson, *Effects of Ascorbic Acid on Peroxidase and Poly phenoloxidase Activities in Fresh-Cut Cantaloupe Melon*", **Journal of Food Science, 66**(9), 2001, pp. 1283- 1286.

[10] S. Supapvanich, G.A. Tucker, *Enzyme changes during softening of cantaloupe melon fruit*, **Australasian Postharvest Conference,** Crowne Plaza Terrigal, NSW, Australia, 12 September, 2007, p. 87.

[11] P. Marian, H. Leslie, *Stain Reduction Discussion*, **The Book and Paper Group Annual, 20**, 2001, pp. 1-5.

[12] A. Taha, *Experimental study to evaluate the physiochemical treatments effect on old paper manuscripts properties applied on selected objects*, **Master's Thesis**, Conservation Department, Faculty of Archaeology, Cairo University, 2010.

[13] H. Arai, *Foxing caused by Fungi: twenty-five years of study*, **International Biodeterioration and Biodegradation**, **46**, 2000, pp.181-188.

[14] E. Perkin, **Analytical Methods for Atomic Absorption Spectroscopy**, Printed in the United States of America, Perkin-Elmer Inc., 1996.

[15] L. Tang, *Determination of Iron and Copper Content in 18th and 19th Century Books by Flameless Atomic Absorption Spectroscopy*, **Journal of the American Institute for Conservation, 17**(2), 1978, pp. 19-32.

[16] I. Fridovich, *Superoxide Anion Radical (O_2), Superoxide Dismutases, and Related Matters*, **The Journal of Biological Chemistry, 272**(30), 1995, pp. 1-15.

[17] K. Sebnem, Y. Fikret, *Determination of anti-oxidant activities in some melon (Cucumis melo L.) Varieties and cultivars under salt stress*, **Journal of Horticultural Science and Biotechnology, 81**, 2006, pp. 627 - 630.

Received: January, 14, 2016
Accepted: September, 15, 2016w