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Kinetic study of non-reactive iron removal from iron-gall inks

[a,b]Antonio C. A. da Costa*, [b]Fernanda do N. Corrêa, [a]Gustavo de S. Sant'Anna,
[c]Gisele B. Tonietto, [c]José Marcus de O. Godoy, [c]Rodrigo de A. Gonçalves,
[d]Márcia T. S. Lutterbach

[a]*Museu de Astronomia e Ciẹncias Afins,*
Rua General Bruce 586, Bairro Imperial de São Cristóvão, 20921-030, Rio de Janeiro, RJ, Brasil

[b]*Universidade do Estado do Rio de Janeiro, PPG-EQ,*
Rua São Francisco Xavier 524, Maracanã, 20550-900, Rio de Janeiro, RJ, Brasil

[c]*Pontifícia Universidade Católica do Rio de Janeiro, Departamento de Química,*
Rua Marquẹs de São Vicente 255, Gávea, 22451-900, Rio de Janeiro, RJ, Brasil

[d]*Instituto Nacional de Tecnologia, Laboratório de Biodegradação e Biodeterioração,*
Avenida Venezuela 82, Praça Mauá, 20081-312, Rio de Janeiro, RJ, Brasil

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The removal of non-reactive iron for different combinations of Fe^{2+} and tannic acid in iron-gall inks, via calcium phytate solutions, was studied. In parallel, the non-reactive iron removal kinetics was investigated using the pseudo first-order and second-order kinetic models. The results showed that the use of a dilute solution of calcium phytate to wash the impregnated paper strips removed the non-reactive iron from iron-gall inks in approximately 15 min in stoichiometric and non-stoichiometric combinations of iron and tannic acid. A second washing of the paper strips after an accelerated ageing, showed a distinct kinetic behaviour, with iron removal taking place simultaneously but apparently via a different mechanism. The use of a reference calcium phytate solution exhibited the same behaviour, suggesting that the use of dilute solutions as iron removal agents would represent less damage to historical documents. The results of kinetic modelling showed that all the combinations of Fe^{2+} and tannic acid used fitted the pseudo first-order kinetic model, when dilute and reference phytate solutions were tested as iron-desorbing agents.

Keywords: iron-gall ink, phytate, kinetic modelling, iron stabilisation

Introduction

Iron-gall ink was used extensively between the 12th and 19th centuries in the Western world and in Brazil up to the initial decades of the 20th century (Rouchon & Bernard, 2015). Western civilisation owes much of its documentary memory to the stability of these inks (Kolar & Strlič, 2006; Albro & Biggs, 2008). Artisans who produced iron-gall inks in the past followed a common recipe, although some variations were to be observed in the formulae used (Botti et al., 2005; Rouchon et al., 2013). The standard formulation has four basic ingredients: gall nuts, ferrous sulphate, gum arabic as thickener and an aqueous medium such as wine, vinegar, ethanol or water. The tannic acid in the gall nuts reacts with the iron of the ferrous sulphate, yielding a water-soluble complex known as ferrous gallotannate. Due to this solubility, the ink readily penetrates the surface of the cellulosic supports, making its removal difficult. After exposure to oxygen, a dark water-insoluble pigment of ferric gallotannate is formed, resistant to removal and degradation

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*Corresponding author, e-mail: antoniocosta@mast.br

over time (Cleveland, 2000; James, 2000; Jančovičová et al., 2007; Hahn, 2010).

The problems caused by iron-gall inks are widely known and have long been the subject of study. In 1765, the English chemist William Lewis published a treatise on the stability of iron-gall inks and in 1898 the first conference on the subject was held in Saint Gallen, Switzerland. These were the starting points for scientific and systematic research into the causes of this degenerative process (Neevel & Reissland, 2005; Hanus et al., 2009). Depending on the conditions under which documents containing iron-gall inks are stored, the natural ageing process can promote corrosion on the surface of the paper, causing significant and irreversible damage to documents. In these cases, the damage usually observed is the formation of holes, halos and whitening and migration of the ink (Eusman & Mensch, 2000; Botti et al., 2005; Rouchon et al., 2011a). According to the literature, the corrosiveness of iron-gall inks occurs in two main ways: first, hydrolysis of the cellulose (support) is facilitated due to the acidity of the ink, which usually has an initial pH of between 2.0 and 3.0 (Rouchon-Quillet et al., 2004). Beyond the presence of gallic acid (which already gives an acid character to the ink), the reaction of this component with ferrous sulphate for the formation of gallotannic complex leads to the release of sulphuric acid (Trengove, 1970). Secondly, the oxidation of cellulose is accelerated by the oxygen present in the environment and due to Fenton reactions. This complex set of reactions is catalysed by Fe^{2+} and reactive oxygen species, such as peroxides, leading to the formation of more reactive radicals, such as the hydroxyl (Rouchon et al., 2011a, 2011b; Malešič et al., 2014). Due to the long-standing lack of knowledge of the stoichiometry of the reaction, most of the historical recipes for iron-gall inks present an excess of Fe^{2+} relative to the amount of tannin. This promotes a direct action of the ink on the depolymerisation process of the cellulose (Neevel, 1995). The large number of historical documents that have resisted the action of time for millennia, when stored under appropriate conditions, confirm cellulose as being one of the most resilient organic materials in nature. Cellulose can, however, undergo hydrolysis due to the acidity and presence of free transition metals (commonly present in iron-gall inks) during natural ageing (Kolar & Strlič, 2006). Accordingly, the procedure for stabilisation of the oxidation of iron-gall ink documents requires the addition of alkali to neutralise the acid hydrolysis (de-acidification) and antioxidants to inhibit the oxidation process catalysed by metals in the Fenton reaction (Malešič et al., 2005).

A wide variety of antioxidants may be used to intervene in the oxidative degradation of cellulose. According to the mechanism, they can be classified into two groups: those that interrupt the chain reaction of free radicals catalysed by transition metals and those that inhibit or retard the formation of free radicals from its unstable precursors, particularly hydroperoxides (Scott, 1997). Several methodologies for the stabilisation and preservation of historical documents have been studied and applied in the past. However, the most frequently used is the so-called "calcium phytate method" (Neevel, 1995).

The phytic acid is a natural antioxidant present in seeds, whose main function is to block the unsaturated fatty acid oxidation which is catalysed by iron. Hence, in the treatment of historical documents, this compound belongs to the class which inhibits the formation of free radicals (Botti et al., 2005). Phytate (phytic acid, *myo*-inositol hexaphosphate) is the phytic acid in its salt form. The most commonly used are calcium and magnesium phytates. The high solubility of sodium phytate contributes to its migration to the edges of the paper during drying, causing stains, thus explaining its limited use. Because phytate is a powerful chelating agent, it has the ability to form complexes or precipitates with some polyvalent cations such as Fe^{2+} and Fe^{3+}. Depending on the phytate/iron ratio in the solution, the formation of mono phytate, di-, tri- or tetra-ferric phytate is expected. Iron coordination sites react with phytate, thus preventing this ion from remaining free to participate in Fenton reactions (Rouchon, 2011b).

The methodology for the treatment consists of immersing the document in a calcium phytate solution for a certain time. Next, the document must undergo de-acidification, so that the final pH does not favour the acid hydrolysis of cellulose. The most commonly used de-acidification agent is calcium carbonate. While it is the most widely used method, treatment with calcium phytate entails some side-effects such as migration of the ink and change in its colour (Malešič et al., 2014).

The present work sought to study four iron-gall ink preparations with different amounts of iron (stoichiometric and non-stoichiometric iron/tannin ratio) and the effect of contact time with two phytate solutions of different concentrations. The kinetics of the action of phytate solutions in the removal of free iron ions will indicate the minimum contact time between inks and phytate solutions in order to improve the process of conservation and protection of the historical documents from excessive contact to aqueous solutions.

Experimental

For preparation of the iron-gall inks used in the present work, $FeSO_4 \cdot 7\ H_2O$ (Vetec, Rio de Janeiro, Brasil), tannic acid (Vetec, Rio de Janeiro, Brasil), gum arabic (Vetec, Rio de Janeiro, Brasil) and 95 vol. % ethanol (Vetec, Rio de Janeiro, Brasil) were used. Table 1 presents the composition of the inks used.

Ink B was formulated with stoichiometric amounts

Table 1. Chemical composition of iron-gall ink formulations (amounts for 50 mL of ink in water)

Ink	$FeSO_4 \cdot 7H_2O$/g	Tannic acid/g	Gum arabic/g	Ethanol/mL
A	0.5	5.5	2.0	5.0
B	1.0	5.5	2.0	5.0
C	2.0	5.5	2.0	5.0
D	10.0	5.5	4.0	5.0

Table 2. Chemical composition of phytate solution for non-reactive iron removal

Solution	Phytic acid/mL	$CaCO_3$/g	Water/L
A (Diluted)	0.875	0.22	1.0
B (Reference)	1.75	0.44	1.0

of iron and tannic acid, and is regarded as the reference ink. Ink A presents half of the total amount of iron in comparison to Ink B. This simulates the reactivity of Fe^{2+} in the presence of excess tannic acid. Inks C and D were prepared with double and ten times higher concentrations of iron than in Ink B, respectively. After the initial reaction, the inks were exposed to air for 24 h to strengthen the colour after the formation of the gallotannic complex. After this step, the inks were kept in sealed amber vials at ambient temperature.

Impregnation of inks on paper strips

Initially, 20.0 mL of ink was transferred into a 50 mL beaker and then Whatman no. 1 paper strips were immersed vertically in each ink for 5 min. Each paper strip was 6 cm × 1 cm. This procedure was stopped when the ink reached 2.0 cm in the height on the paper strip, resulting in a total area of 2.0 cm^2 of ink impregnation. Next, the paper strips were dried in air for 24 h and placed in a controlled chamber at 100 ℃ for 5 d in glass tubes, in accordance with ASTM (da Costa et al., 2013).

This procedure was followed by a treatment with calcium phytate to remove the non-reactive iron. Next, a new accelerated ageing step and a new phytate treatment were conducted, in order to simulate another cycle of ageing of the paper in the absence of non-reactive iron. In that case, no further oxidation of iron was expected.

Calcium phytate solutions for non-reactive Fe^{2+} removal

Two calcium phytate solutions were prepared using an aqueous solution of phytic acid (Aldrich, Rio de Janeiro, Brasil) and $CaCO_3$ (Vetec, Rio de Janeiro, Brasil). The amounts used for the preparation of the solutions are detailed in Table 2.

Solution B was prepared in accordance with the methodology described by Neevel (1995), and used as a reference solution. Solution A was prepared with half the recommended concentration of phytate in order to evaluate the efficiency of the removal of Fe^{2+} by the diluted solutions. First, calcium carbonate was added to phytic acid solution in a beaker, and the mixture was stirred until a homogeneous brown pulp was formed. This slurry was dissolved in 100 mL of distilled water and the final volume was adjusted to 1.0 L volumetric flask. Under constant stirring, the pH was adjusted to 5.5–6.0 by adding NH_4OH (Vetec, Rio de Janeiro, Brasil).

Kinetics of iron removal by calcium phytate solution

After accelerated ageing, all the paper strips impregnated with the inks were washed two times with each phytate solution. 5.0 mL of each phytate solution were added to glass tubes and the paper strips were immersed. The kinetic test of iron removal by phytate solutions was performed by contact of the extractant with the strips of paper for 1 min, 2 min, 3 min, 5 min, 10 min, 15 min, 30 min, 45 min and 60 min. The strips were then dried in the ambient atmosphere for 24 h and returned to the oven for further accelerated ageing under the conditions previously described. Next, the samples were subjected to a second wash with the phytate solutions in triplicate ageing in order to simulate the durability and stability of the paper in the future. The iron content in all the samples was quantified by atomic absorption spectrometry.

Kinetic modelling of iron removal by phytate

A kinetic study of iron removal from the paper strips impregnated with iron-gall ink was performed. This modelling sought to ascertain when the iron removal achieved equilibrium with the liquid phase (phytate solution). Two different kinetic models were used to fit the experimental data. The pseudo first-order Lagergren model (Eq. (1)) was first considered, where: C_e (mg L^{-1}) and C (mg L^{-1}) are the concentrations of desorbed iron at the equilibrium and at any time t, respectively; k_1 is the Lagergren rate constant. By integrating Eq. (1) between the limits, $t = 0$ to $t =$

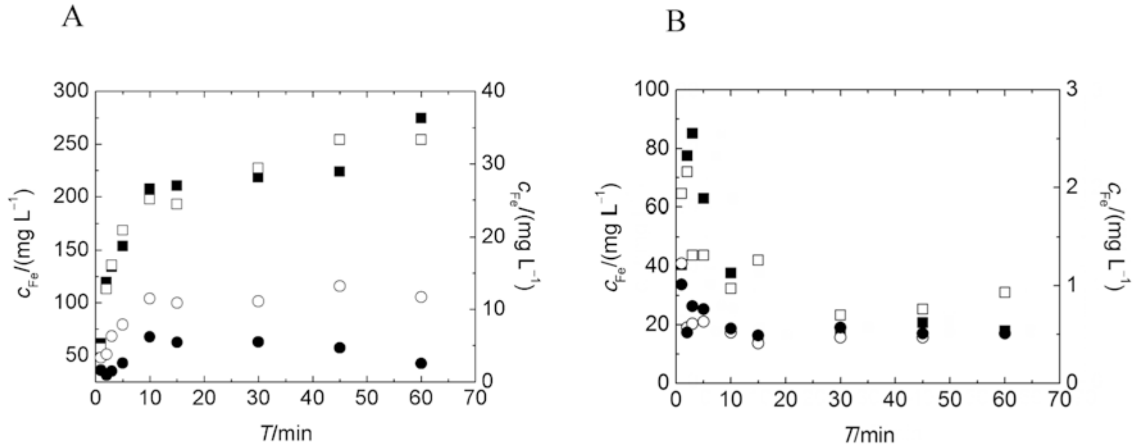

Fig. 1. Iron concentrations in calcium phytate solution A obtained after 1st (A) and 2nd (B) washings. Ink A (●); Ink B (○); Ink C (■); Ink D (□). The right y axis of each graph refers to Inks A, B and C. The left y axis refers to Ink D.

t and $C = 0$ to $C = C_{\mathrm{e}}$, it becomes Eq. (2).

$$\frac{\mathrm{d}C}{\mathrm{d}t} = k_1(C_{\mathrm{e}} - C) \tag{1}$$

$$\log(C_{\mathrm{e}} - C) = \log(C_{\mathrm{e}}) - \left(\frac{k_1}{2.303}\right) t \tag{2}$$

The linear plots of $\log(C_{\mathrm{e}} - C)$ against t are possible if the C_{e} value must be pre-estimated by extrapolating the experimental data to $t \to \infty$. The second-order model is based on the assumption that the rate of release of iron to the solution is proportional to the square of the number of unoccupied sites (Eq. (3)), where: k_2 is the rate constant of a second-order reaction. By integrating Eq. (3) for the boundary conditions $t = 0$ to $t = t$ and $C = 0$ to $C = C_{\mathrm{e}}$, the linear form of the model is obtained (Eq. (4)), where C_{e} and k_2 can be calculated from the slope and the interception of the t/C plot against t. By plotting t/C against t, a straight line is obtained for all the concentrations, by which the second-order rate constant (k_2) and C_{e} values could be determined.

$$\frac{\mathrm{d}C}{\mathrm{d}t} = k_2(C_{\mathrm{e}} - C)^2 \tag{3}$$

$$\frac{t}{C} = \left(\frac{1}{k_2}\right)(C_{\mathrm{e}})^2 + \left(\frac{1}{C_{\mathrm{e}}}\right) t \tag{4}$$

Analytical determination of iron

Iron quantifications were performed with the help of a high resolution atomic absorption spectrometer, ContrAA 300 (AnalytikJena AG, Jena, Germany), equipped with an air/acetylene flame for iron atomisation. High-purity acetylene was used as fuel for the flame (Linde Gases, Rio de Janeiro, Brazil) and the mixture flux of the gases was equal to 85 L h^{-1}.

All reagents used in this study were of analytical grade. The preparation of all solutions was from a 1.000 mg L^{-1} iron stock solution (Merck, Darmstadt, Germany). High-purity water was used, with resistivity of up to 18.2 MΩ cm, using a water purification system Master System All (Gehaka, São Paulo, Brazil). All measurements were performed in triplicate.

The main line for iron (248.327 nm) was selected for the readings. In order to achieve more suitable analytical signals, the measurement periods were equal to 3 s. The limit of detection and limit of quantification were calculated as 3 and 10 times, respectively. All the samples were previously tested and absorbance signals were obtained against the standard solution of 4.0 mg L^{-1}. In the event that the signals from the test samples were higher than the highest concentration of a standard solution used to construct the calibration curve, the test solution was diluted to fit the calibration range.

Results and discussion

Figs. 1 and 2 show the concentrations of iron measured by atomic absorption spectrometry in the phytate solutions used, in both the first and the second washings.

In both the first and second washings, and also for the two phytate solutions used, the concentration of iron in the washing solutions increased from inks A to D. This observation is in accordance to the predicted behaviour from inks A to D. Increasing free-iron concentrations were found, amenable to oxidation by atmospheric air and, consequently, additional free iron could be removed by phytate solutions, once the phytate concentration was fixed. To confirm this assumption, direct measurements on paper strips after washing need to be performed in further studies.

Phytate solutions removed higher amounts of iron in the first wash than in the second, indicating a marked decrease in iron removal from the structure of the paper. The first wash, in both cases (phytate solutions A and B), showed increasing Fe^{2+} concentrations

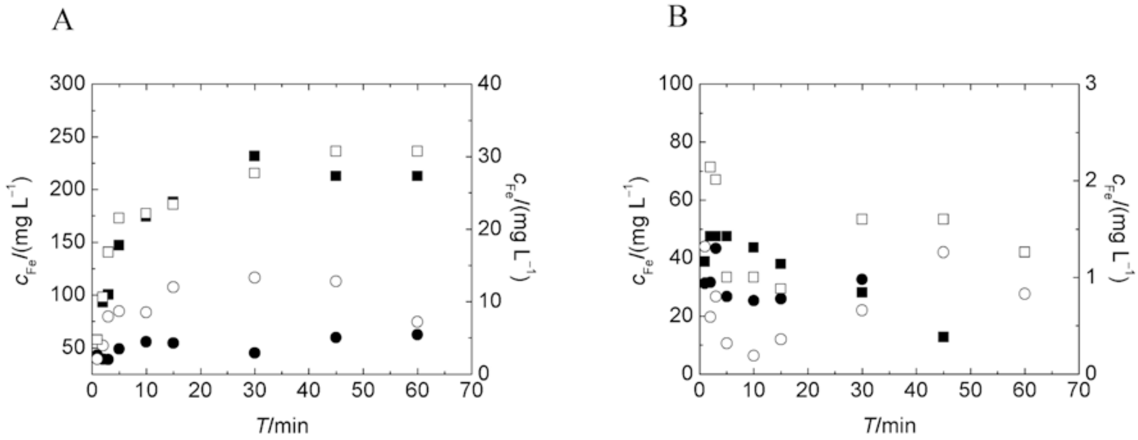

Fig. 2. Iron concentrations in calcium phytate solution B obtained after 1st (A) and 2nd (B) washings. Ink A (●); Ink B (○); Ink C (■); Ink D (□). The right y axis of each graph refers to Inks A, B and C. The left y axis refers to Ink D.

for all the inks investigated. This is a good indication of the Fe^{2+} desorption equilibrium, between 15 min and 30 min, in the first wash. Subsequent washes need to be investigated to assess their effectiveness and the frequency of contacts with aqueous baths requires further investigation (Rouchon et al., 2009).

From Figs. 1 and 2, specifically in the first washing, a small increase in iron concentration in the first minutes of removal was noted. Except for Ink D, the others appear to achieve equilibrium in the early stages of the process. This is probably due to its much higher iron concentration. A complete kinetic evaluation is needed for stabilisation of the ink. In the second wash, all the inks exhibited the same tendency, with a reduction in the amount of iron removed in the initial 5 minutes of washing. This indicates that subsequent washings of the paper do not require longer than five minutes to achieve the maximal removal of iron.

Due to the greater amount of iron in ink D, the second wash with phytate solutions exhibited a different tendency of iron removal. In the first three minutes, the second wash removed considerable quantities of iron. However, for the remaining inks (A, B and C), differences between the amounts of iron removed in the first and second washings, indicated that the second wash removed negligible amounts of iron. It may also be noted that the second wash can be used for an extended time since equilibrium was reached rapidly. The results revealed that the phytate solutions could be very effective in the treatment of a wide range of documents with different types of iron-gall inks.

Kolar et al. (2007) studied the stabilisation of iron-gall inks by using magnesium phytate. In that work, the researchers used an ink prepared with a tannin/iron ratio double that of ink D in the present work. Whatman paper strips impregnated with iron-gall inks were aged at 70 ℃ and 65 % relative humidity for 11 d. After that process, the paper strips were submerged in a calcium phytate solution (at the same concentration as the phytate solution B, from the present work), for 15–20 min, followed by magnesium phytate for 15 min. According to the results, the calcium phytate removed 44 % of the iron present in the paper and the magnesium phytate solution removed 42 % of the iron, indicating that there were no marked differences between calcium and magnesium sulphates.

In the work of Rouchon et al. (2011b), a combination of SEM, ICP and XANES techniques was used to study the action of phytate solutions on damaged manuscripts, due to the iron-gall inks. The researchers used an ink prepared with half of the tannin/iron ratio used for ink D. The paper strips containing the ink, aged at 70 ℃ and 65 % relative humidity for 6 d, were immersed in a phytate solution (the same as the reference phytate solution in the present work), at different pH values, from 4.8 to 6.0, for 15 min. The calcium phytate solution removed approximately 30 % of the iron (in comparison with the initial iron concentration used in the preparation of the ink). In particular, at pH 6.0, iron removal was around 40–45 %.

In agreement with the results observed in the present work, Rouchon et al. (2011a) observed that iron solubilisation and equilibrium occurred in up to 30 minutes. This, however, can alter from ink to ink and also depends on the methodology adopted to study kinetics.

Due to the presence of reducing substances in the paper, not all Fe^{2+} is oxidised to Fe^{3+}; due to this, even after centuries, old recipes still present substantial amounts of Fe^{2+}. On the other hand, this ion can markedly accelerate the degradation of cellulose, by oxidation through two basic mechanisms: the direct production of organic radicals and its further oxidation; and production of hydrogen peroxide decomposed by Fe^{2+} to hydroxyl radical and one hydroxide ion (Neevel, 1995). Due to its reactivity, hydroxyl radicals are usually considered as being mainly responsible for cellulose degradation through oxidation (Robert et al., 2002).

Dzinavatonga et al. (2015) evaluated the risk of the degradation of some historical documents through the determination of the valence state of iron using Mössbauer spectroscopy. This technique was used to determine the relative contribution of Fe^{2+} ions in relation to the total amount of iron in a manuscript. The authors observed that the document contained both Fe^{2+} (21 %) and Fe^{3+} (79 %) and that the aqueous samples contained just Fe^{3+}. Neevel (1995) used this same technique, obtaining a concentration of Fe^{2+} of approximately 20 % when studying a manuscript from the 18th century, clearly corroded by the ink.

Wagner et al. (2004) observed that the distribution of Fe^{2+} ions was homogeneous in the bulk of the liquid ink, being more concentrated in the paper-ink interface, while Fe^{3+} was predominantly on the surface of the paper. Yue et al. (2014) reported that most Fe^{3+} ions were distributed as complexes or precipitated on the surface of the paper, while the amount of free Fe^{3+} was quite low, in contrast to the high amount of free Fe^{2+} amenable to oxidation.

Batterham and Rai (2008) conducted an investigation of the chemical and physical properties of six types of paper, prior to and after accelerated ageing, in order to compare natural and accelerated ageing. The authors observed that papers naturally aged for 27 years were the equivalent of papers artificially aged for 3 d at (105 ± 2) ℃.

Consequently, it is reasonable to assume that the age of the paper strips after artificial ageing used in the present study is 18 years. Considering the amount of ferrous sulphate added to each ink, it may be accepted that the oxidation of Fe^{2+} to Fe^{3+} was not complete on the support, due to the short period of time, thus leaving a considerable amount of Fe^{2+} ions remaining. The phytic acid forms complexes over a wide range of pH values (1.0–12.0) with a variety of polyvalent cations, preferentially from the left to the right, namely: Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+} (Maenz et al., 1999). By increasing the concentration of phytate, more iron phytate is formed and more Fe^{3+} is dissolved.

It could also be observed that, during the first washing of the paper strips, the formation of a thick layer of ink on the surface of the paper made possible its physical removal, followed by complexation of the Fe^{2+} ions and Fe^{3+} still present in the inks. In the second washing, only minor quantities of Fe^{2+} were present on the paper strips. It can also be considered that the higher the concentration of calcium phytate, the Fe^{2+} which was oxidised to Fe^{3+} (as a consequence of the second accelerated ageing) was removed in the form of iron phytate complex.

Table 3. Removal of iron as a function of iron-gall ink composition

Ink	Iron removed mg L^{-1}
A	5.3
B	10.0
C	21.7
D	190.9

The results are summarised in Table 3. A direct correlation between the amount of iron added and removed in the first wash can be observed. This lack of proportionality when compared to other inks may be explained by two factors: possible analytical errors and, most likely, the formation of a dense oxidised iron layer deposited on the surface of the paper strips, forming a type of shield or contributing to the formation of crystals, which prevent the efficient removal of Fe^{2+} ions from the inner layers. In order to confirm the mass balance for iron, a direct quantification of iron on the paper strips should be performed. In this case, a single treatment of de-acidification with calcium phytate solutions is not sufficient to prevent the ink from undergoing a new oxidation, because the corrosion caused by the oxidation catalysed by Fe^{2+} is temporarily blocked (Orlandini, 2009). This happens because the Fe^{2+} ions are again oxidised to Fe^{3+} after a second artificial ageing (Burgaud et al., 2006). This would explain the significant concentration of iron ions (40 mg L^{-1}) in the second wash. Hence, it is clear that the removal kinetics is the same irrespective of the amount of iron added, up to a certain concentration; the exception to this behaviour is found in ink D, the composition of which is far from stoichiometric. La Camera (2007) examined the crystals formed in iron-gall inks on drawings from the collection of the Department of Paintings and Photographs of Boston Fine Arts Museum. Ink crystals were more frequently observed in paintings and documents in which a substantial amount of ink remained on the paper surface. Instrumental analysis identified the chemical composition of crystalline material as sulphates, especially iron sulphate. The ink composition and the site where these crystals were formed were examined by means of accelerated ageing of twelve sets of samples. Each set included twenty mixtures of ink with different ferrous sulphate/tannin/gum arabic ratios. The experiments revealed an increase in crystallisation, after accelerated ageing, for samples containing high concentrations of ferrous sulphate and minimal concentrations of binder gum. The corrosion of iron-gall inks is markedly influenced by ageing, storage, temperature and relative humidity. However, Reissland (2000) noted that two factors, although having a marked impact, are usually disregarded: the amount of ink used and the sizing of the paper. A thick layer of ink is likely to cause more harm than a thin layer, leaving a larger surface area of the support vulnerable to corrosion (Kolar & Strlič, 2006). Similarly, a paper with little or no sizing absorbs ink more readily than the

Table 4. Kinetic parameters of iron removal

Phytate/Ink	Pseudo first-order R^2	Pseudo first-order Theoretical $C_e/(\text{mg mL}^{-1})$	Pseudo first-order Experimental $C_e/(\text{mg mL}^{-1})$	Second-order R^2	Second-order Theoretical $C_e/(\text{mg mL}^{-1})$	Second-order Experimental $C_e/(\text{mg mL}^{-1})$
A/A	0.6241	5.50	6.20	0.3389	4.1	6.20
A/B	0.9573	10.50	11.50	0.7762	14.1	11.50
A/C	0.9918	28.30	25.10	0.2800	83.3	25.10
A/D	0.8962	160.40	210.50	0.9096	238.1	210.50
B/A	0.4859	2.80	4.40	0.7026	3.9	4.40
B/B	0.8774	12.60	12.00	0.1558	51.5	12.00
B/C	0.9908	37.40	23.40	0.2286	144.9	23.40
B/D	0.9594	174.30	187.90	0.7143	344.8	187.90

fibres in a hard-sized paper, where the ink will tend to deposit on the surface.

Kinetic modelling of iron removal

The results of kinetic modelling are shown in Table 4. Both phytate solution A and B removed the non-reactive iron from iron-gall ink paper in accordance with a reaction model of pseudo-first order. This is confirmed by the values of the correlation coefficients of the straight lines fitting the experimental data prior to equilibrium (Figs. 1 and 2). For example, when phytate solution A was used for iron removal, the R^2 values ranged from 0.6241 to 0.9918. By contrast, the results from the second-order model ranged from 0.2800 to 0.9096. This is an indication that the experimental data fitted the model of Lagergren's pseudo-first order more accurately than the second-order model.

If the values for the correlation coefficients are considered for solution B, according to the first-order model, the values ranged from 0.4859 to 0.9908, whereas for the second-order model these coefficients ranged from 0.1558 to 0.7143. This is an indication that the fit to the second-order model was less suitable. A comparison between the theoretical and experimentally observed values for the concentration of non-reactive iron also confirms the applicability of the first-order model.

These results complement earlier studies, where the non-reactive iron removal kinetics and stoichiometry considerations of the reaction were taken into account. The present results provide valuable information about the stabilisation of the process of deterioration of the paper due to the chemical action of iron-gall ink. This can help in enhancing the stability of the ink and consequent preservation of much of the cultural heritage (da Costa et al., 2013, 2014).

Conclusions

The iron removal kinetics from paper strips impregnated with iron-gall inks was rapid, taking approximately 15 min with the use of both extraction solutions and different combinations of iron and tannic acid. A wash solution of calcium phytate was capable of removing most of the non-reactive iron from inks. A second washing (after accelerated ageing of the paper) removed small quantities of iron, indicating a start to the stabilisation of the ink oxidation process. Calcium phytate dilute solutions were as efficient for iron removal as the reference solution. Consequently, reduced structural damage to papers and documents is expected. The kinetic model of pseudo first-order fitted the experimental data more accurately than the second-order model, confirming a rapid kinetics, which affords the simultaneous operation of treatment baths on documents. These tests provided new knowledge for the preventative conservation of cultural heritage, introducing aspects of kinetic modelling of iron removal in documents printed (or written) with iron-gall ink.

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