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A NEW APPROACH TO THE TREATMENT OF IRON GALL INK CORROSION USING PLANT BIOMASS

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ABSTRACT

Iron gall ink (IGI) was the most common writing ink for centuries, meanwhile one of the major responsible factors for paper degradation. Corrosive constituents are responsible for acid hydrolysis and metal-catalyzed oxidation. The study proposes a new stabilization treatment using two aquatic plants biomass. Handmade biomass interleaving paper (BIP) was produced from duckweed Lemna gibba L. Lemnaceae (L. gibba) and water hyacinth, Eichhornia crassipes (E. crassipes).The produced BIP offered a promising synergy of deacidification and stabilization of model and historical samples. The treatment impact was evaluated on thermally aged and on post treated model inked paper using pH measurement, Fe^{2+}detection and colorimetry. Moreover, removal capacity of corrosive metal ions; Zn^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, and $Pb^{2+}$was assessed. The BIP biosorption and preference of corrosive transition metals were evaluated using atomic absorption spectroscopy (AAS) and combined scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDX). All produced BIP absorbed transition metals in different concentrations, particularly L-BIP treatment gave the maximum removal of corrosive metals after treatment for 24 h in the order Fe > Mn > Cu > Zn > Pb.

KEYWORDS: Iron gall ink; corrosion; historical paper; stabilization; metal biosorption.

1. INTRODUCTION

Since its first appearance on an Egyptian papyrus in the 1stcentury AD, iron gall ink (IGI) was the universal writing and drawing material on a wide range of archival objects till the 20th century(Eusman1999; Kolar et al. 2012).The ink was originally produced by mixing gall extract, vitriol, and gum arabic with an aqueous medium (Krekel1999). Unfortunately, IGI contains destructive components, which are responsible for the degradation of cellulose. Uncombined Fe2+and other high mobile metal ions impurities, cause acid hydrolysis, low pH and metal-catalyzed oxidation known as ink corrosion (Wunderlich 1994; Neevel 1995;Banik 1997;Krekel 1999; Bulska and Wagner 2004; Kolar et al. 2006; Potthast et al. 2008; Zervos 2010;Malešič et al. 2014).The paper degradation by ink corrosion develops through the formation of organic radicals followed by oxidation and the formation of hydroxyl radicals from hydrogen peroxide according to Fenton reaction. In these processes, Fe2+contributesin the formation of organic radicals and peroxides and works as a catalyst for Fenton reaction, furthermore, its continuous reproduction promotes cyclic corrosion reactions (Zucchiatti, et al. 2005; Hastrup, et al. 2011).However, other transition metals, like copper play a greater role in the oxidative decay and breakdown of cellulose through Fenton-like reaction (Banik et al. 1981; Neevel 1999; 2000; Reiβland 1999; Eusman 1999; Kolar et al. 2003; Valenzuela, et al. 2008). The Fenton reactions take place when transition metals are in the reduced form, e.g. Cu+ or Fe2+. Glucoseand superoxide effectively reduce Cu2+ and Fe3+respectively (Wardman and Candeias1996; Selih et al 2007).Light and humidity also increase ink corrosion and migration of Fe2+out of the ink regions, causing brown ink haloes (Neevel 1999; Kanngieβer et al., 2004). As paper degradation goes on fading of ink color, perforation and loss of mechanical strength take place (Poggi et al. 2010).This in fact is a real threat for archival cultural heritage which requires more effort to find out a non-invasive and effective treatment.

Several stabilization methods have been implemented through the last three decades to prevent paper degradation by ink corrosion (Van Gulik and Kersten-Pampiglione 1994; Neevel 1995; Neevel and Reiβland 1997; Van Gulik 1997; Reiβland 1999; Neevel 2000; Zappala and De Stefani 2005;Tse et al. 2005;Botti et al. 2005;Kolar et al. 2007; Henniges et al. 2008; Potthast et al. 2008: Zervos and Alexopoulou 2015). But negative side effects could not be avoided (Henniges et al. 2006; Selih et al. 2007; Hahn et al. 2008; Zervos and Alexopoulou 2015; Alexopoulou and Zervos 2016). Recently, treatment with buffer and antioxidants impregnated interleaving papers was a major improvement (Malešič et al. 2012; 2014).

This work proposes a new conservation treatment of IGI paper corrosion using biomass interleaving paper (BIP), produced from aquatic plants; Duckweed Lemna gibba and Water hyacinth Eichhorniacrassipes. These plants biomass are known to be effective biosorpents for heavy metal ionse.g.,Cu2+, Zn2+, Fe2+,Co2+, Ni2+, Cd2+, and Pb2+. They have been used successfully for phytoremediation because of their strong removal capacities of toxic metals and metalloids (Schneider et al. 1995; Vajpayee et al. 1995; Tkalec et al. 1998; Schneider and Rubio 1999; Axtell et al. 2003;Weis and Weis 2004; González-Muñoz et al. 2006; Panayotova et al. 2007; Liu et al. 2007; Krishna and Polprasert 2008; Mishra and Tripathi 2009; Chaudhary and Sharma 2014; Allam et al. 2015). It is suggested that metals sequestrated in the biomass turn into biominerals. This mechanism is still not very well understood. Lemna spp. for example assimilates metals in sugars, peptides, proteins and some organic acids. This is sometimes defined as nucleus of biomineralisation (Mann et al. 1989: Bovet et al. 2000; Mazen et al. 2004; Mkandawire and Dudel 2005; 2007). However, it was evidenced that the main mechanism involved in biosorption was ion exchange between monovalent metals as counterions present in the macrophytes biomass and heavy metal ions in addition to protons taken up from water (Miretzky et al. 2006). The exchange adsorption and/or surface precipitation can take place onto plant biomass surfaces (Schneider et al. 2001). The current study proposes that the potential biosorption of plant biomass can be useful for the selective removal of destructive heavy metal ions and replacement with beneficial ions.

2. MATERIALS AND PREPARATION

2.1 Preparation of ink

For the preparation of model ink; 7.688 g of oak galls powder was mixed with 66.8 ml distilled water and stored for 3 days. Then 2.528 g $FeSO_4$.$7H_2O$, 0.2 g NaCl, 2 ml of 10% acetic acid and 0.318 g $KAl(SO_4)_2.12H_2O$(Sigma -Aldrich, Chemie Gmbh, UK) were added. The obtained mixture stored for 2 weeks with alternative agitation and filtration (Wunderlich1994; Krekel 1999; Senvaitiene et al. 2005).The similarity between the prepared model ink and an authentic 19th century IGI sample was confirmed using Jasco 6100 FTIR spectrometer, with TGS detector, Japan. FTIR spectra are given in (Fig.1).

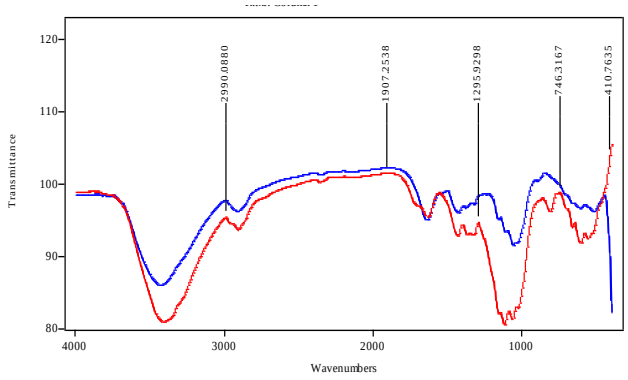


Figure 1 FTIR transmission spectra show the similarity between the model (red line) and an authentic IGI (blue line).

2.2 Preparation of model inked paper

Model inked paper is prepared by blotting a 1cm width solid ink line on Whatman no. 1 pure cellulose fiber filter paper. The model inked paper was cut into75 x 25 mm coupons. 3 replicates were dedicated for testing each variable. All of 48 coupons were subjected to artificial ageing (cycle 1)to maximize paper corrosion. Thermal ageing was undertaken in the oven for 48 hours at 90 °C in a sealed box at 75% RH using KCl saturated aqueous solution (Poggi et al. 2010). After ageing ink haloes were observed indicating development of ink corrosion

2.3 Preparation of biomass interleaving paper (BIP)

To produce the (BIP)fresh aquatic plants, Lemna gibba L. Lemnaceae (L. gibba)and water hyacinth, Eichhornia crassipes (E.crassipes) were collected from Abu-humuslocal ponds in El-Beheira governorate of Egypt (Lat: 31° 5' 49.2504", Long: 30° 18' 41.1444"). They were initially washed with tap water to remove debris. Odd materials were removed and left to air dry before drying in oven at 60o C for 24 hours. Dried biomass of E. crassipes was cut then blended to fine powder < 4 mm long, while L. gibba was blended to fine grains. Each 50 gm of blended plants were mixed with 75ml of distilled water to make three different kinds of biomass pastes. The resulting wet pastes were spread separately over 30x 40 cm glass plates, over a polyethylene (PE) sheet to prevent sticking. Pastes were lightly hand pressed and flattened, covered with PE sheets then further flattened with a rolling pin and left uncovered to air dry for 24 h. By drying-BIP, E/L-BIP and L-BIP sheets are created (Fig.2), with thicknesses3.25 mm, 3.95mm and 5 mm respectively. These sheets were cut into the same size as model inked-paper coupons.

Figure 2 BIP sheet (left) and BIP stripes (upright).

2.4 Treatment of model and historical samples

Aged model inked-paper were treated by E-BIP, E/L-BIP and L-BIP by placing each model inked-paper coupon upside down on one of BIP strips under pressure of 0.013psiand left for 1, 7, 12 and 24 h at 25° C and 65 % ±5 RH. The treatment was repeated on an authentic 19th century fragment. After treatment BIP strips were removed and kept frozen below – 20°Cbefore the assessment of metals contents.

3. METHODS AND ANALYSIS

3.1 pH measurements

BIP treated model inked coupons were subjected to pH measurement before and after treatment and after post accelerated ageing (cycle 2) in which the procedures described in cycle 1were repeated to evaluate the resistance of treated model inked coupon against further corrosion. pH was measured on ink line and on ink border (within 5 mm next to ink line)according to the standard test; Tappi 509 om-088. This was performed using (PHM62, Radiometer, Copenhagen) pH meter with a contact electrode.

The pH of the authentic fragment was measured before and after treatment with an equal size of L-BIP for 24 h at 25°C and 65 % ± 5RH.

3.2 SEM-EDX examination and analysis

The historical fragment was examined and analyzed before and after treatment using SEM-EDX (FEI Quanta 200 ESEM FEG, with tungsten electron source, at 20KV) to determine change in transition metals concentration on ink line and ink border.

3.2.1 Detection of Fe^{2+}

Fe^{2+}detection in model inked paper before treatment, after treatment with L-BIP and after cycle 2 accelerated ageing was undertaken using the non-bleeding bathophenanthroline indicator paper (Pel Preservation Equipment Ltd, UK).

3.2.2 Color change test

To determine the color of cycle 1 aged ink as the reference and the color change after treatment with

L-BIP for 1, 7, 12 and 24 h, Color-Eye® Spectrophotometer (OPTIMATCH 3100) was used. The values of the ink color are measured using CIE L* a* b*coordinates. This test has not been undertaken for the historical paper because of small sample area.

3.3 AAS analysis

Transition metals Zn, Cu, Fe, Mn and Pb contents in the E-BIP, E/L-BIP and L-BIP were determined before and after treatment using AAS (Shimadzu - AA-6650). Samples were digested using dry ashing at 430-600°C then diluted with 1:1 (10% HCl: H_2O) and then filtrated. The amount of light absorbed by the atomized element is measured. Wavelength absorbed in the flame is proportional to the concentration of the element in the sample. Data are statistically analyzed using SPSS software with two –way ANOVA version 18. This enabled the presentation of the selective total absorbance capacity of E-BIP, E/L-BIP and L-BIP of transition metals and the rate of absorbance of different metals.

4. RESULTS

4.1 Deacidification

The pH values of ink line and ink borders of untreated cycle 1 aged model inked-paper were measured and compared with treated and aged cycle 2 model inked-paper. Results presented in Table 1providea general trend of pH values of treated model inked-papers towards less acidic; they were noticeably neutralized in some cases reaching the peaks at7.1 and 7.5.on ink line and ink border respectively, although remained unchanged after cycle 2 ageing. The acidity was reduced on the ink line as well as on the ink borders where ions migration took place. The pH increased with treatment time, the 24 h treatment gave remarkable pH rise by L-BIP treatment on ink line and ink border, from 5.6 to 7.1 and from 6.1 to 7.5 respectively. pH values on ink line and border of the historical fragment (Table 2) approached neutrality after treatment. This agrees with the above results. The treatment with L-BIP for 24 h under test conditions stabilized ink line and neutralized ink border of the authentic fragment.

Table 1. pH values of ink line and ink borders of cycle 1 aged model inked-paper before and after treatment with E-BIP, E/L-BIP and L-BIP for 1, 7, 12 and 24 h compared with the values after cycle 2 ageing (pH*).

The average standard deviation of pH for three measurements was < 0.3.

Tested samples		*Time/h*	Test area			
			Ink line		Ink border	
			pH	pH*	pH	pH*
Untreated		0	5.6	5.4	6.1	6.0
BIPpaper	E	1	6.4	6.3	6.2	6.2
		7	6.5	6.5	6.5	6.3
		12	6.6	6.5	6.5	6.4
		24	6.7	6.7	7.0	6.9
	E/L	1	6.3	6.3	6.7	6.6
		7	6.4	6.3	6.8	6.8
		12	6.6	6.4	7.1	7.0
		24	6.8	6.7	7.3	7.2
	L	1	6.5	6.4	6.9	6.8
		7	6.8	6.7	6.9	6.9
		12	6.9	6.8	7.1	7.0
		24	7.1	7.0	7.5	7.4

Table 2. pH values of historical paper fragment before and after treatment with L-BIP for 24 h.

Before treatment		After treatment	
Ink line	Ink border	Ink line	Ink border
5.5	6.0	6.6	7.0

The average standard deviation of pH for three measurements was < 0.3.

4.2 Fe^{2+} decrease

Fe^{2+}detection in cycle 1 aged model inked paper before treatment, after treatment with L-BIP and after cycle 2 accelerated ageing was undertaken. In this test Fe^{2+} concentration is semi-quantitatively assessed as indicated by the intensity of the magenta color complex formed (Neevel and Reiβland 2005; Albro et al. 2008). Results indicated that Fe^{2+} concentration decreased by increasing treatment time up to 24 h.

4.3 Color change

Using CIE L* a* b* system the color was described and color changes were numerically evaluated. Ink color of (cycle 1) aged model inked paper was measured and compared with values measured after L-BIP treatment for 1, 7, 12 and 24 h (Fig.3).The values of L*,a*,b* and ΔE*of treated and untreated aged reference were compared. Results proved that a limited change of lightness and ΔE^*_{ab} after L-BIP treatment has occurredespeciallyafter12h. The darkness of ink has increased.

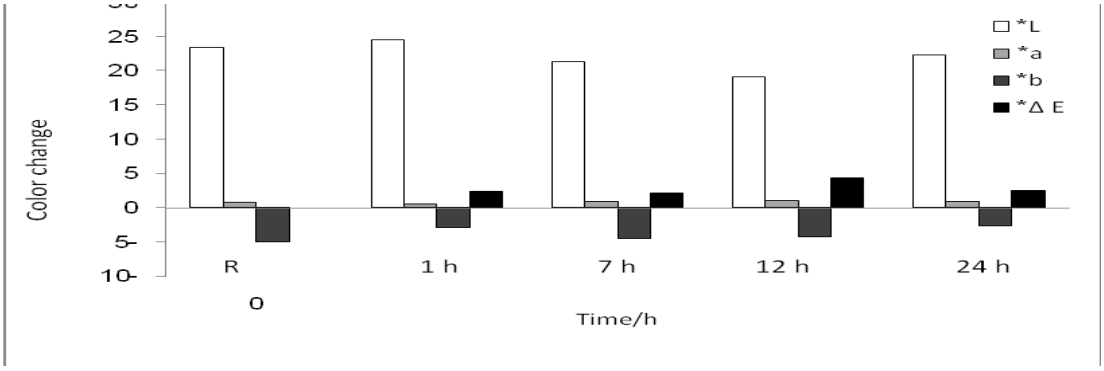
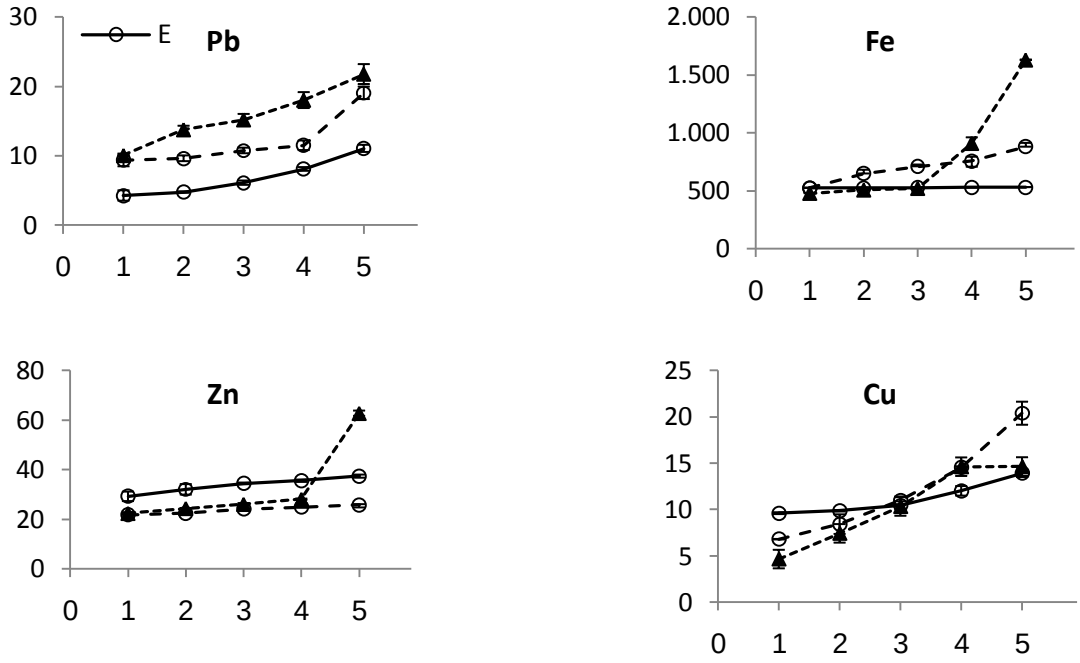


Figure 3 Color coordinates values of untreated model ink reference(R), compared to L-BIP treated ink for 1, 7, 12 and 24 h.



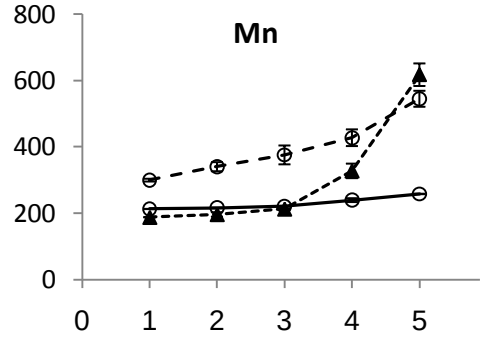


Figure 4.Absorbance of transition metals (ppm/t) by E-BIP, E/L-BIP and L-BIP, where (1) in the horizontal axe represents untreated control, (2, 3, 4, and 5) represent 1, 7, 12 and 24 h treatment time respectively.

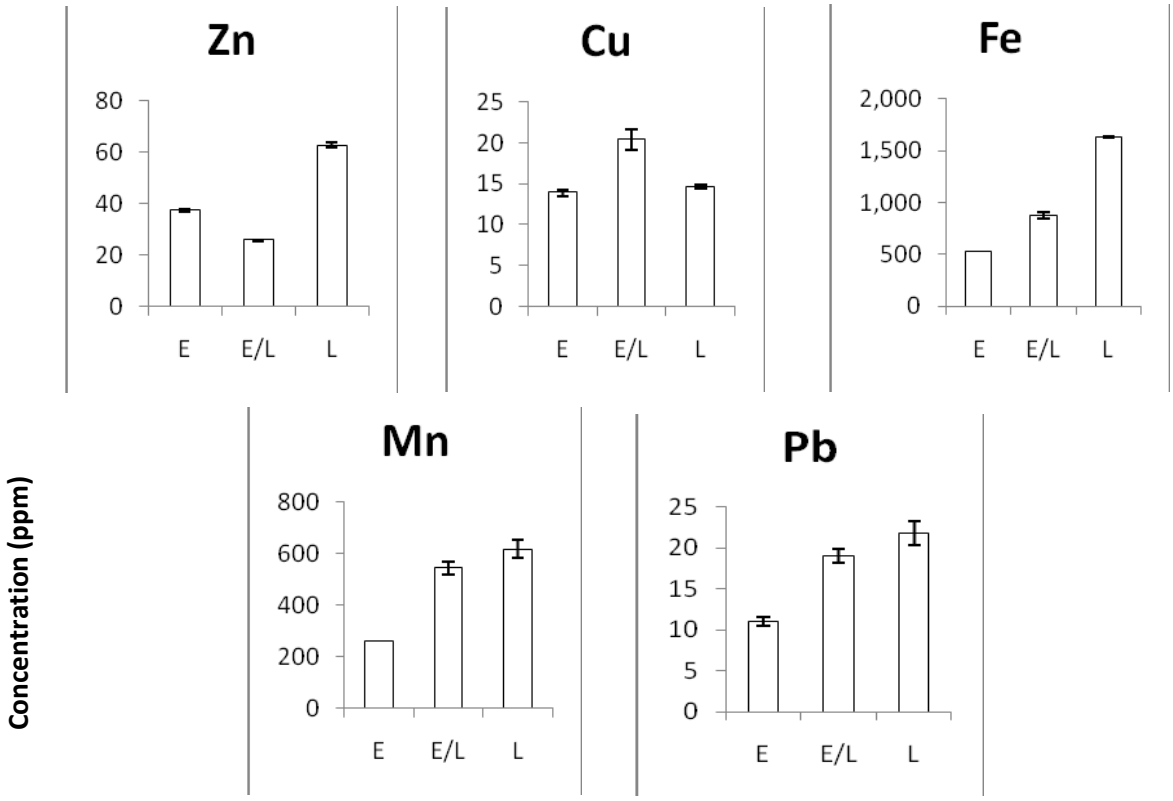


Figure 5. Absorbance capacity demonstrated by E-BIP, E/L-BIP and L-BIP for Zn, Cu, Fe, Mn and Pb.

4.4 Stabilization

Corrosive transition metals Zn, Cu, Fe, Mn and Pb were absorbed by E-BIP, E/L-BIP and L-BIP, metal content was evaluated before and after treatment of model cycle 1 aged inked- paper by AAS. The increase in metals concentration indicates their absorbance by BIP. The total absorbance capacity of transition metals and the rate of absorbance of different metals after 1, 7, 12 and 24 h treatment are presented in (Fig.4).

The adsorption increased by time under test conditions. Treatment with L-BIP gave the maximum removal of transition metals after 24 h treatment in the order Fe > Mn > Cu >Zn > Pbas shown in (Fig. 5).

The authentic historical fragment shown typical IGI induced corrosion, cracked up ink and deteriorated cellulose fibers(Fig. 6). It was treated with L-BIP for 24 h.Then examined and analysed by SEM-EDX. Results given in (Figs. 7A and7B) indicated the removal ofZn, Cu, Fe, Mn and Pb. However, alkaline metals such as Na, Mg and K insignificantly increased.

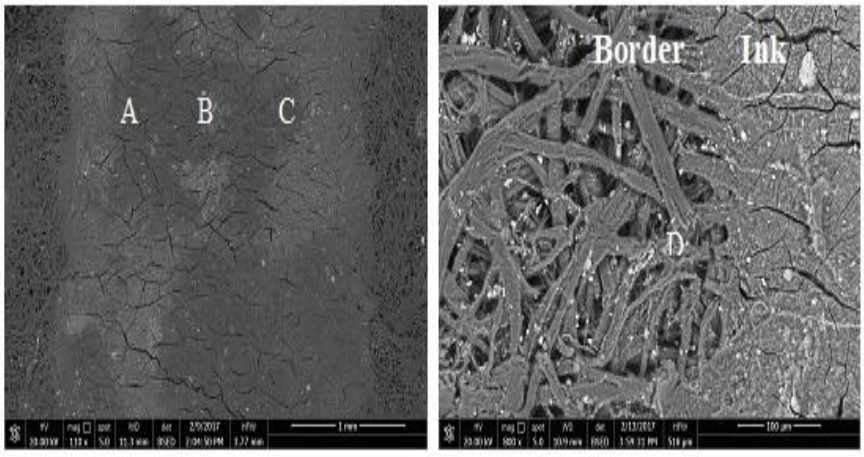
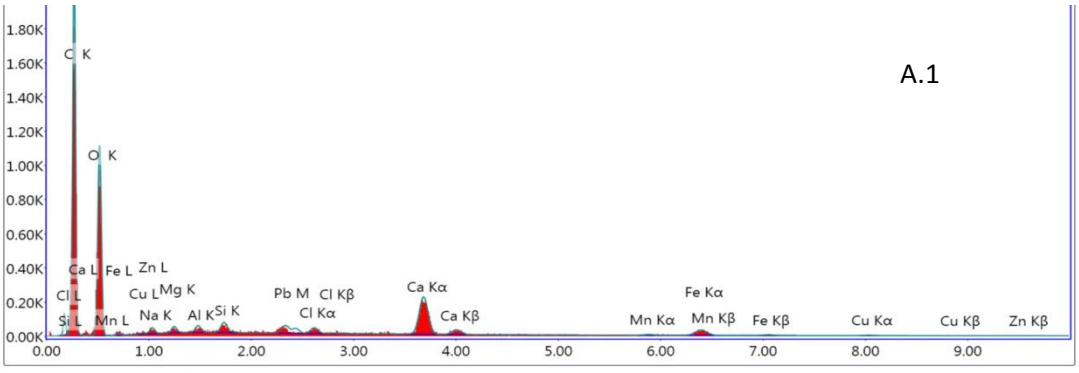
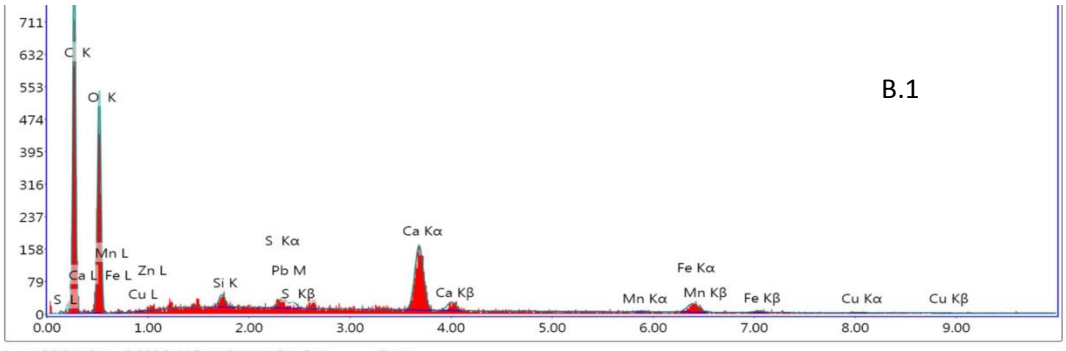
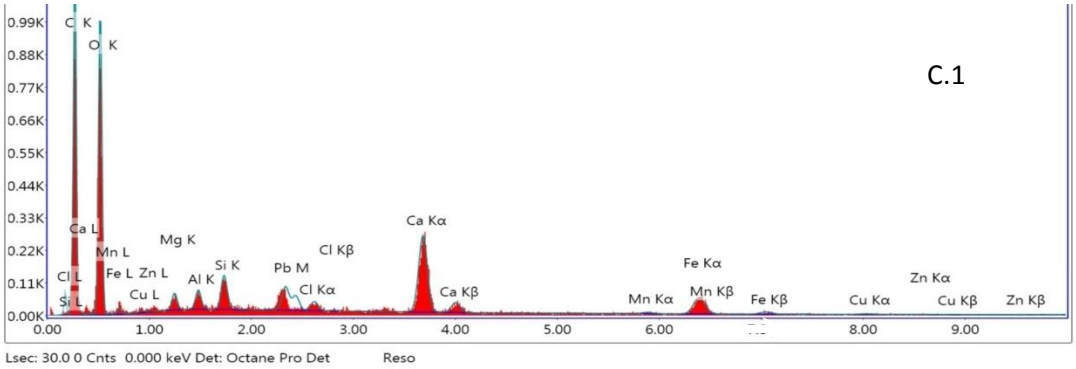


Figure 6. SEM micrographs of the historical fragment showing analyzed spots of IGI line A, B and C (left)and ink border analyzed spot D (right), the corresponding analysis results before treatment are given no.1.,and no. 2., together with the letter, for after treatment analysis.







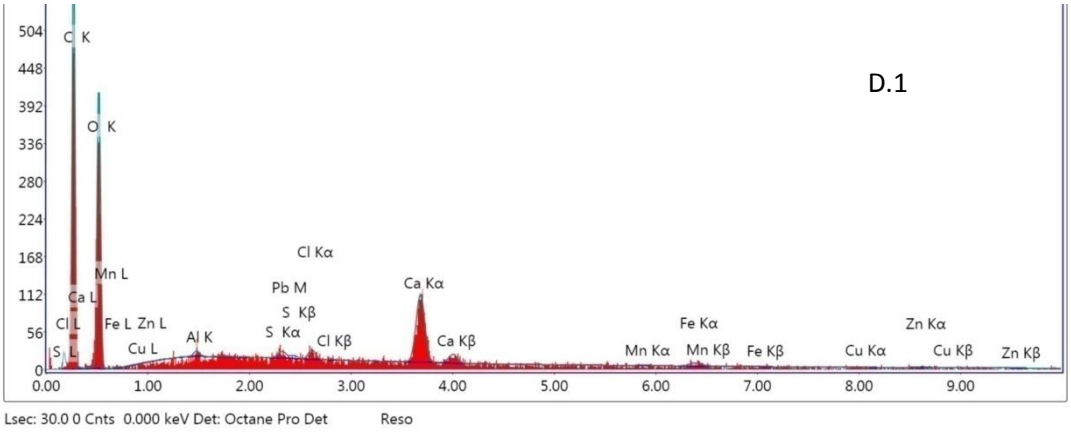
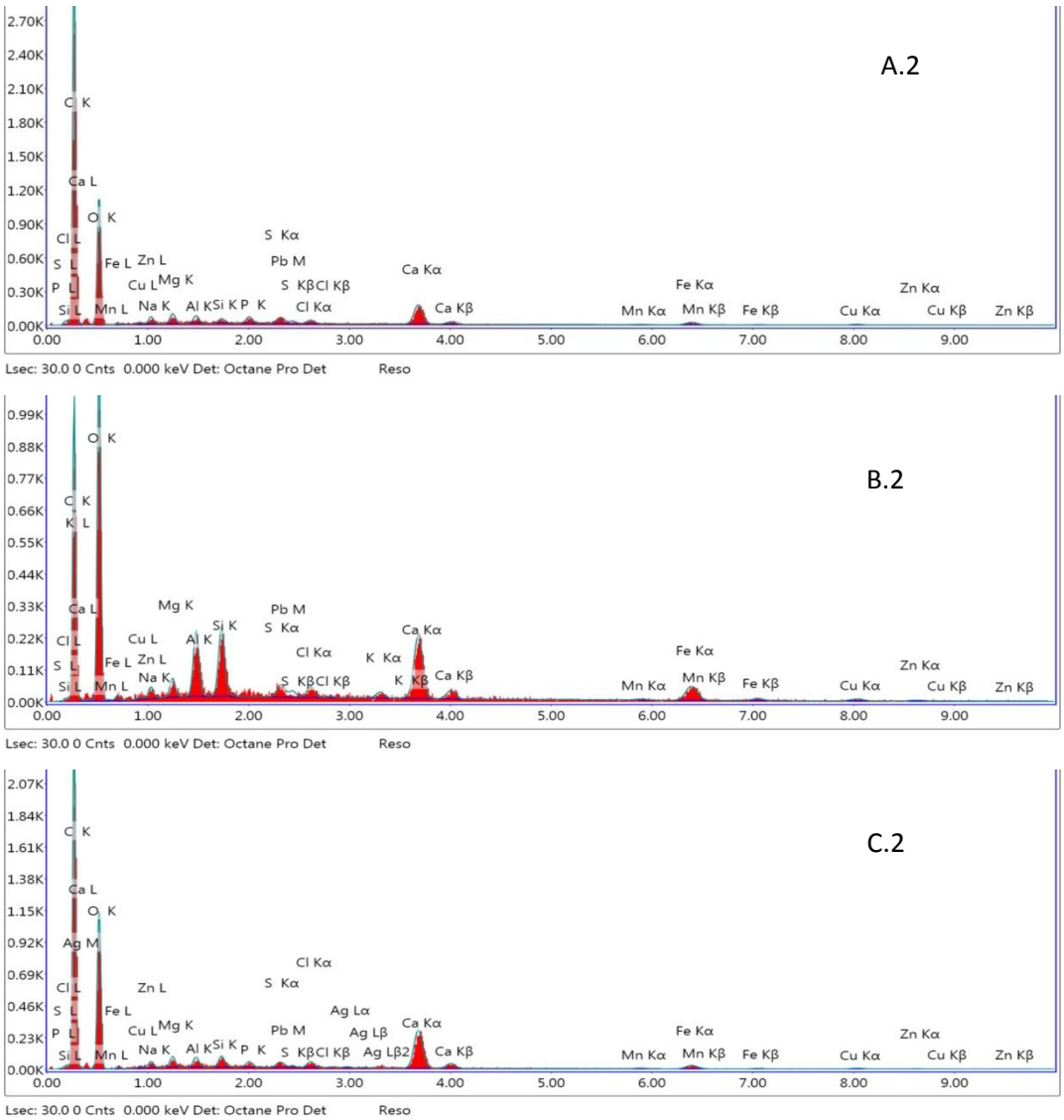


Figure 7A. EDX analysis spectraofthe historicalsample before treatment. Spots A.1, B.1 and C.1 are taken on the ink line while, spot D.1 is taken on the ink border.



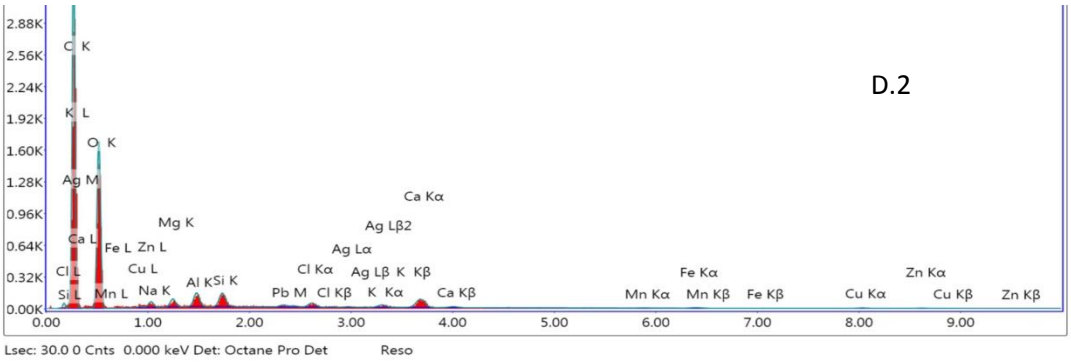


Figure 7B. EDX analysis spectra of the historical sample after treatment. Spots A.2, B.2 and C.2 are taken on the ink line while, spot D.2 is taken on the ink border.

DISCUSSION

As neutralization is an essential key factor for the preservation of paper, it was important to assess the deacidification impact of the BIP treatment on model and historical inked papers.The treatment with L-BIP proved to be the most efficient in neutralizing acidic inked-paper if compared with E-LBIP and E/L-BIP treatments. The stability against ageing after neutralization is evidenced by theslight pH change after cycle 2 ageing. Stabilizing pH around 6.5 to 7.5 is known to protect paper from acid hydrolysis and oxidative ink corrosion meanwhile it controls ions migration risk (Poggi et al. 2010; Rouchon et al. 2013). Moreover, the catalytic activity of metal ions is minimizedat neutrality. Another advantage is that although the stabilization was achieved by L-BIP treatment, the critical pH value (≥ 8) which may increase the catalytic activity of iron and copper (Strlic et al. 2003) has never been reached. Desorption of alkaline elements such as Mg and Na may provide a reservoir against further acidification. Controlling pH governs the degradation rate through Fenton and Fenton-like reactions. Ink-catalyzed degradation of cellulose can also be inhibited(Strlic et al. 1998; Margutti et al. 2001; Poggi et al. 2010; Whitmore 2011). Inhibition of ink corrosion wasindicated by the decrease in Fe^{2+}content;this revealedthe treatment efficiency and enhanced stability of the ink (Proost et al. 2003). In fact high and fluctuated humidity in storage conditions cause color change of IGI (Fuchs 1999; Reiβland and Cowan 2002).Yellow iron oxides e.g. goethite FeO(OH) may form in a few years, in addition to the formation of white layers of potassium alum KAl $(SO_4)_2$ and zinc sulphate ($ZnSO_4$). L-BIP treatment resulted in a little darkness ofIGI, this may due to Fe^{3+} desorption. Darkening of the inkenhances the document legibility (Zervos 2006).The absorption capacity of transition metals is affected by pH of the paper as the uptake of heavy metal cations decreases from pH 6 to 2.5 (Kratochvil and Volesky 1998).The binding of heavy metals in this pH range is determined primarily by the dissociation degree of the weakly acidic groups (Miretzky et al. 2006). This may explain the significant increase of metals removal associated with pH increase in both ink line and ink borders. This was most likely to take place in the ink borders as adsorption was favored at pH ≥ 6.

Previous studies explained that ions exchange can take place between Na^+, K^+ and $Fe^{3+}$and heavy metal ions i.e., Pb^{2+}, Cu^{2+}, Zn^{2+}, H^+ (Kratochvil and Volesky 1998; Schneider and Rubio 1999; Schneider et al.,2001). The main functional group in the ion exchange reactions at neutral pH is the carboxyl group present in the plant tissues which increases with higher protein content. The metal binding probably occurs with the free carboxyl groups present in some amino acids of the protein chains, which are responsible for the metal complexation (Li et al. 1998). The removal of Fe^{2+} ionscan minimize the oxidative damage (Tkalec et al., 1998),while desorption of $Fe^{3+}$is suggested to increase the advantages of the treatment for restoring faded IGI manuscripts. This if confirmed by further studies would be a breakthrough in the conservation treatments of archival cultural heritage.

The removal of transition metals is suggested to prevent a series of galvanic corrosion and preferential dissolution of more anodic metals in the ink i.e., Zn^{2+} and Fe^{2+} whereas reduction takes place of less anodic i.e., Cu^{2+}. Multiple galvanic coupling is expected to be created. Low concentrations of the more anodic metals result in higher corrosion potentials of the galvanic cells (Fontana and Greene 1984). Consequently, the presence of more reactive metals like Zn^{2+}can preventFe^{2+}oxidation, whereas Cu^{2+}initiates Fe^{2+} dissolution.

Heavy metals removal preferencebydead biomass in this study differs from that of the established living plant experiments (Hegazy et al. 2009; Li et al. 2016).The maximum removal of Cu^{2+} by E. Crassipesin other experiments was achievednear neutral values. The decrease in the uptake capacity at lower pH

values can be explained by the occupation of H^+ ions instead of Cu^{2+} ions in the binding sites (Schneider and Rubio 1999).

The production of BIPfrom nonliving plant biomass proved to becost effective and non-invasive alternative for stabilization treatment of IGI induced corrosion. This green technologyis easyapplicable and non-destructive.The fact that the biomass can be loaded with metals and subsequently eluded (Schneider et al. 2001) makes it worth recyclable.Future work is underway to the development of the suggested treatment, and testing different conditions to increase its effectiveness.

6. CONCLUSION

Deacidification and stabilization of iron gall ink induced- corrosion of historical paper were achieved by a new treatment using biomass interleaving paper (BIP). Lemna gibba and Eichhornia crassipes were used to producethe biomass paper. Lemna gibba biomass paper gave the bestabsorption capacity of corrosive metals after 24 h treatment in the order Fe > Mn > Cu > Zn > Pb.

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